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Authors

Wang, Y.Z.

Littlejohn, D.

Chang, S.G.

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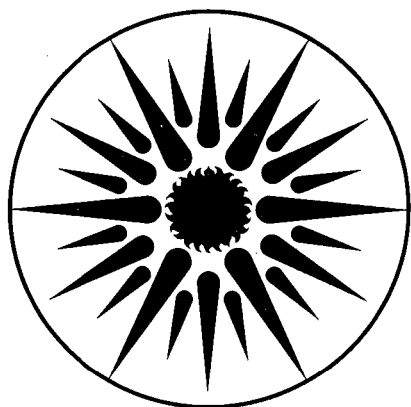
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Oxidation of Aqueous Sulfite Ion by Nitrogen Dioxide

Y.Z. Wang[†], David Littlejohn, and S.G. Chang^{*}

Lawrence Berkeley Laboratory
Energy and Environment Division
Berkeley, California 94720

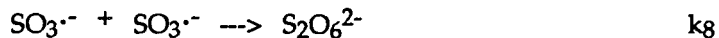
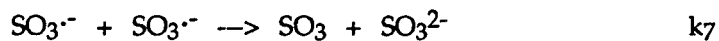
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[†] On leave from the Research Center for Environmental Sciences, Academia Sinica, Beijing, Peoples Republic of China.

^{*} 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



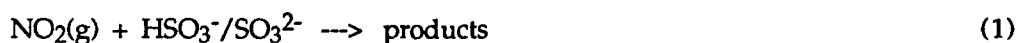
of $k_7/k_8 = 1.8 \pm 0.2$ at 20°C in 0.8 M NaOH and derive values of $k_7 = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $k_8 = 2.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

Introduction

The reaction of nitrogen dioxide with sulfite ion is important in both air pollution chemistry and in control of flue gas emissions.¹ There have been a number of studies on this reaction system, yet the details of the reaction mechanism have not been clearly established.²⁻¹⁰ 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. Nash² determined the relative rate of reaction involving NO₂ 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 NO₂.

Takeuchi et al³ used a plane interface contactor to calculate reaction rates from the observed removal of NO₂ from the gas phase by sulfite and hydrogen sulfite solutions. Second order rate constants for the following reactions are listed in Table I.



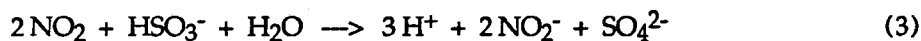
The second report by Takeuchi and coworkers⁴ found that oxygen slowed the rate of absorption of NO₂ by sulfite solutions, and that antioxidants counteracted this effect.

Sato et al⁵ investigated the products of the reaction of NO₂ 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.⁶

Rosenberg and Grotta⁷ observed the oxidation by NO₂ and NO of dissolved sulfur dioxide in calcium hydroxide slurries. They found that NO inhibited oxidation and that NO₂ promoted oxidation. Anionic products other than sulfate were not analyzed.

Lee and Schwartz⁸ investigated the reaction of NO₂ and S(IV) (where S(IV) collectively represents SO₃²⁻ and HSO₃⁻) by bubbling a low concentration of NO₂ in N₂ 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



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 Schwartz⁹ also studied the dissolution of 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.³

Huie and Neta¹⁰ included the reaction of NO_2 with SO_3^{2-} in their pulse radiolysis study of one electron transfer reactions of NO_2 and ClO_2 . A rate constant of $k_1 = \sim 3.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH 12.1 was derived. In comparing rate constants for the reactions of $\text{ClO}_2 + \text{X}$ with the rate constants for the analogous reactions of $\text{NO}_2 + \text{X}$, they found that ClO_2 reactions were faster than the NO_2 reactions, except when $\text{X} = \text{SO}_3^{2-}$. 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 NO_2 with S(IV) was later reported by Clifton and co-workers¹¹. The reaction was studied over a range of pH 5.3 to 13 using pulse radiolysis to generate aqueous 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 HSO_3^- and SO_3^{2-} . It was proposed that the reaction proceeds via one or more intermediates to form stable products.

In an attempt to clarify the reaction mechanism, we have investigated the products of the reaction of NO_2 with SO_3^{2-} and HSO_3^- . Gas mixtures containing NO_2 were flowed over solutions of SO_3^{2-} and 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 cm^2 . A gas mixture of NO_2 in N_2 , or NO_2 in N_2 and O_2 , 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 NO_2 absorption. This flow rate kept the amount of NO_2 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 NO_x 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% NO_2 in N_2 (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 NO_2 concentration was investigated using NO_2 concentrations of 900 to 9000 ppm. At 1000 ppm NO_2 , the equilibrium concentration of N_2O_4 is about 7 ppm.¹² 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 $600\text{--}1400 \text{ cm}^{-1}$. The amounts of the ions present in solution were determined by comparison with an internal reference such as carbonate, perchlorate, or boric acid.¹³

