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Authors
Wang, Y.Z.
Littlejohn, D.
Chang, S.G.

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Oxidation of Aqueous Sulfite Ion by Nitrogen Dioxide

Y.Z. Wang†, David Littlejohn, and S.G. Chang*

Lawrence Berkeley Laboratory
Energy and Environment Division
Berkeley, California 94720

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† On leave from the Research Center for Environmental Sciences, Academia Sinica, Beijing, Peoples Republic of China.

* Author to whom correspondence should be addressed.
Abstract

The formation of products from the reaction of nitrogen dioxide, with and without the presence of oxygen, in aqueous sulfite and hydrogen sulfite solutions has been studied by Raman spectroscopy. The products observed include nitrite, nitrate, sulfate and dithionate ions. The product distribution at low pH is complicated by the formation of nitrogen sulfonates from the reaction of nitrite ion with hydrogen sulfite ion. A possible mechanism is presented for the reaction of aqueous nitrogen dioxide with sulfite ion to generate the observed products. From the product distribution observed, we obtain a branching ratio for the reactions

\[
\begin{align*}
\text{SO}_3^{2-} + \text{SO}_3^{2-} &\rightarrow \text{SO}_3^{-} + \text{SO}_3^{2-} \quad k_7 \\
\text{SO}_3^{2-} + \text{SO}_3^{-} &\rightarrow \text{S}_2\text{O}_6^{2-} \quad k_8
\end{align*}
\]

of \( k_7/k_8 = 1.8 \pm 0.2 \) at 20°C in 0.8 M NaOH and derive values of \( k_7 = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \) and \( k_8 = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \).
Introduction

The reaction of nitrogen dioxide with sulfite ion is important in both air pollution chemistry and in control of flue gas emissions. There have been a number of studies on this reaction system, yet the details of the reaction mechanism have not been clearly established. The reaction process may be complicated by the presence of one or more sulfur oxyanion radicals.

Early studies established that the reaction was fast but did not determine the reaction products. Nash determined the relative rate of reaction involving NO$_2$ with a number of compounds at pH 7 and pH 13, including sulfite/hydrogen sulfite at pH 7. It was suggested that the compounds underwent nucleophilic attack by NO$_2$.

Takeuchi et al. used a plane interface contactor to calculate reaction rates from the observed removal of NO$_2$ from the gas phase by sulfite and hydrogen sulfite solutions. Second order rate constants for the following reactions are listed in Table I.

\[
\text{NO}_2(g) + \text{HSO}_3^-/\text{SO}_3^{2-} \rightarrow \text{products} \quad (1)
\]

\[
\text{NO}_2(g) + \text{NO}_2(g) + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{NO}_2^- + \text{NO}_3^- \quad (2)
\]

The second report by Takeuchi and coworkers found that oxygen slowed the rate of absorption of NO$_2$ by sulfite solutions, and that antioxidants counteracted this effect.

Sato et al. investigated the products of the reaction of NO$_2$ with sulfite and hydrogen sulfite solutions. A number of anions, including nitrite, nitrate, sulfate, dithionate, and nitrogen sulfonates were found. The nitrogen sulfonates can be formed by the reaction of nitrite with hydrogen sulfite.

Rosenberg and Grotta observed the oxidation by NO$_2$ and NO of dissolved sulfur dioxide in calcium hydroxide slurries. They found that NO inhibited oxidation and that NO$_2$ promoted oxidation. Anionic products other than sulfate were not analyzed.

Lee and Schwartz investigated the reaction of NO$_2$ and S(IV) (where S(IV) collectively represents SO$_3^{2-}$ and HSO$_3^-$) by bubbling a low concentration of NO$_2$ in N$_2$ through S(IV) solutions. The reaction was studied at pHs 5.8 and 6.4 using conductivity. Their results
suggested the presence of a long-lived intermediate in the reaction. The measured second order rate constant of $2 \times 10^6 \text{M}^{-1} \text{s}^{-1}$ did not display a pH dependence over the limited pH range studied. The analyzed reaction products were consistent with an overall stoichiometry of

$$2 \text{NO}_2 + \text{HSO}_3^- + \text{H}_2\text{O} \rightarrow 3 \text{H}^+ + 2 \text{NO}_2^- + \text{SO}_4^{2-} \quad (3)$$

The studies suggested the presence of a long-lived intermediate in the reaction. While no $\text{S}_2\text{O}_6^{2-}$ was observed, the sensitivity of the detection method was not specified. Lee and Schwartz also studied the dissolution of $\text{NO}_2$ in water with a similar experimental system. They obtained a value of $k_{\text{hyd}} = 1.0 \pm 0.1 \times 10^8 \text{M}^{-1} \text{s}^{-1}$, quite close to the value reported by Takeuchi et al.

