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# Decomposition of the Nitrosyldisulfonate Free-Radical Anion in Strongly Alkaline Solutions

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The decomposition of the moderately stable free-radical nitrosyldisulfonate ion, $\cdot ON(SO_3)_2^{2-}$, in strongly alkaline solution (1–5 *m* $OH^-$) is first order in radical concentration and first order in hydroxide ion concentration. The products are nitrate ion, hydroxylaminetrisulfonate ion, and hydroxylaminedisulfonate ion. Decomposition of the last ion to sulfite ion, which reacts with the radical, increases the rate of radical loss.

## Introduction

This paper is the final experimental report of the studies conducted in our laboratories on the decomposition of the free-radical nitrosyldisulfonate ion, $\cdot ON(SO_3)_2^{2-}$, which has found use as an ESR standard and a selective oxidizer for some organic compounds. In our last paper,[2] we reported the decomposition in nonaqueous solvents and proposed a mechanism for decomposition. In this paper, we report the kinetics of decomposition in strongly alkaline solutions which supports the proposed mechanism. We also report kinetic data for the accompanying decomposition of a product, hydroxylaminedisulfonate.

## Experimental Section

**Materials.** Potassium nitrosyldisulfonate was prepared and purified as described earlier.[3] It was analyzed by reaction with iodide ion, with the released iodine being titrated with standard thiosulfate solution. With fresh samples, the purity was 99.0% or greater. A colorimetric purity measurement was made at the beginning of each kinetic run at 545 nm (ϵ 20.8 $M^{-1}$ $cm^{-1}$). The run was continued only if the purity was 99.0% or greater.

Potassium hydroxylaminedisulfonate, $HON(SO_3K)_2 \cdot 2H_2O$, was prepared by the reaction of sodium hydrogen sulfate and sodium nitrite at 0 °C. The product was precipitated from solution with potassium nitrate, recrystallized from 1 N hydroxide, and stored in a vacuum desiccator. The purity was determined by two methods: oxidation with ferric ion[4] and gravimetric barium sulfate determination after hydrolysis. The purity was found to be at least 97.8% in all cases.

Potassium hydroxylaminetrisulfonate, $ON(SO_3K)_3$, was prepared by the oxidation of potassium hydroxylaminedisulfonate with lead dioxide. After being washed with cold water and absolute ethanol, the salt was stable and was stored in a vacuum desiccator. The purity was determined by precipitation of the highly insoluble salt with the $Co(NH_3)_6^{3+}$ cation. The orange salt was collected on a filter, washed with cold water, and dried at 100 °C for 1 h. The purity was found to be at least 99.8%.

Other substances used were reagent grade and were used as obtained from the suppliers.

**Product Analysis.** Nitrite ion production was followed at 355 nm (ϵ 23.5 $M^{-1}$ $cm^{-1}$) during the initial part of the decomposition while the concentrations of the other products were very low. The absorptivity of the radical is low (ϵ 5.70 $M^{-1}$ cm¯1) at this wavelength, but was corrected for with the formula

$$C_{\text{nitrite}} = \frac{A_{335\text{nm}} - \left[\dfrac{A_{545\text{nm}}}{20.8} \times 5.7\right]}{23.5}$$

used to calculate the concentration of nitrite ion. This could only be used in the first part of the decomposition before the other products became concentrated enough to absorb significantly.

At the completion of the decomposition, nitrite ion was determined by reduction with iodide and titration of the liberated iodine with thiosulfate solution under a carbon dioxide atmosphere.

No sulfite ion was detected during or at the end of the decomposition, but on standing overnight, small amounts of sulfite were produced.

At the end of the reaction, the solution was acidified and barium chloride was added. A precipitate was not apparent at first but slowly formed as the hydroxylaminedisulfonate and -trisulfonate present slowly hydrolyzed, releasing sulfate ion.

The hydroxylaminetrisulfonate ion present was determined by gravimetric precipitation with hexaamminecobalt(III) ion. The precipitate was collected on a filter, washed, dried, and weighed. The filtrate was analyzed for hydroxylaminedisulfonate by ferric ion reduction described earlier.