Results

A typical Raman spectrum of an alkaline reaction mixture is shown in Figure 1. The spectrum is of a solution of 1 M SO_3^{2-} + 1 M NaOH + .03 M ClO_4^- exposed to 5000 ppm NO_2 in N_2 for 1 hour. The peaks shown are NO_2^- at 818 cm^{-1} , ClO_4^- at 934 cm^{-1} , SO_3^{2-} at 967 cm^{-1} , SO_4^{2-} at 981 cm^{-1} , 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 HSO_3^- at pH 5.5 exposed to 5000 ppm NO_2 in 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} , SO_4^{2-} at 981 cm^{-1} , 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 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 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 SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$ generally agree quite well with the loss of SO_3^{2-} , indicating good mass balance for sulfur.

The effect of the NO_2 gas phase concentration on the reaction is illustrated in Figure 3. The rate of oxidation from the disappearance of SO_3^{2-} shows a linear dependence on the NO_2 concentration. The $\text{SO}_4^{2-}/\text{S}_2\text{O}_6^{2-}$ ratio is unaffected by the amount of NO_2 in the gas phase. The $\text{NO}_2^-/\text{SO}_4^{2-}$ ratio apparently decreases slightly above 5000 ppm NO_2 , but this may be within experimental error and not significant. There is a marked effect of oxygen on the oxidation of SO_3^{2-} . Figure 4 shows the increase in the S(IV) oxidation rates with and without oxygen as a function of gas phase 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 NO_2 present is much less than what would be obtained by extrapolating the $\text{NO}_2 + \text{O}_2$ data to zero NO_2 concentration. This suggests that NO_2 acts as an initiator for S(IV) oxidation by O_2 .

The effect of oxygen in the gas mixture on the reaction chemistry is shown in Figure 5. The $\text{SO}_4^{2-}/\text{S}_2\text{O}_6^{2-}$ ratio shows a fairly linear dependence on the gas phase concentration of oxygen. The effect of oxygen on the $\text{NO}_2^-/\text{SO}_4^{2-}$ ratio is less pronounced. The NO_2^- rate of production is relatively unaffected by oxygen, while the rate of SO_4^{2-} production increases.

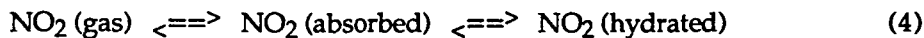
The runs with SO_3^{2-} concentrations less than 1 M showed significantly more NO_3^- relative to NO_2^- . This is due to the decrease in the rate of the $\text{NO}_2 + \text{SO}_3^{2-}$ reaction relative to the NO_2 and N_2O_4 hydrolysis reactions. The runs done at higher temperatures had higher $\text{SO}_4^{2-}/\text{S}_2\text{O}_6^{2-}$ 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 NO_2 with HSO_3^- , 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 hydroxyimidodisulfate^{14,15} (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 NO_2 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 NO_2 with S(IV) and reaction (2) is given in Table I. For the latter reaction, bubbling studies and experiments in which NO_2 is generated in solution are in reasonably good agreement. This is not the case for the values of

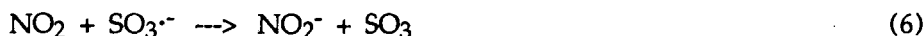
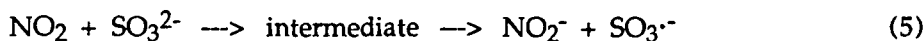
the $\text{NO}_2 + \text{S(IV)}$. Experiments in which the S(IV) solution is contacted with gaseous NO_2 have yielded values of the rate constant that are significantly less than those obtained by pulse radiolysis, in which the NO_2 is generated in solution. This suggests that there may be an intermediate step between absorption of NO_2 and its reaction with S(IV) . One possibility is a hydration process that is the limiting step in the bubbling experiments.



This could be analogous to the NO hydration process discussed by Nunes and Powell¹⁶ in their study of $\text{NO} + \text{SO}_3^{2-}$. The hydration process could be reasonably independent of pH, as observed by Lee and Schwartz.⁸ The hydrated NO_2 could then react with SO_3^{2-} at the rate observed by Clifton et al.¹¹