Huie and Neta included the reaction of $\text{NO}_2$ with $\text{SO}_3^{2-}$ in their pulse radiolysis study of one electron transfer reactions of $\text{NO}_2$ and $\text{ClO}_2$. A rate constant of $k_1 = 3.5 \times 10^7 \text{M}^{-1} \text{s}^{-1}$ at pH 12.1 was derived. In comparing rate constants for the reactions of $\text{ClO}_2 + X$ with the rate constants for the analogous reactions of $\text{NO}_2 + X$, they found that $\text{ClO}_2$ reactions were faster than the $\text{NO}_2$ reactions, except when $X = \text{SO}_3^{2-}$. From the comparison, the rate constant for $\text{NO}_2 + \text{SO}_3^{2-}$ would be expected to be at least an order of magnitude slower than measured if it proceeded by the same mechanism as the other reactions. They suggested that the $\text{NO}_2 + \text{SO}_3^{2-}$ reaction was not proceeding via outer-sphere electron transfer.

A more detailed investigation of the reaction of $\text{NO}_2$ with $\text{S(IV)}$ was later reported by Clifton and co-workers. The reaction was studied over a range of pH 5.3 to 13 using pulse radiolysis to generate aqueous $\text{NO}_2$. The reaction products were not measured. The observed pH dependence in the rate constant did not appear to be directly related to the relative proportions of $\text{HSO}_3$ and $\text{SO}_3^{2-}$. It was proposed that the reaction proceeds via one or more intermediates to form stable products.

In an attempt of clarify the reaction mechanism, we have investigated the products of the reaction of $\text{NO}_2$ with $\text{SO}_3^{2-}$ and $\text{HSO}_3^-$. Gas mixtures containing $\text{NO}_2$ were flowed over solutions of $\text{SO}_3^{2-}$ and $\text{HSO}_3^-$ and the solutions were periodically analyzed.
Experimental Section

The reaction was studied by placing 10 mL of a solution containing sulfite or hydrogen sulfite in a small long-necked bulb. The solution was stirred at about 200 rpm with a magnetic stirrer and had a surface area of approximately 9 cm². A gas mixture of NO₂ in N₂, or NO₂ in N₂ and O₂, was flowed through an inner tube coaxial with the neck of the bulb, over the top of the solution, and out of the neck. The gas flow rate was generally 1.4 L/min. A few measurements were made at other flow rates to observe the effect of flow rate on NO₂ absorption. This flow rate kept the amount of NO₂ absorbed by the solution to less than 20% of the initial concentration. The inlet and outlet concentrations could be alternately monitored with a Thermoelectron 14A chemiluminescent NOₓ analyzer. The solutions were prepared by dissolving sodium sulfite or sodium metabisulfite in house deionized water had been passed through another deionizing column, stored in a plastic container, and degassed with argon. The gas mixtures were prepared by mixing 2.6% NO₂ in N₂ (Matheson) with research grade nitrogen, and oxygen when desired. The initial S(IV) concentration was generally 1.0 M, although a few measurements were made at lower concentrations. The sodium sulfite solutions were generally prepared with 0.8 M sodium hydroxide. The ionic strengths of the solutions were in the range of 3.8 to 6.1 M. Reagent grade chemicals were used in solution preparation.

The effect of NO₂ concentration was investigated using NO₂ concentrations of 900 to 9000 ppm. At 1000 ppm NO₂, the equilibrium concentration of N₂O₄ is about 7 ppm. The oxygen concentration in the gas mixtures ranged from 0 to 5%. The majority of the studies were done at 20°C, with a few measurements made at higher temperatures. For analysis, the solution was sampled by collecting a small amount in a 1 mm diameter glass tube. Raman spectra of the samples were obtained over a range of 600 - 1400 cm⁻¹. The amounts of the ions present in solution were determined by comparison with an internal reference such as carbonate, perchlorate, or boric acid.
Results