**Kinetic Data.** The loss of nitrosyldisulfonate radical was followed spectrophotometrically at 545 nm. The solutions with hydroxide ion (0.01–5.00 m) were prepared in volumetric flasks and a sample was immediately withdrawn for analysis. If it had decomposed more than slightly, it was discarded. The solutions were transferred to polyethylene containers and placed in a constant-temperature bath held at ±0.03 °C of the desired temperature. Aliquots were withdrawn

**Table I.** Nitrite Ion Production during the Initial Part of the Decomposition As Determined Spectrophotometrically

| | Amt, mmol | | |
|---|---|---|---|
| Time, s | Nitrosyl-disulfonate ion lost | Nitrite ion produced | % of N found as nitrite ion |
| | 1.40 m NaOH | | |
| 0.00 | 0.00 | | |
| 500 | 0.106 | 0.0277 | 26.1 |
| 1000 | 0.207 | 0.0528 | 25.5 |
| 1500 | 0.298 | 0.0745 | 25.0 |
| | 3.0 m NaOH | | |
| 0.00 | 0.00 | | |
| 1000 | 0.767 | 0.197 | 25.7 |
| 1500 | 1.106 | 0.271 | 24.5 |

periodically for analysis and then discarded. A Beckman DU, a Beckman DK2, and a Cary 15 spectrophotometer were used. Etching of the cells was found to be negligible over the period of time the alkaline solutions were in them.

Some additional runs were made with added bromine, sulfite, sulfate, hydroxylaminedisulfonate, or hydroxylaminetrisulfonate ions. The ionic strengths of the solutions were adjusted with potassium nitrate.

Rate constants were calculated with the aid of an H-P Model 9100B calculator to which a H-P calculator plotter, Model 9125A, was interfaced. Premade program no. 90803 was used which utilized a least-squares regression analysis to fit a linear equation to the experimental data.

## Results

**Products of the Decomposition.** Nitrite ion concentrations determined spectrophotometrically during the initial stages of the reaction indicated that about 25% of the nitrogen from the nitrosyldisulfonate ion which had decomposed was found as nitrite ion, as shown in Table I. As the decomposition proceeded, the rate of production of nitrite ion increased; and at the completion of the decomposition, 28% of the nitrogen was present as nitrite ion.

Sulfate ion was not detected among the products, and sulfate ion added during the decomposition did not react with nitrosyldisulfonate or any of its decomposition products. So, if it were formed, it would have been detected.

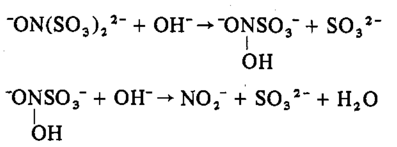
If sulfite ion was formed, it would have reacted rapidly with nitrosyldisulfonate ion and so would not be expected to be found among the products. The hydroxylamine ion found after the reaction accounted for 22% of the nitrogen, and the hydroxylaminetrisulfonate ion found accounted for 49% of the nitrogen.

With these analyses, 96% of the nitrogen and 95.5% of the sulfur were accounted for. This suggests the reaction

$$4\cdot ON(SO_3)_2^{2-} + OH^- \rightarrow NO_2^- + HON(SO_3)_2^{2-} + 2ON(SO_3)_3^{3-}$$

modified by a slight side reaction.

The hydroxylaminedisulfonate ion in strongly basic solution reverts back to nitrite and sulfite ions in a two-step process



$$^-ON(SO_3)_2^{2-} + OH^- \rightarrow {}^-O\underset{OH}{N}SO_3^- + SO_3^{2-}$$

$$^-O\underset{OH}{N}SO_3^- + OH^- \rightarrow NO_2^- + SO_3^{2-} + H_2O$$

This accounts for the apparent increase in the nitrite ion and loss of hydroxylaminedisulfonate ion. The deviation from first-order kinetics in the decomposition of the nitrosyldisulfonate ion can be accounted for by its reaction with the sulfite ion produced

$$SO_3^{2-} + \cdot ON(SO_3)_2^{2-} \rightarrow {}^-ON(SO_3)_2^{2-} + \cdot SO_3^-$$