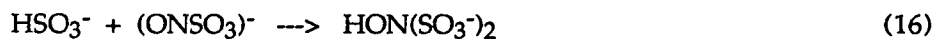
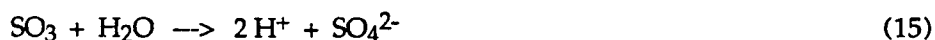
A viable mechanism for the reaction of NO_2 with S(IV) must be capable of accommodating the observations of previous studies and this study. These include the presence of dithionate in the reaction products, the pH dependence obtained by Clifton et al,¹¹ and the exceptionally fast rate constant when compared to the $\text{ClO}_2 + \text{SO}_3^{2-}$ reaction. As noted by Clifton et al,¹¹ the $\text{ClO}_2 + \text{SO}_3^{2-}$ reaction proceeds primarily by electron transfer¹⁷ and an electron transfer reaction between NO_2 and SO_3^{2-} would be expected to be slower than the observed rate constant. Sarala et al¹⁸ discuss electron transfer reactions between SO_3^{2-} and metal ion complexes and their relationship to Marcus theory. They note that SO_3^{2-} reacts more quickly with MnO_4^- 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 $\text{NO}_2 + \text{SO}_3^{2-}$ 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.





A second possible mechanism is similar to that proposed by Clifton et al.¹¹

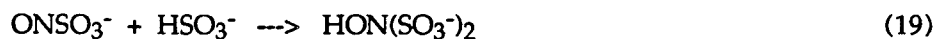
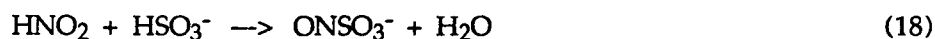


For either mechanism, we attribute the formation of NO_3^- primarily to NO_2 and N_2O_4 hydrolysis, reactions (2) and (17).



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 Schwartz⁸ after the end of NO_2 addition could be attributed to the formation and hydrolysis of hydroxyimidodisulfate and other nitrogen sulfonates.^{14,15}



The second mechanism presented here does not provide a well-established pathway for dithionate production. In contrast, the process by which $\text{S}_2\text{O}_6^{2-}$ is formed from $\text{SO}_3^{\cdot-}$ has been studied by several investigators.¹⁹⁻²² The sulfite radical undergoes second order decay into two channels (reactions 7 and 8). The SO_3 produced reacts rapidly with H_2O to form SO_4^{2-} .

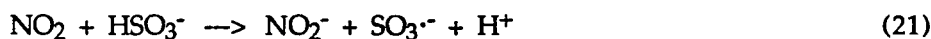
(reaction 9).¹⁸ Hayon et al¹⁹ obtained a value of $k = 5.5 \pm 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the second order decay rate constant for $\text{SO}_3^{\cdot-}$. However, the branching ratio for reactions 7 and 8 has not been determined. Eriksen²⁰ noted that less $\text{S}_2\text{O}_6^{2-}$ 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 $-\text{d}[\text{SO}_3^{2-}]/\text{dt} \sim 3 \times 10^{-5} \text{ M s}^{-1}$ (see Table I) as a typical rate for reaction (5) under the conditions studied. A value of $[\text{NO}_2] \sim 1 \times 10^{-12} \text{ M}$ is obtained using this rate with $k_5 \sim 3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $[\text{SO}_3^{2-}] \sim 1 \text{ M}$. Using the steady-state approximation for $\text{SO}_3^{\cdot-}$ and the assumption that reaction (6) is not important, we can obtain an estimate of $[\text{SO}_3^{\cdot-}] \sim 2 \times 10^{-7} \text{ M}$. 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 $\text{SO}_3^{\cdot-}$ will react via (7) and (8), rather than (6). On this basis, we can use the concentrations of SO_4^{2-} and $\text{S}_2\text{O}_6^{2-}$ that we have measured to calculate a value of 1.8 ± 0.2 for k_7/k_8 at 20°C and in 0.8 M NaOH. Using the rate constant measured by Hayon et al¹⁹, 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 Schwartz⁸, the assumptions used above to determine k_7/k_8 would not necessarily hold, and more of the $\text{SO}_3^{\cdot-}$ may react with

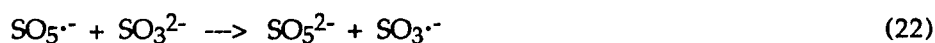
NO_2 or the nitrogen sulfonates, yielding less $\text{S}_2\text{O}_6^{2-}$. They obtained stoichiometric ratios of $[\text{NO}_2^-]/[\text{S(IV)}]_0 = 1.5 \pm 0.4$ and $[\text{H}^+]/[\text{S(IV)}]_0 = 2.5 \pm 0.4$. The value of the first ratio could be explained if reaction (6) becomes competitive with 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 HSO_3^- .



These reactions should be fairly rapid. At low pH conditions, hydrolysis of nitrogen sulfonates will also contribute to hydrogen ion production. NO_2 is a sufficiently strong oxidant²³ to oxidize hydroxyimidodisulfate to nitrosodisulfonate,^{24,25} so there are a number of possible reaction pathways available.