A typical Raman spectrum of an alkaline reaction mixture is shown in Figure 1. The spectrum is of a solution of 1 M $\text{SO}_3^{2-}$ + 1 M $\text{NaOH}$ + 0.03 M $\text{ClO}_4^-$ exposed to 5000 ppm $\text{NO}_2$ in $\text{N}_2$ for 1 hour. The peaks shown are $\text{NO}_2^-$ at 818 cm$^{-1}$, $\text{ClO}_4^-$ at 934 cm$^{-1}$, $\text{SO}_3^{2-}$ at 967 cm$^{-1}$, $\text{SO}_4^{2-}$ at 981 cm$^{-1}$, $\text{NO}_3^-$ at 1050 cm$^{-1}$, and $\text{S}_2\text{O}_6^{2-}$ at 1092 cm$^{-1}$. A Raman spectrum of a reaction mixture of 1 M acetate + 0.9 M $\text{HSO}_3^-$ at pH 5.5 exposed to 5000 ppm $\text{NO}_2$ in $\text{N}_2$ for 0.5 hour is shown in Figure 2. The peaks in the spectrum include acetic acid at 893 cm$^{-1}$, acetate at 930 cm$^{-1}$, $\text{SO}_4^{2-}$ at 981 cm$^{-1}$, $\text{HSO}_3^-$ at 1023 and 1052 cm$^{-1}$, and nitrogen sulfonates at 1083 cm$^{-1}$ and 1097 cm$^{-1}$. The peaks for the latter compounds are labeled as HADS and ATS for hydroxyimidodisulfate and nitridotrisulfonate, respectively. Nitrite is absent in detectable quantities because of its conversion to nitrogen sulfonates. Nitrate and dithionate may be present, but their peaks are masked by the $\text{HSO}_3^-$ peak and the ATS peak. Because of this, only high pH conditions were used for product determination. The Raman spectra were analyzed to obtain profiles of concentration vs time for the conditions studied. There is some uncertainty in the determination of low concentrations of the products, particularly with species such as $\text{NO}_2^-$ that do not Raman scatter strongly. Therefore, slopes were found to be a better measure of the reaction progress than the individual concentration measurements. Values for the slopes were obtained by linear least squares fits and the values obtained for the change in concentration with time are listed in Table II. The build up of $\text{SO}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ generally agree quite well with the loss of $\text{SO}_3^{2-}$, indicating good mass balance for sulfur.

The effect of the $\text{NO}_2$ gas phase concentration on the reaction is illustrated in Figure 3. The rate of oxidation from the disappearance of $\text{SO}_3^{2-}$ shows a linear dependence on the $\text{NO}_2$ concentration. The $\text{SO}_4^{2-}/\text{S}_2\text{O}_6^{2-}$ ratio is unaffected by the amount of $\text{NO}_2$ in the gas phase. The $\text{NO}_2^-/\text{SO}_4^{2-}$ ratio apparently decreases slightly above 5000 ppm $\text{NO}_2$, but this may be within experimental error and not significant. There is a marked effect of oxygen on the oxidation of $\text{SO}_3^{2-}$. Figure 4 shows the increase in the S(IV) oxidation rates with and without oxygen as a function of gas phase $\text{NO}_2$ concentration. The lower line was obtained without
oxygen and the upper line was obtained with 3% oxygen in the gas mixture. The S(IV) oxidation rate due to oxygen without any NO₂ present is much less than what would be obtained by extrapolating the NO₂ + O₂ data to zero NO₂ concentration. This suggests that NO₂ acts as an initiator for S(IV) oxidation by O₂.

The effect of oxygen in the gas mixture on the reaction chemistry is shown in Figure 5. The SO₄²⁻/S₂O₆²⁻ ratio shows a fairly linear dependence on the gas phase concentration of oxygen. The effect of oxygen on the NO₂⁻/SO₄²⁻ ratio is less pronounced. The NO₂⁻ rate of production is relatively unaffected by oxygen, while the rate of SO₄²⁻ production increases.

The runs with SO₃²⁻ concentrations less than 1 M showed significantly more NO₃⁻ relative to NO₂⁻. This is due to the decrease in the rate of the NO₂ + SO₃²⁻ reaction relative to the NO₂ and N₂O₄ hydrolysis reactions. The runs done at higher temperatures had higher SO₄²⁻/S₂O₆²⁻ ratios than equivalent runs done at 20°C.