$$\cdot SO_3^- + \cdot ON(SO_3)_2^{2-} \rightarrow ON(SO_3)_3^{3-}$$

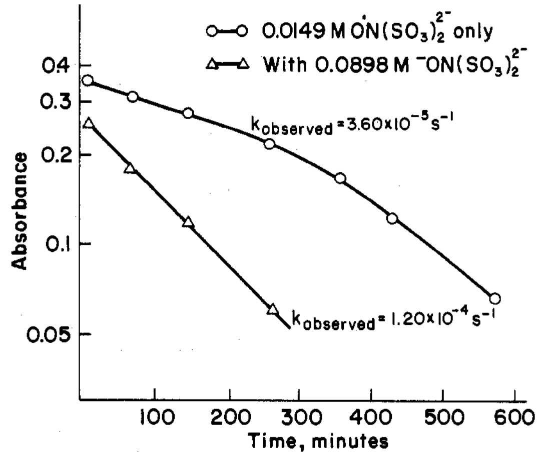


**Figure 1.** Effect of hydroxylaminedisulfonate ion on the decomposition of nitrosyldisulfonate ion.

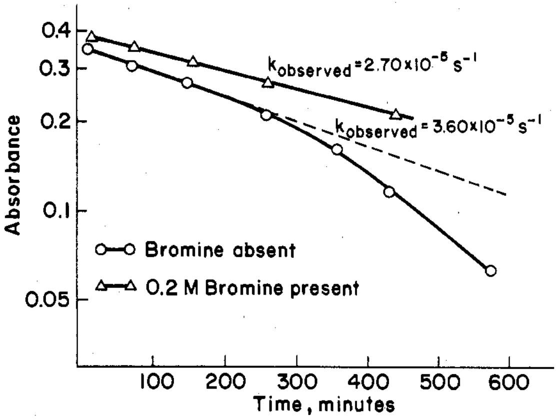


**Figure 2.** Effect of added bromine on the decomposition of nitrosyldisulfonate ion in 3 *m* sodium hydroxide solution.

To test this, a series of experiments was designed in which separate solutions of the same nitrosyldisulfonate ion concentration had increasing amounts of hydroxylaminedisulfonate ion added at the beginning of the decomposition. As Figure 1 shows, the rate of color loss increased and there was no deviation from first-order kinetics. This was due to the high and essentially constant concentration of hydroxylaminedisulfonate ion. This was tried with all the other decomposition products, but no change was observed. Added sulfite ion does speed up the color loss, however.

Bromine was tried as an oxidizing agent to oxidize the sulfite before it could react as above, but the reaction rate decreased by only one-fourth rather than one-half, as expected, and the reaction remained first order to completion, as shown in Figure 2. It was then determined in a separate experiment that bromine was oxidizing the hydroxylaminedisulfonate ion produced back to nitrosyldisulfonate ion. This accounts for the reduction in the rate of radical loss and for the lack of deviation from first-order kinetics.

**Kinetics of the Decomposition.** The decomposition data were plotted as log (absorbance) vs. time. The reactions appeared to be first order with an increase in rate during the latter part. Table II shows that these first-order rate constants increase as the ionic strengths increase, suggesting that the decomposition involved a reaction between ions of the same charge. The rate constants were calculated for zero ionic strength using data from solutions of various ionic strengths. Table III shows the negligible effect on the rate constant of varying the initial nitrosyldisulfonate ion concentration.

Rate constants were obtained at 25, 35, and 45 °C. An Arrhenius plot, Figure 3, gave an activation energy of 4.7

**Table II.** Rate Constants for the Decomposition of 0.000 374 M Nitrosyldisulfonate

| [NaOH], *m* | Activity of NaOH,[5] *m* | Ionic strength | Obsd first-order rate const × $10^6$, $s^{-1}$ |
|---|---|---|---|
| 0.01 | 0.009 | 0.344 | 0.47 |
| 0.10 | 0.077 | 0.344 | 0.66 |
| 0.50 | 0.344 | 0.344 | 1.00 |
| 0.50 | 0.344 | 0.960 | 1.60 |
| 1.00 | 0.678 | 0.960 | 8.40 |
| 1.40 | 0.960 | 0.960 | 9.50 |
| 1.40 | 0.960 | 2.35 | 11.2 |
| 2.00 | 1.42 | 2.35 | 15.1 |
| 3.00 | 2.35 | 2.35 | 28.0 |
| 3.00 | 2.35 | 5.39 | 36.0 |
| 4.00 | 3.61 | 5.39 | 36.0 |
| 5.00 | 5.39 | 5.39 | 90.0 |