Adding O_2 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 NO_2 , the rate of sulfite oxidation is very small, much less than the rate of sulfite oxidation due to NO_2 alone at a much lower concentration. This indicates that NO_2 contributes to sulfite autoxidation. While the data in Figure 4 have been linearly extrapolated to zero NO_2 concentration, the actual S(IV) oxidation rate would be expected to curve downward toward zero as the NO_2 concentration approaches zero. As the NO_2 concentration is increased to the point where it can provide a sufficient concentration of radicals to sustain the O_2 -S(IV) oxidation process, the overall rate would be expected to increase substantially.

Huie and Neta²⁶ indicate that O_2 reacts rapidly with $\text{SO}_3^{\cdot-}$ to form $\text{SO}_5^{\cdot-}$. The $\text{SO}_5^{\cdot-}$ formed can react with sulfite ion.¹⁹



HSO_5^- (Caro's acid) will react rapidly with S(IV).²⁷ While the chemistry associated with $\text{SO}_5^{\cdot-}$ and $\text{SO}_4^{\cdot-}$ has not been fully established,²⁸ their involvement in the chemistry appears to enhance the NO_2 - 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 S(IV) oxidation. The additional NO_3^- may be formed by oxidation of NO_2^- by $\text{SO}_5^{\cdot-}$.

We made an attempt to identify intermediates in solution by collecting Raman spectra of flowing solutions of SO_3^{2-} through which 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 NO_2^- and $\text{SO}_3^{\cdot-}$. The presence of O_2 in the NO_2/N_2 mixture increases the rate of oxidation of SO_3^{2-} and the increase is much greater than the oxidation caused by O_2/N_2 mixtures without 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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Table I

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

study	pH	k ($\text{M}^{-1} \text{s}^{-1}$)
Takeuchi et al ³	~9	6.6×10^5
	~4	1.5×10^4
Lee and Schwartz ⁸	5.8 - 6.4	2×10^6
Huie and Neta ¹⁰	12.1	$\sim 3.5 \times 10^7$
Clifton et al ¹¹	5.3	1.24×10^7
	13	2.95×10^7

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

study	pH	k ($\text{M}^{-1} \text{s}^{-1}$)
Takeuchi et al ³		0.74×10^8
Lee and Schwartz ⁹	5.8 - 6.4	1.0×10^8
Treinin and Hayon ^a		$0.47 \times 10^8 + \text{first order term}$
Gratzel et al ^a		0.65×10^8
Komiyama and Inoue ^a		0.42×10^8

a: from Table V in Lee and Schwartz⁹

Table II

Condition	Rate of Change of Concentration in M s ⁻¹				
	SO ₃ ²⁻	SO ₄ ²⁻	S ₂ O ₆ ²⁻	NO ₂ ⁻	NO ₃ ⁻
1000 ppm NO ₂ 1 M SO ₃ ²⁻ no O ₂	-6.33e-6	2.57e-6	1.83e-6	7.15e-6	0.47e-6
3000 ppm NO ₂ 1 M SO ₃ ²⁻ no O ₂	-22.9e-6	9.99e-6	5.63e-6	2.85e-6	1.71e-6
5000 ppm NO ₂ 1 M SO ₃ ²⁻ no O ₂	-32.6e-6	13.8e-6	8.94e-6	38.4e-6	2.36e-6
7000 ppm NO ₂ 1 M SO ₃ ²⁻ no O ₂	-4.95e-5	2.16e-5	1.28e-5	5.24e-5	0.65e-5
9000 ppm NO ₂ 1 M SO ₃ ²⁻ no O ₂	-6.39e-5	3.27e-5	1.57e-5	7.35e-5	1.18e-5
1000 ppm NO ₂ 1 M SO ₃ ²⁻ 3% O ₂	-36.6e-6	32.9e-6	1.87e-6	10.9e-6	0.48e-6
3000 ppm NO ₂ 1 M SO ₃ ²⁻ 3% O ₂	-5.95e-5	4.91e-5	0.60e-5	3.86e-5	0.31e-5
5000 ppm NO ₂ 1 M SO ₃ ²⁻ 3% O ₂	-8.12e-5	6.45e-5	0.85e-5	5.08e-5	0.45e-5
5000 ppm NO ₂ 1 M SO ₃ ²⁻ 1% O ₂	-5.58e-5	3.43e-5	1.06e-5	6.10e-5	0.30e-5
5000 ppm NO ₂ 1 M SO ₃ ²⁻ 2% O ₂	-6.64e-5	4.62e-5	1.01e-5	5.29e-5	0.30e-5
5000 ppm NO ₂ 1 M SO ₃ ²⁻ 5% O ₂	-10.7e-5	8.89e-5	0.84e-5	5.08e-5	0.41e-5
5000 ppm NO ₂ 0.4 M SO ₃ ²⁻ 3% O ₂	-4.34e-5	3.09e-5	0.52e-5	2.04e-5	0.83e-5
5000 ppm NO ₂ 0.6 M SO ₃ ²⁻ 3% O ₂	-7.33e-5	5.74e-5	0.75e-5	3.40e-5	0.59e-5