Discussion

Many of the previous studies did not fully take into consideration the formation of nitrogen sulfonates from the reaction of NO₂ with HSO₃⁻, and their influence on the solution chemistry.⁶ All of the studies that have performed product analysis have found nitrite ion. Once formed, nitrite ion can react with S(IV) under neutral or acidic conditions to produce hydroxyimidodisulfate¹⁴,¹⁵ (referred to as hydroxylamine disulfonate, or HADS, in some early publications) and other nitrogen sulfonates. The H⁺ production observed by Lee and Schwartz⁸ that occurred after addition of NO₂ to solution could be due, at least in part, to hydrolysis of nitrogen sulfonates. Under suitable conditions, the nitrogen sulfonates can hydrolyze or oxidize during ion chromatographic analysis to yield sulfate, possibly giving inaccurate product distributions.

A comparison of the rate constants for the reaction of NO₂ with S(IV) and reaction (2) is given in Table I. For the latter reaction, bubbling studies and experiments in which NO₂ is generated in solution are in reasonably good agreement. This is not the case for the values of
the NO₂ + S(IV). Experiments in which the S(IV) solution is contacted with gaseous NO₂ have yielded values of the rate constant that are significantly less that those obtained by pulse radiolysis, in which the NO₂ is generated in solution. This suggests that there may be an intermediate step between absorption of NO₂ and its reaction with S(IV). One possibility is a hydration process that is the limiting step in the bubbling experiments.

\[
\text{NO}_2 (\text{gas}) \overset{\text{<==>}}{\longrightarrow} \text{NO}_2 (\text{absorbed}) \overset{\text{<==>}}{\longrightarrow} \text{NO}_2 (\text{hydrated}) \quad (4)
\]

This could be analogous to the NO hydration process discussed by Nunes and Powell\textsuperscript{16} in their study of NO + SO₃²⁻. The hydration process could be reasonably independent of pH, as observed by Lee and Schwartz.\textsuperscript{8} The hydrated NO₂ could then react with SO₃²⁻ at the rate observed by Clifton et al.\textsuperscript{11}

A viable mechanism for the reaction of NO₂ with S(IV) must be capable of accommodating the observations of previous studies and this study. These include the presence of dithionate in the reaction products, the pH dependence obtained by Clifton et al.,\textsuperscript{11} and the exceptionally fast rate constant when compared to the ClO₂ + SO₃²⁻ reaction. As noted by Clifton et al.,\textsuperscript{11} the ClO₂ + SO₃²⁻ reaction proceeds primarily by electron transfer\textsuperscript{17} and an electron transfer reaction between NO₂ and SO₃²⁻ would be expected to be slower than the observed rate constant. Sarala et al.\textsuperscript{18} discuss electron transfer reactions between SO₃²⁻ and metal ion complexes and their relationship to Marcus theory. They note that SO₃²⁻ reacts more quickly with MnO₄⁻ than would be expected by outer-sphere electron transfer. They speculate that this could occur by formation of a transient intermediate, which could also occur in the NO₂ + SO₃²⁻ reaction.

From the results of the studies done to date, we propose two potential reaction schemes. Since it is unlikely that an electron transfer reaction can occur quickly enough to be responsible for the observed reaction rate, one possible mechanism involves formation of an intermediate which rapidly decomposes to nitrite ion and sulfite radical.

\[
\text{NO}_2 + \text{SO}_3^{2-} \rightarrow \text{intermediate} \rightarrow \text{NO}_2^- + \text{SO}_3^{2-} \quad (5)
\]

\[
\text{NO}_2 + \text{SO}_3^{2-} \rightarrow \text{NO}_2^- + \text{SO}_3 \quad (6)
\]
\[ \text{SO}_3^{-} + \text{SO}_3^{-} \rightarrow \text{SO}_3 + \text{SO}_3^{2-} \]  \hspace{1cm} (7)
\[ \text{SO}_3^{-} + \text{SO}_3^{-} \rightarrow \text{S}_2\text{O}_6^{2-} \]  \hspace{1cm} (8)
\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{H}^{+} + \text{SO}_4^{2-} \]  \hspace{1cm} (9)