**Table III.** Effect of Initial Nitrosyldisulfonate ion Concentration on the Observed Rate Constant[a]

| [Nitrosyldisulfonate ion], M | Obsd rate const × $10^5$, $s^{-1}$ | [Nitrosyldisulfonate ion], M | Obsd rate const × $10^5$, $s^{-1}$ |
|---|---|---|---|
| 0.0185 | 2.80 | 0.009 65 | 2.60 |
| 0.0162 | 2.80 | 0.000 345 | 2.50 |
| 0.0146 | 2.80 | | |

[a] These solutions were 3 *m* in sodium hydroxide and had an ionic strength of 2.35.

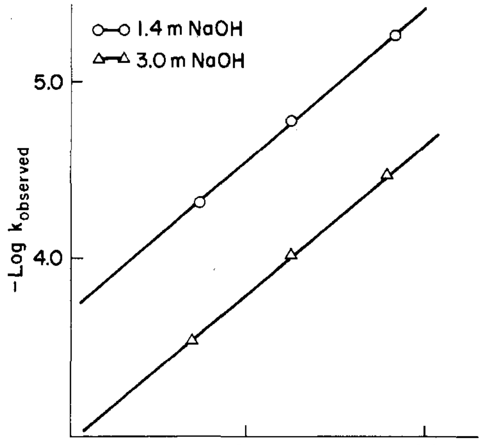


**Figure 3.** Arrhenius plot for the determination of activation energy for the decomposition of nitrosyldisulfonate ion.

kcal/mol in the highly basic solutions.

The effect of the hydroxide ion concentration was evaluated by plotting log [$OH^-$] vs. the log of the observed rate constant and the rate constant was calculated for zero ionic strengths, Figure 4. Both plots gave a slope of 1, which suggests that the reaction is first order in the radical and first order in hydroxide ion. In the high and constant concentration of hydroxide ion, the reaction appears pseudo first order.

## Conclusions

The decomposition seems to proceed by the same mechanism that we proposed in our earlier paper[2] for decomposition in nonaqueous solvents, modified slightly for solvent interaction in the strongly alkaline medium: eq 1–5.

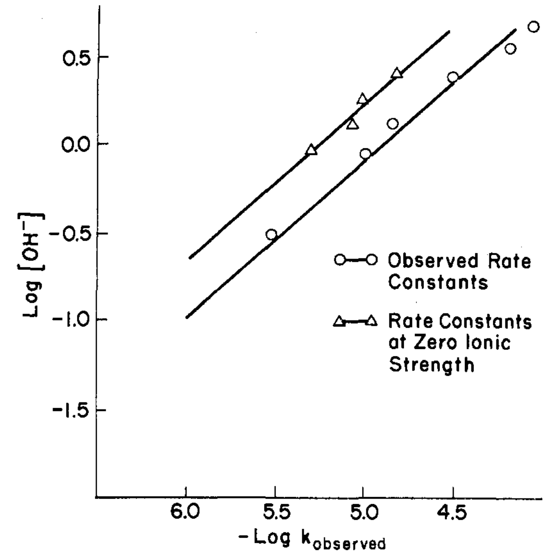
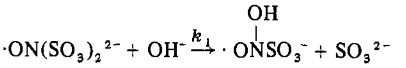
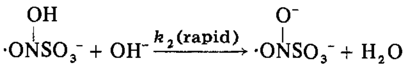


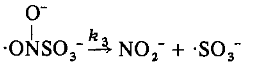
**Figure 4.** Determination of the order of the decomposition with respect to hydroxide ion.