5000 ppm NO ₂ no O ₂ 38°C	1 M SO ₃ ²⁻	-5.04e-5	2.68e-5	1.17e-5	4.37e-5	4.34e-5
5000 ppm NO ₂ no O ₂ 50°C	1 M SO ₃ ²⁻	-5.10e-5	2.78e-5	1.17e-5	4.57e-5	4.98e-5

Table III

Redox Couple	E° (V)	Reference
$\text{NO}_2 / \text{NO}_2^-$	1.04	23
$\text{SO}_3^{\cdot-} / \text{SO}_3^{2-}$	0.72	18
$\text{SO}_3 / \text{SO}_3^{\cdot-}$	0.25	23

Figure Captions

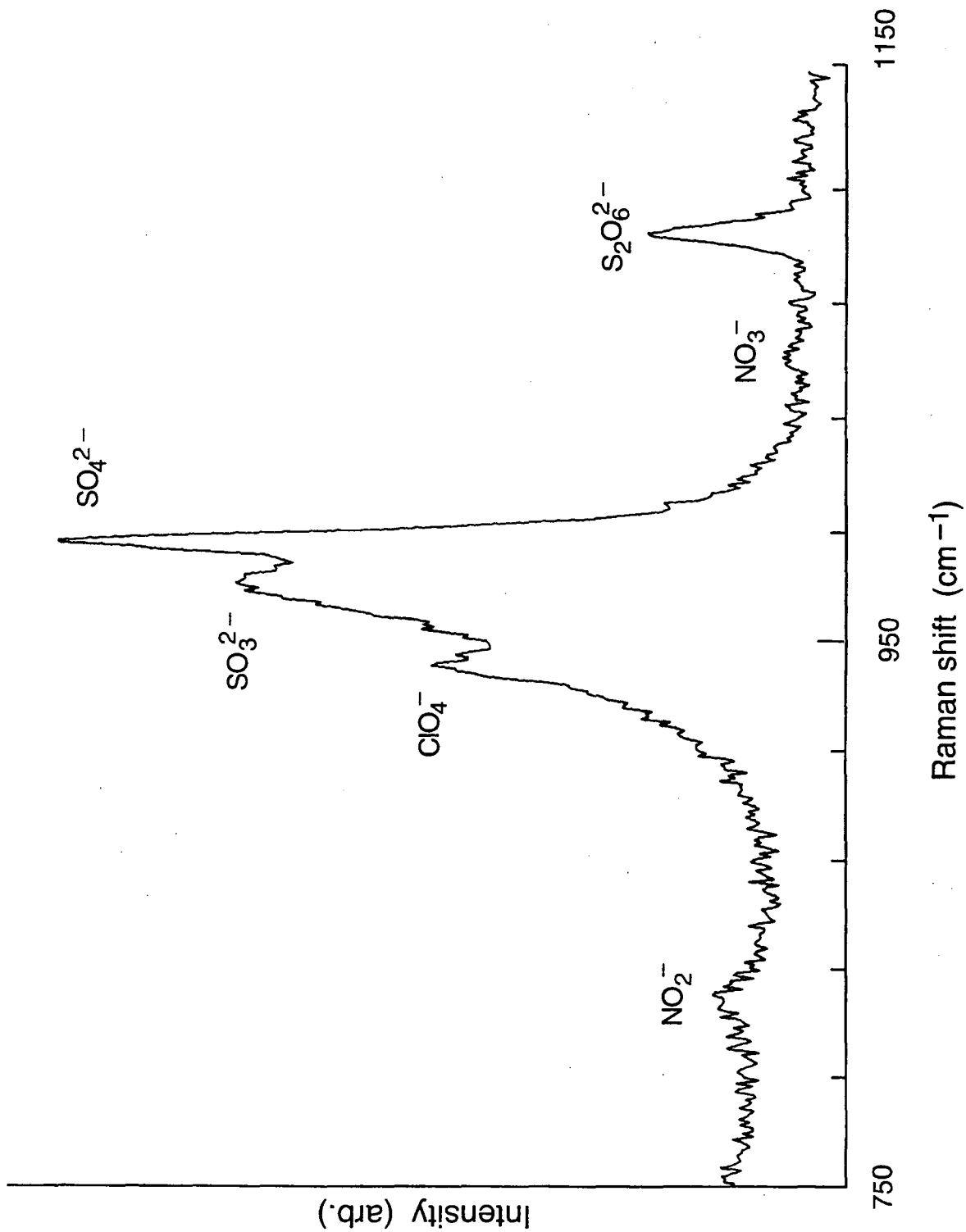
Figure 1. Raman spectrum of 1 M SO_3^{2-} exposed to 5000 ppm NO_2 for 1 hour.