A second possible mechanism is similar to that proposed by Clifton et al.\textsuperscript{11}
\[ \text{NO}_2 + \text{SO}_3^{2-} \rightarrow (\text{O}_2\text{NSO}_3)^{2-} \]  \hspace{1cm} (10)
\[ \text{NO}_2 + (\text{O}_2\text{NSO}_3)^{2-} \rightarrow 2\text{NO}_2^{-} + \text{SO}_3 \]  \hspace{1cm} (11)
\[ \text{NO}_2 + (\text{O}_2\text{NSO}_3)^{2-} \rightarrow \text{NO}_2^{-} + (\text{O}_2\text{NSO}_3)^{-} \]  \hspace{1cm} (12)
\[ \text{SO}_3^{2-} + (\text{O}_2\text{NSO}_3)^{2-} \rightarrow \text{NO}_2^{-} + \text{S}_2\text{O}_6^{2-} \]  \hspace{1cm} (13)
\[ \text{SO}_3^{2-} + (\text{O}_2\text{NSO}_3)^{-} \rightarrow \text{SO}_4^{2-} + (\text{ONS}O_3)^{-} \]  \hspace{1cm} (14)
\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow 2\text{H}^{+} + \text{SO}_4^{2-} \]  \hspace{1cm} (15)
\[ \text{HSO}_3^{-} + (\text{ONS}O_3)^{-} \rightarrow \text{HON}(\text{SO}_3)^{-}_2 \]  \hspace{1cm} (16)

For either mechanism, we attribute the formation of NO$_3^-$ primarily to NO$_2$ and N$_2$O$_4$
hydrolysis, reactions (2) and (17).
\[ \text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow 2\text{H}^{+} + \text{NO}_2^{-} + \text{NO}_3^{-} \]  \hspace{1cm} (17)

This is supported by the increase in NO$_3^-$ concentration with increasing NO$_2$ concentration.

While the reaction of NO$_2$ with SO$_3^{2-}$ does appear to proceed too rapidly for electron
transfer, there is no definite evidence that an intermediate with a substantial lifetime is
involved. We suggest that the H$^+$ generation observed by Lee and Schwartz\textsuperscript{8} after the end of
NO$_2$ addition could be attributed to the formation and hydrolysis of hydroxyimidodisulfate
and other nitrogen sulfonates.\textsuperscript{14,15}
\[ \text{HNO}_2 + \text{HSO}_3^{-} \rightarrow \text{ONSO}_3^{-} + \text{H}_2\text{O} \]  \hspace{1cm} (18)
\[ \text{ONSO}_3^{-} + \text{HSO}_3^{-} \rightarrow \text{HON}(\text{SO}_3)^{-}_2 \]  \hspace{1cm} (19)
\[ \text{HON}(\text{SO}_3)^{-}_2 + \text{H}_2\text{O} \rightarrow \text{HONH}(\text{SO}_3)^{-} + \text{H}^{+} + \text{SO}_4^{2-} \]  \hspace{1cm} (20)

The second mechanism presented here does not provide a well-established pathway for
dithionate production. In contrast, the process by which S$_2$O$_6^{2-}$ is formed from SO$_3^{-}$ has been
studied by several investigators.\textsuperscript{19-22} The sulfite radical undergoes second order decay into two
channels (reactions 7 and 8). The SO$_3$ produced reacts rapidly with H$_2$O to form SO$_4^{2-}$. 
(reaction 9). Hayon et al. obtained a value of $k = 5.5 \pm 1.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ for the second order decay rate constant for $\text{SO}_3^{2-}$. However, the branching ratio for reactions 7 and 8 has not been determined. Eriksen noted that less $\text{S}_2\text{O}_6^{2-}$ is produced at pH 7.55 than pH 4.1.

Since we find no substantive evidence for the second mechanism discussed and it does not provide a good explanation for the observed product distribution or the effect of oxygen, we believe the first mechanism is correct. Using this mechanism, our results can be used to determine the branching ratio of reactions (7) and (8). To do this we assume that the rate of reaction (6) is small compared to reaction (5) and reactions (7) and (8). From the redox couples for the species involved in reactions (5) and (6), listed in Table III, it can be seen that reaction (6) has a more favorable potential than reaction (5).

To verify this assumption, we take a value of $-d[\text{SO}_3^{2-}] / dt = -3 \times 10^{-5} \text{ M s}^{-1}$ (see Table I) as a typical rate for reaction (5) under the conditions studied. A value of $[\text{NO}_2^-] = 1 \times 10^{-12} \text{ M}$ is obtained using this rate with $k_5 = 3 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$ and $[\text{SO}_3^{2-}] = 1 \text{ M}$. Using the steady-state approximation for $\text{SO}_3^{2-}$ and the assumption that reaction (6) is not important, we can obtain an estimate of $[\text{SO}_3^{2-}] = 2 \times 10^{-7} \text{ M}$. With this concentration, the rate of reaction (6) will be small compared to reactions (5), (7), and (8) even if $k_6 = 1 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$, near the diffusion limit. So, most of the $\text{SO}_3^{2-}$ will react via (7) and (8), rather than (6). On this basis, we can use the concentrations of $\text{SO}_4^{2-}$ and $\text{S}_2\text{O}_6^{2-}$ that we have measured to calculate a value of $1.8 \pm 0.2$ for $k_7/k_8$ at $20^\circ\text{C}$ and in $0.8 \text{ M NaOH}$. Using the rate constant measured by Hayon et al., this ratio yields values of $k_7 = 3.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$ and $k_8 = 2.0 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$. The measurements obtained at higher temperatures suggest that the ratio $k_7/k_8$ increases with temperature. Since the temperature dependence of most of the reactions in solution is unknown, it is difficult to quantify the temperature effect. We were not able to obtain a reliable measure of this ratio from the experiments done at pH 8 and below because of the appearance of nitrogen sulfonates in the reaction mixtures. Sulfate is produced in the reactions forming some of these compounds.