$$\cdot ON(SO_3)_2^{2-} + OH^- \xrightarrow{k_1} \cdot O\overset{OH}{\overset{|}{N}}SO_3^- + SO_3^{2-} \tag{1}$$



$$\cdot O\overset{OH}{\overset{|}{N}}SO_3^- + OH^- \xrightarrow{k_2(\text{rapid})} \cdot O\overset{O^-}{\overset{|}{N}}SO_3^- + H_2O \tag{2}$$

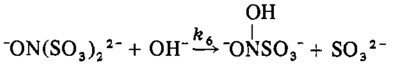


$$\cdot O\overset{O^-}{\overset{|}{N}}SO_3^- \xrightarrow{k_3} NO_2^- + \cdot SO_3^- \tag{3}$$

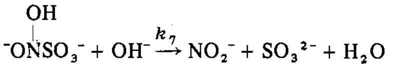
$$\cdot ON(SO_3)_2^{2-} + SO_3^{2-} \xrightarrow{k_4} {}^-ON(SO_3)_2^{2-} + \cdot SO_3^- \tag{4}$$

$$\frac{2[\cdot ON(SO_3)_2^{2-} + \cdot SO_3^- \xrightarrow{k_5} ON(SO_3)_3^{3-}]}{\underset{(0)}{4(\cdot ON(SO_3)_2^{2-})} \rightarrow \underset{(III)}{NO_2^-} + \underset{(-I)}{{}^-ON(SO_3)_2^{2-}} + \underset{(-I)}{2ON(SO_3)_3^{3-}}} \tag{5}$$

The equation for the overall reaction also satisfies the oxidation number changes in the disproportionation. This mechanism predicts that 25% of the nitrogen would be found as hydroxylaminedisulfonate ion, but only 22% was found in this form. Nitrite ion should also account for 25%, but 28% was found at the end of the decomposition. Hydroxylaminetrisulfonate should account for 50%, and 49% was found in this form. The decrease in hydroxylaminedisulfonate ion and the increase in nitrite ion can be accounted for by the reversion of the former ion, i.e., the reverse process for the formation of the hydroxylaminedisulfonate,[6] eq 6 and 7.



$${}^-ON(SO_3)_2^{2-} + OH^- \xrightarrow{k_6} {}^-O\overset{OH}{\overset{|}{N}}SO_3^- + SO_3^{2-} \tag{6}$$



$${}^-O\overset{OH}{\overset{|}{N}}SO_3^- + OH^- \xrightarrow{k_7} NO_2^- + SO_3^{2-} + H_2O \tag{7}$$

As the hydroxylaminedisulfonate ion is formed from the decomposition of the radical, it slowly decomposes. The sulfite ion formed rapidly reacts with the radical, causing the deviation from the first-order kinetics. Added bromine rapidly oxidized the hydroxylaminedisulfonate as it was formed back to nitrosyldisulfonate, so there was no deviation from first-order kinetics.

As reactions 2–5 are all much more rapid than reaction 1, it is possible to derive a rate expression for the loss of the radical by using steady-state approximations for the concentrations of $SO_3^{2-}$, $\cdot SO_3^-$, $ON(OH)SO_3^-$, and $ON(O^-)SO_3^-$. The expression thus derived is

$$-d[\cdot ON(SO_3)_2^{2-}]/dt = 4k_1[\cdot ON(SO_3)_2^{2-}] + 4k_6[{}^-ON(SO_3)_2^{2-}]$$

During the initial part of the reaction when the product ${}^-ON(SO_3)_2^{2-}$ concentration is low, the decomposition is first order but starts to increase as that product is formed and starts to revert to $SO_3^{2-}$ and $NO_2^-$ ions.

**Table IV.** Second-Order Rate Constant for the Decomposition of Nitrosyldisulfonate Ion with No Correction Made for the Ionic Strength