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.

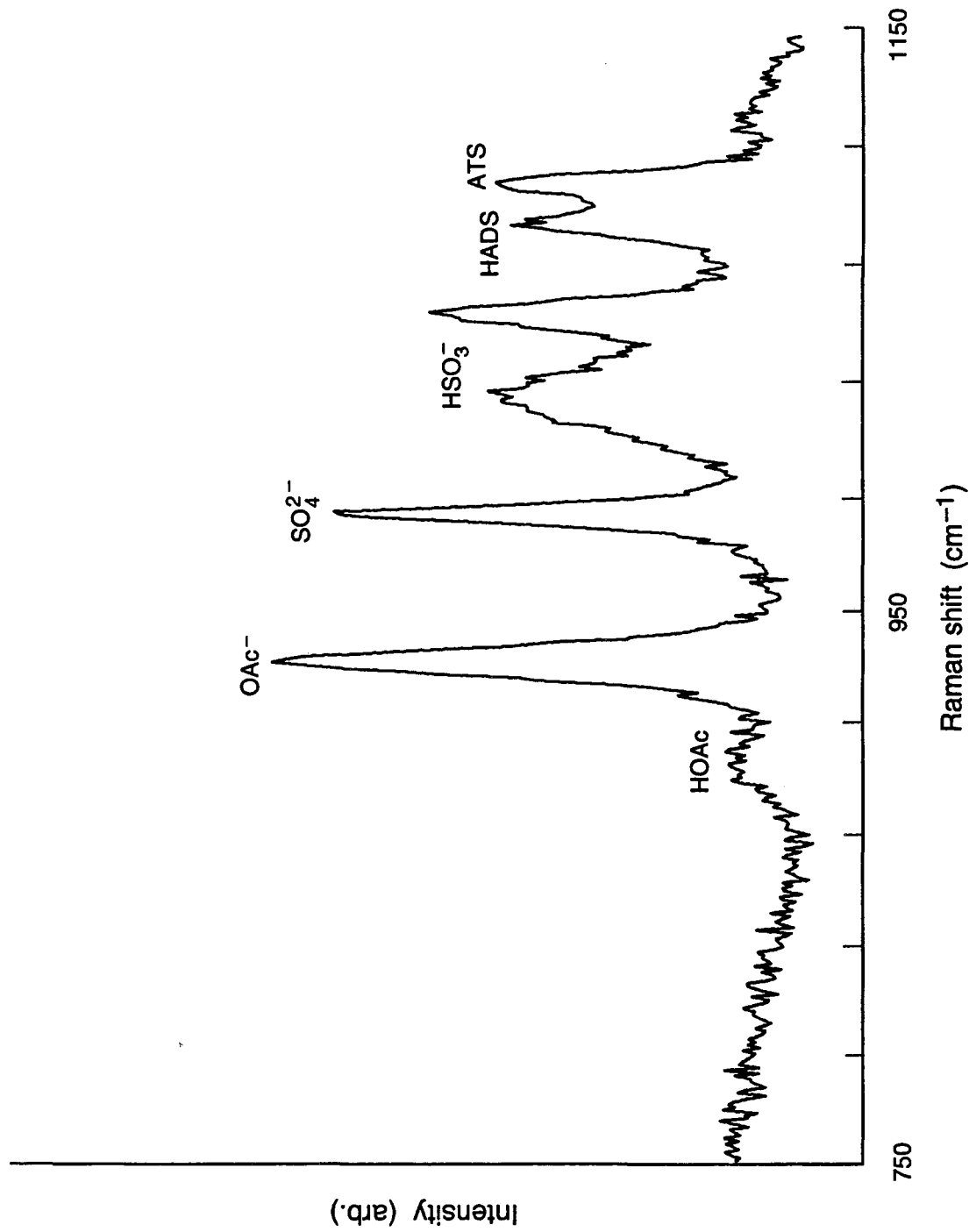
Figure 4. S(IV) oxidation rate as a function of NO_2 concentration with and without O_2 .

Figure 5. Effect of gas phase O_2 concentration on ratios of reaction products.