At the low reactant concentrations used by Lee and Schwartz, the assumptions used above to determine $k_7/k_8$ would not necessarily hold, and more of the $\text{SO}_3^{2-}$ may react with
NO₂ or the nitrogen sulfonates, yielding less S₂O₆²⁻. They obtained stoichiometric ratios of 
\[ \frac{[\text{NO}_2^-]}{[\text{S(IV)}]}_0 = 1.5 \pm 0.4 \] and \[ \frac{[\text{H}^+]}{[\text{S(IV)}]}_0 = 2.5 \pm 0.4 \]. The value of the first ratio could be 
explained if reaction (6) becomes competitive with reaction (5) at low S(IV) concentrations. We 
are not aware of any measurements of the rate of reaction (6). H⁺ production comes from 
reaction (9) as well as reactions involving HSO₃⁻.

\[
\text{NO}_2^- + \text{HSO}_3^- \rightarrow \text{NO}_2^- + \text{SO}_3^{2-} + \text{H}^+ \tag{21}
\]

These reactions should be fairly rapid. At low pH conditions, hydrolysis of nitrogen sulfonates 
will also contribute to hydrogen ion production. NO₂ is a sufficiently strong oxidant²³ to 
oxidize hydroxyimidodisulfate to nitrosodisulfonate,²⁴,²⁵ so there are a number of possible 
reaction pathways available.

Adding O₂ to the gas mixture passed over the sulfite solution had the effect of 
increasing the rate of sulfite oxidation and increasing the \([\text{SO}_4^{2-}]/[\text{S}_2\text{O}_6^{2-}]\) ratio. In the absence 
of NO₂, the rate of sulfite oxidation is very small, much less than the rate of sulfite oxidation 
due to NO₂ alone at a much lower concentration. This indicates that NO₂ contributes to sulfite 
autoxidation. While the data in Figure 4 have been linearly extrapolated to zero NO₂ 
concentration, the actual S(IV) oxidation rate would be expected to curve downward toward 
zero as the NO₂ concentration approaches zero. As the NO₂ concentration is increased to the 
point where it can provide a sufficient concentration of radicals to sustain the O₂ -S(IV) 
oxidation process, the overall rate would be expected to increase substantially.

Huie and Neta²⁶ indicate that O₂ reacts rapidly with SO₃⁻⁻ to form SO₅⁻⁻. The SO₅²⁻ 
formed can react with sulfite ion.¹⁹

\[
\begin{align*}
\text{SO}_5^{2-} + \text{SO}_3^{2-} & \rightarrow \text{SO}_5^{2-} + \text{SO}_3^{2-} \tag{22} \\
\text{SO}_5^{2-} + \text{SO}_3^{2-} & \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \tag{23} \\
\text{SO}_5^{2-} + \text{H}^+ & \leftrightarrow \text{HSO}_5^- \tag{24} \\
\text{HSO}_5^- + \text{SO}_3^{2-} & \rightarrow \text{H}^+ + 2 \text{SO}_4^{2-} \tag{25} \\
\text{SO}_4^{2-} + \text{SO}_3^{2-} & \rightarrow \text{SO}_4^{2-} + \text{SO}_3^{2-} \tag{26} \\
\text{SO}_4^{2-} + \text{NO}_2^- & \rightarrow \text{SO}_4^{2-} + \text{NO}_2 \tag{27}
\end{align*}
\]
HSO$_5^-$ (Caro's acid) will react rapidly with $\text{S(IV)}$.$^{27}$ While the chemistry associated with $\text{SO}_5^{2-}$ and $\text{SO}_4^{2-}$ has not been fully established,$^{28}$ their involvement in the chemistry appears to enhance the $\text{NO}_2^- \text{-SO}_3^{2-}$ oxidation process and increase the amount of sulfate and nitrate in solution. The effects of oxygen on the $\text{NO}_2^- + \text{SO}_3^{2-}$ reaction would appear to be in better agreement with the first mechanism presented rather than the second mechanism, since the latter does not provide an established process to explain the increased $\text{S(IV)}$ oxidation. The additional $\text{NO}_3^-$ may be formed by oxidation of $\text{NO}_2^-$ by $\text{SO}_5^{2-}$.