| Concentration of [NaOH], molality *m* | Activity of NaOH,[5] *m* | Obsd first-order rate const, $4k_1[OH]$, $s^{-1} \times 10^{-5}$ | Second-order rate const, $4k_1$, $s^{-1}$ $M^{-1} \times 10^{-5}$ | Second-order rate const, $k_1$, $s^{-1}$ $M^{-1} \times 10^{-6}$ |
|---|---|---|---|---|
| 0.50 | 0.344 | 0.10 | 0.29 | 0.73 |
| 0.50 | 0.344 | 0.16 | 0.46 | 1.15 |
| 1.00 | 0.678 | 0.84 | 1.20 | 3.00 |
| 1.40 | 0.960 | 0.95 | 0.99 | 2.48 |
| 1.40 | 0.960 | 1.10 | 1.00 | 2.50 |
| 2.00 | 1.42 | 1.50 | 1.10 | 2.75 |
| 3.00 | 2.35 | 2.70 | 1.10 | 2.75 |
| 3.00 | 2.35 | 3.60 | 1.50 | 3.75 |
| 4.00 | 3.61 | 7.00 | 1.90 | 4.75 |
| 5.00 | 5.39 | 9.00 | 1.70 | 4.25 |

**Table V.** Rate Constant, $k_6$, for the Decomposition of Hydroxylaminedisulfonate Ion[a]

| Obsd rate const $\times 10^5$, $s^{-1}$ | [Hydroxylaminedisulfonate ion] $\times 10^2$, M | $k_7 \times 10^6$, $s^{-1}$ |
|---|---|---|
| 4.80 | 1.49 | 5.0 |
| 8.80 | 3.30 | 6.5 |
| 12.0 | 9.00 | 3.9 |

[a] These solutions were 3 *m* in sodium hydroxide and had an ionic strength of 2.35. The nitrosyldisulfonate ion concentration was $1.49 \times 10^{-2}$ M.

**Table VI.** Effect of Bromine on the Rate Constant for Decomposition of Nitrosyldisulfonate Ion

| [NaOH], *m* | Temp, °C | $10^5 k_{obsd}$, $s^{-1}$ |  | Ratio of rates for Br present: Br absent |
|---|---|---|---|---|
|  |  | Br absent | Br present |  |
| 5.00 | 25.0 | 9.0 | 7.0 | 0.77 |
| 3.00 | 25.0 | 3.6 | 2.7 | 0.74 |
| 2.00 | 25.0 | 2.4 | 1.5 | 0.63 |
| 3.00 | 35.0 | 7.9 | 6.2 | 0.79 |
| 1.40 | 35.0 | 4.4 | 3.4 | 0.77 |
| 3.00 | 45.0 | 23.5 | 16.0 | 0.71 |
| 1.40 | 45.0 | 16.0 | 13.5 | 0.83 |

During the course of decomposition, the reaction is pseudo first order (as the hydroxide ion concentration is held constant) so $k_{obsd}$ is actually $4k_1[OH^-]$. These $k_1$ values are shown in Table IV.

It is possible to estimate rate constant values for the hydroxylaminedisulfonate reversion from the experiments involving added hydroxylaminedisulfonate ion, as

$$k_6 = \frac{\text{rate obsd} - 4k_1[\cdot ON(SO_3)_2{}^{2-}]}{4[{}^-ON(SO_3)_2{}^{2-}]}$$

These values of $k_6$ are shown in Table V.

The proposed mechanism was further confirmed by the runs with added bromine which oxidized the product hyroxylaminedisulfonate back to nitrosyldisulfonate. The proposed mechanism would require the rate of loss of the radical to decrease one-fourth, as was found to be the case, as shown in Figure 2 and Table VI.

## Summary

The decomposition of nitrosyldisulfonate ion in strongly alkaline solution can be explained in terms of a pseudo-first-order decomposition and a side reaction involving the reversion of a decomposition product. In the first-order decomposition, the breaking of a nitrogen–sulfur bond is the initial and rate-determining step. This initial step probably involves the formation of an activated complex by an $S_N2$ replacement of sulfite ion by hydyroxide ion. The reaction is first order in both hydroxide ion and nitrosyldisulfonate ion. The pronounced effect of ionic strength on the observed rate constants indicates that the reaction involves ions of similar charge. The activation energy for the formation of the activated complex is only 4.7 kcal/mol which suggests that this is an easy complex to form.

**Registry No.** $\cdot ON(SO_3)_2{}^{2-}$, 15177-44-3; ${}^-ON(SO_3)_2{}^{2-}$, 62107-68-0; $OH^-$, 14280-30-9; $Br^-$, 7726-95-6.

## References and Notes

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