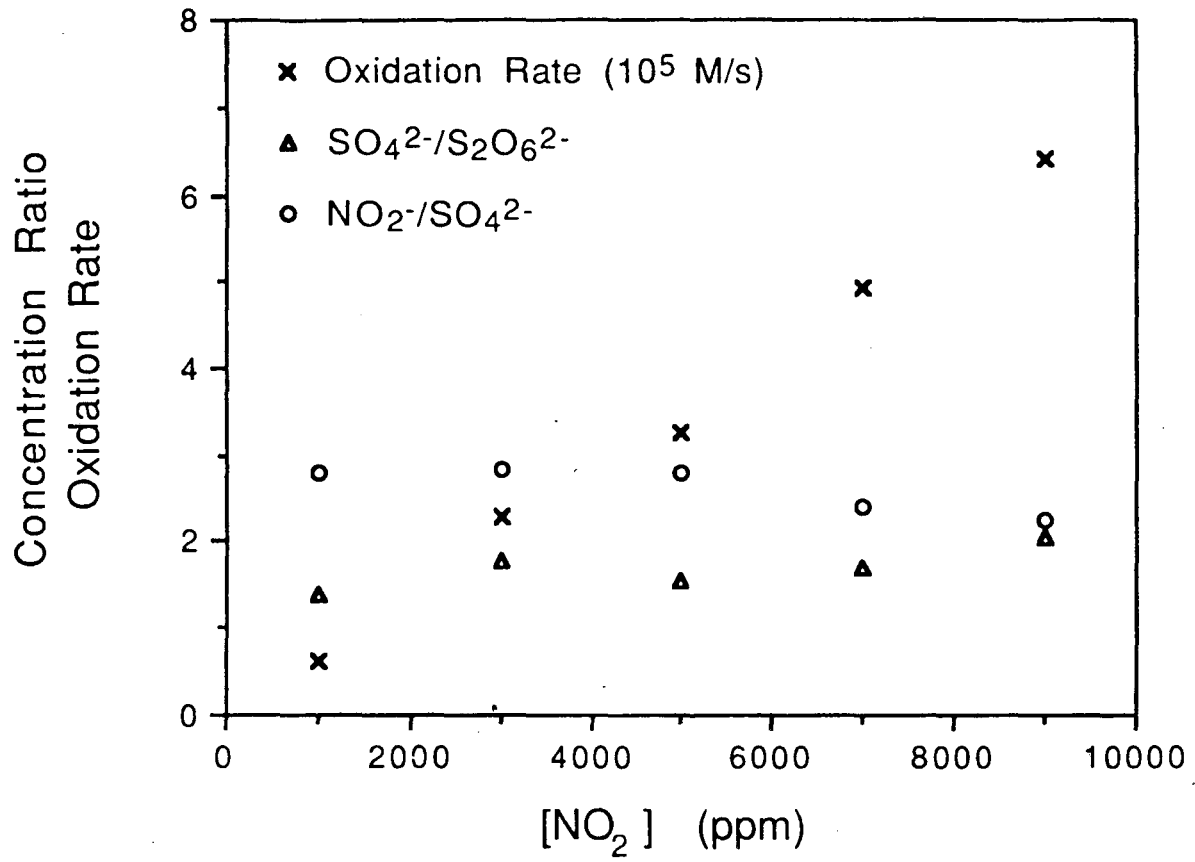
XBL9110-7077

Figure 1



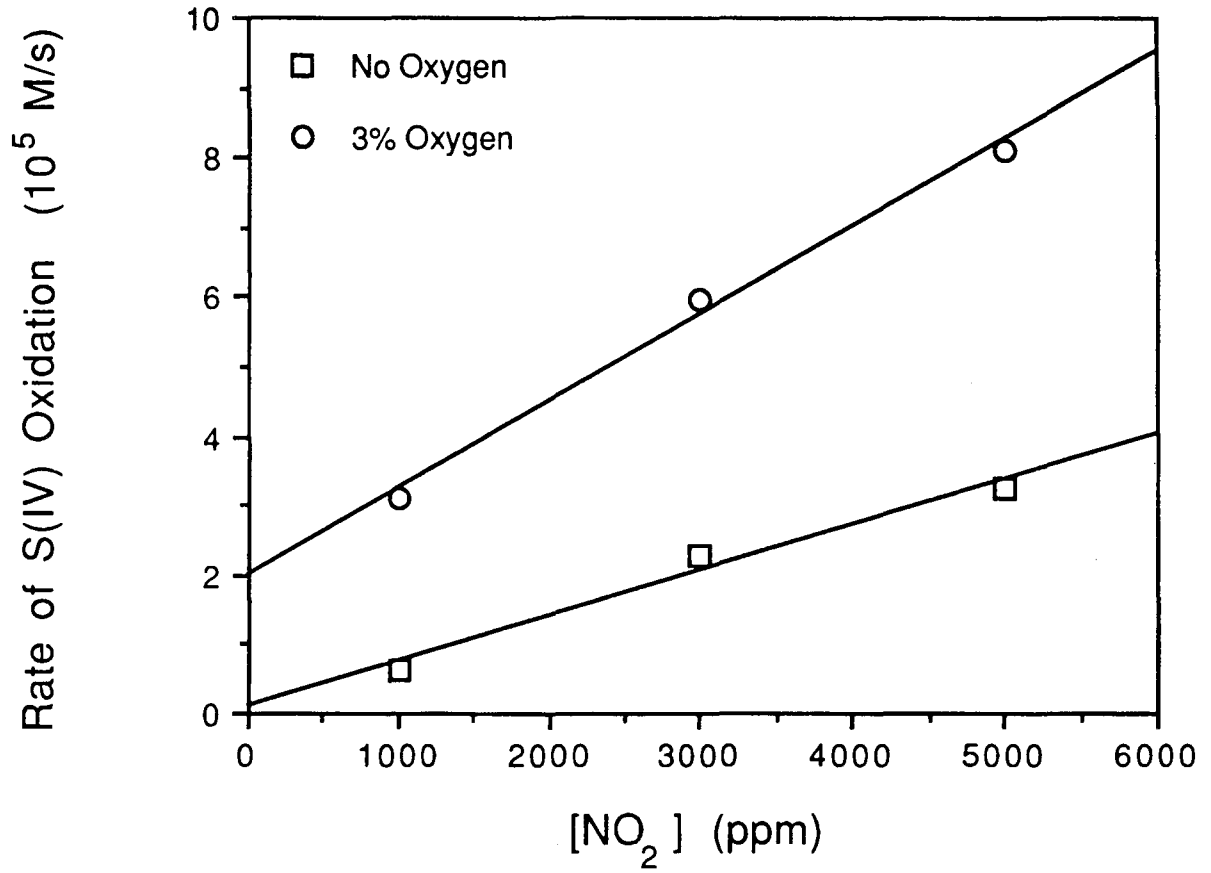
XBL9111-7083

Figure 2