We made an attempt to identify intermediates in solution by collecting Raman spectra of flowing solutions of $\text{SO}_3^{2-}$ through which $\text{NO}_2$ had been bubbled through. The time delay between bubbling and observation was less than 5 seconds. No unidentified peaks that might be associated with an intermediate were observed. The method is not particularly sensitive and an intermediate may be too reactive to be detectable after 5 seconds.

In conclusion, we find no compelling evidence for the formation of a long-lived intermediate from the reaction of $\text{NO}_2^- + \text{SO}_3^{2-}$. The reaction appears to proceed primarily to form $\text{NO}_3^-$ and $\text{SO}_4^{2-}$. The presence of $\text{O}_2$ in the $\text{NO}_2/N_2$ mixture increases the rate of oxidation of $\text{SO}_3^{2-}$ and the increase is much greater than the oxidation caused by $\text{O}_2/N_2$ mixtures without $\text{NO}_2$. Using the first reaction mechanism presented and the product distribution observed in our experiments, we obtain a measure of the branching ratio for reactions (7) and (8) of $k_7/k_8 = 1.8 \pm 0.2$.

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References

### Table I

Reported Values of the Rate Constant for $\text{NO}_2\text{(g)} + \text{S(IV)} \rightarrow \text{products}$

<table>
<thead>
<tr>
<th>Study</th>
<th>pH</th>
<th>$k \text{ (M}^{-1} \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Takeuchi et al$^3$</td>
<td>$-9$</td>
<td>$6.6 \times 10^5$</td>
</tr>
<tr>
<td></td>
<td>$-4$</td>
<td>$1.5 \times 10^4$</td>
</tr>
<tr>
<td>Lee and Schwartz$^8$</td>
<td>5.8 - 6.4</td>
<td>$2 \times 10^6$</td>
</tr>
<tr>
<td>Huie and Neta$^{10}$</td>
<td>12.1</td>
<td>$-3.5 \times 10^7$</td>
</tr>
<tr>
<td>Clifton et al$^{11}$</td>
<td>5.3</td>
<td>$1.24 \times 10^7$</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>$2.95 \times 10^7$</td>
</tr>
</tbody>
</table>

Reported Values of the Rate Constant for $\text{NO}_2\text{(g)} + \text{NO}_2\text{(g)} + \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{NO}_2^- + \text{NO}_3^-$

<table>
<thead>
<tr>
<th>Study</th>
<th>pH</th>
<th>$k \text{ (M}^{-1} \text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Takeuchi et al$^3$</td>
<td></td>
<td>$0.74 \times 10^8$</td>
</tr>
<tr>
<td>Lee and Schwartz$^9$</td>
<td>5.8 - 6.4</td>
<td>$1.0 \times 10^8$</td>
</tr>
<tr>
<td>Treinin and Hayon$^a$</td>
<td></td>
<td>$0.47 \times 10^8 + \text{first order term}$</td>
</tr>
<tr>
<td>Gratzel et al$^a$</td>
<td></td>
<td>$0.65 \times 10^8$</td>
</tr>
<tr>
<td>Komiyama and Inoue$^a$</td>
<td></td>
<td>$0.42 \times 10^8$</td>
</tr>
</tbody>
</table>

$a$: from Table V in Lee and Schwartz$^9$
Table II
Rate of Change of Concentration in M s$^{-1}$

<table>
<thead>
<tr>
<th>Condition</th>
<th>SO$_3^{2-}$</th>
<th>SO$_4^{2-}$</th>
<th>S$_2$O$_6^{2-}$</th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppm NO$_2$</td>
<td>-6.33e-6</td>
<td>2.57e-6</td>
<td>1.83e-6</td>
<td>7.15e-6</td>
<td>0.47e-6</td>
</tr>
<tr>
<td>3000 ppm NO$_2$</td>
<td>-22.9e-6</td>
<td>9.99e-6</td>
<td>5.63e-6</td>
<td>2.85e-6</td>
<td>1.71e-6</td>
</tr>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-32.6e-6</td>
<td>13.8e-6</td>
<td>8.94e-6</td>
<td>38.4e-6</td>
<td>2.36e-6</td>
</tr>
<tr>
<td>7000 ppm NO$_2$</td>
<td>-4.95e-5</td>
<td>2.16e-5</td>
<td>1.28e-5</td>
<td>5.24e-5</td>
<td>0.65e-5</td>
</tr>
<tr>
<td>9000 ppm NO$_2$</td>
<td>-6.39e-5</td>
<td>3.27e-5</td>
<td>1.57e-5</td>
<td>7.35e-5</td>
<td>1.18e-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>SO$_3^{2-}$</th>
<th>SO$_4^{2-}$</th>
<th>S$_2$O$_6^{2-}$</th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppm NO$_2$</td>
<td>-36.6e-6</td>
<td>32.9e-6</td>
<td>1.87e-6</td>
<td>10.9e-6</td>
<td>0.48e-6</td>
</tr>
<tr>
<td>3000 ppm NO$_2$</td>
<td>-5.95e-5</td>
<td>4.91e-5</td>
<td>0.60e-5</td>
<td>3.86e-5</td>
<td>0.31e-5</td>
</tr>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-8.12e-5</td>
<td>6.45e-5</td>
<td>0.85e-5</td>
<td>5.08e-5</td>
<td>0.45e-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>SO$_3^{2-}$</th>
<th>SO$_4^{2-}$</th>
<th>S$_2$O$_6^{2-}$</th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-5.58e-5</td>
<td>3.43e-5</td>
<td>1.06e-5</td>
<td>6.10e-5</td>
<td>0.30e-5</td>
</tr>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-6.64e-5</td>
<td>4.62e-5</td>
<td>1.01e-5</td>
<td>5.29e-5</td>
<td>0.30e-5</td>
</tr>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-10.7e-5</td>
<td>8.89e-5</td>
<td>0.84e-5</td>
<td>5.08e-5</td>
<td>0.41e-5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>SO$_3^{2-}$</th>
<th>SO$_4^{2-}$</th>
<th>S$_2$O$_6^{2-}$</th>
<th>NO$_2^-$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-4.34e-5</td>
<td>3.09e-5</td>
<td>0.52e-5</td>
<td>2.04e-5</td>
<td>0.83e-5</td>
</tr>
<tr>
<td>5000 ppm NO$_2$</td>
<td>-7.33e-5</td>
<td>5.74e-5</td>
<td>0.75e-5</td>
<td>3.40e-5</td>
<td>0.59e-5</td>
</tr>
<tr>
<td>Condition</td>
<td>5000 ppm NO₂</td>
<td>1 M SO₃²⁻</td>
<td>no O₂</td>
<td>38°C</td>
<td>5000 ppm NO₂</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>--------------</td>
<td>-----------</td>
<td>------</td>
<td>------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td>-5.04e-5</td>
<td>2.68e-5</td>
<td>1.17e-5</td>
<td>4.37e-5</td>
<td>4.34e-5</td>
</tr>
<tr>
<td>Redox Couple</td>
<td>$E^0$ (V)</td>
<td>Reference</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
<td>-----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{NO}_2^- / \text{NO}_2^+$</td>
<td>1.04</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SO}_3^{2-} / \text{SO}_3^{2-}$</td>
<td>0.72</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{SO}_3^-/ \text{SO}_3^-$</td>
<td>0.25</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure Captions

Figure 1. Raman spectrum of 1 M SO$_3^{2-}$ exposed to 5000 ppm NO$_2$ for 1 hour.

Figure 2. Raman spectrum of a reaction mixture of NO$_2$ + 0.9 M HSO$_3^-$ in 1 M acetate.

Figure 3. Effect of gas phase NO$_2$ concentration on oxidation rate and reaction products.

Figure 4. S(IV) oxidation rate as a function of NO$_2$ concentration with and without O$_2$.

Figure 5. Effect of gas phase O$_2$ concentration on ratios of reaction products.
Figure 3
Figure 4

Rate of S(IV) Oxidation ($10^5$ M/s)

- □ No Oxygen
- ○ 3% Oxygen

[NO$_2^-$] (ppm)

XBL 919-2068
Figure 5

- \( \text{SO}_4^{2-}/\text{S}_2\text{O}_6^{2-} \)
- \( \text{NO}_2^-/\text{SO}_4^{2-} \)