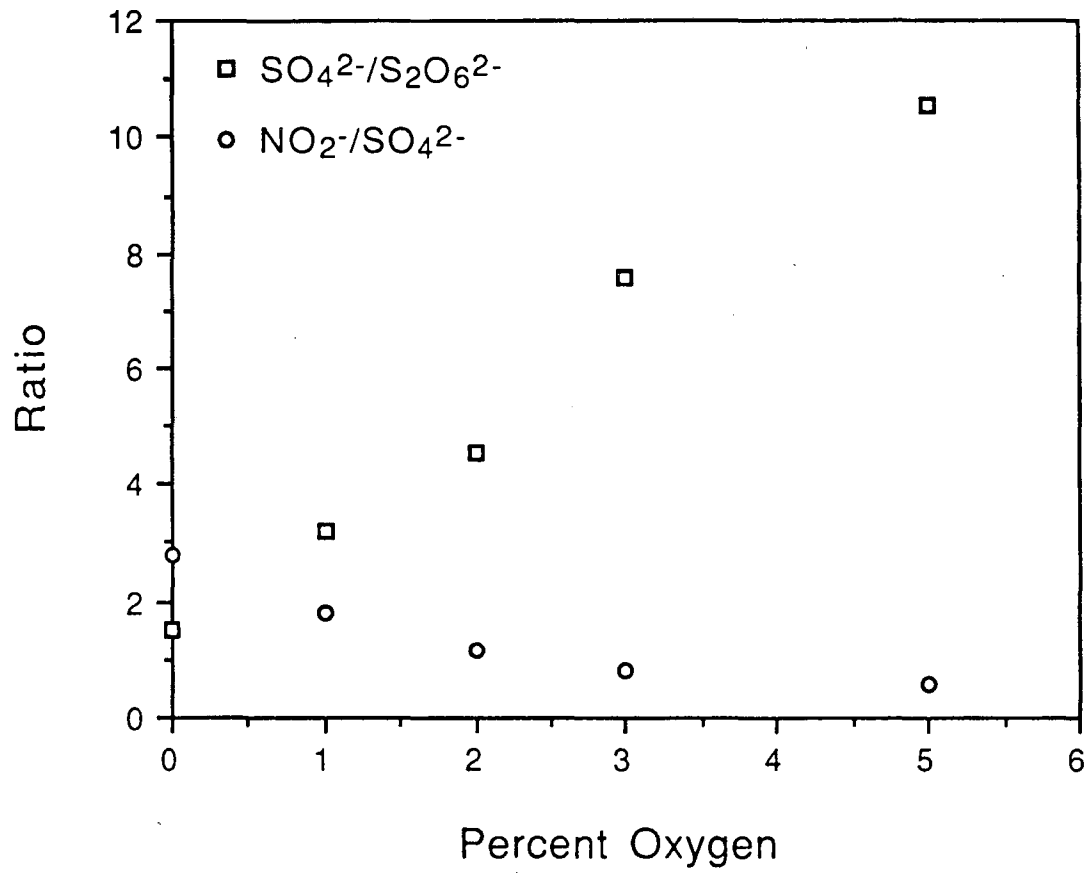
XBL 919-2066

Figure 3



XBL 919-2068

Figure 4



XBL 919-2067

Figure 5

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720