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KINETICS OF THE REACTION OF NITRIC OXIDE WITH SULFITE
AND BISULFITE IONS IN AQUEOUS SOLUTION

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Abstract

The kinetics of the reaction of nitric oxide with sulfite and bisulfite ions was studied over a pH range of 4 to 10 by monitoring the reaction product, N-nitrosohydroxylamine-N-sulfonate (NHAS), using a rapid-mixing, continuous-flow and stopped-flow system. The kinetics of the reaction can be described as

$$\frac{d[\text{NHAS}]}{dt} = k_a [\text{NO}][\text{HSO}_3^-] + k_b [\text{NO}][\text{SO}_3^{2-}]$$

where $k_a = 32 \pm 10$ and $k_b = 620 \pm 100$ in units of $\text{M}^{-1} \text{sec}^{-1}$ at $T = 298\text{K}$. The reaction was also studied at 284K and 323K. The hydrolysis rate of NHAS was determined over a pH range of 4 to 6.

There have been several studies¹⁻⁴ of the reaction of nitric oxide with dissolved sulfur dioxide, but there is disagreement about the kinetics of the system. An early study was done by Terres and Lichti¹, who observed the decrease in pressure of nitric oxide in the presence of K_2SO_3 , $KHSO_3$, and $SO_2 \cdot H_2O$. They were unable to obtain rate constants, but decided that a $(ONSO_3)^{2-}$ intermediate was involved, and that the reaction between nitric oxide and bisulfite ion was first order in both species. Nunes and Powell² investigated the reaction of NO with SO_3^{2-} at pH 13-14 by observing the decrease in pressure of NO over the sulfite solution in a well-stirred reactor. The rate expression they obtained consisted of a sulfite dependent term and a sulfite independent term. Takeuchi *et al.*³ observed the loss of nitric oxide diluted with nitrogen after it either flowed over a sulfite solution surface or was bubbled through a sulfite solution. They found the reaction had second order dependence on nitric oxide and zero order dependence on sulfite concentration. Their results indicated the reaction was very fast. Martin *et al.*⁴ used a stopped-flow system to observe the reaction between dissolved nitric oxide and dissolved sulfur dioxide at $pH \leq 3$ by monitoring $SO_2 \cdot H_2O$ at 280 nm. They found that the reaction was very slow and could only obtain an upper limit for the rate. In view of the disagreement of these studies, we decided to investigate the reaction system in an attempt to remove the ambiguity associated with it.

Experimental

To avoid difficulties with the diffusion rate of nitric oxide influencing the observed rate or reaction, we decided to monitor the reaction of sulfite and bisulfite ions with dissolved nitric oxide rather than nitric oxide gas. A continuous-flow rapid-mixing system which could also be used in the stopped-flow mode was used for the experiments. Both tanks for the reactant solutions were filled with water and degassed by passing argon through them. Nitric oxide for the experiments was purified by passing it through a concentrated sodium hydroxide solution and then through a cold trap at dry ice temperature. The treated nitric oxide was then passed through one of the tanks until the solution was saturated. A lower flow of nitric oxide was passed through the solution during the experiments. The sulfite and/or bisulfite solution was prepared by weighing out

reagent grade sodium sulfite and/or sodium metabisulfite. The pH of the solutions was adjusted by the addition of sodium hydroxide or hydrochloric acid, if necessary. After preparation, the two solutions were passed through flowmeters and a mixer and then into either a 1 cm or 5 cm pathlength UV cell. The cell was located in a temperature-controlled compartment in a Cary 219 spectrophotometer. The pH of the mixed solution was monitored with an in-line pH probe downstream of the cell.

Ackermann and Powell⁵ found that the only product of the reaction of NO with SO_3^{2-} was N-nitrosohydroxylamine-N-sulfonate (NHAS), which has a strong UV absorption. We prepared NHAS by the method given in the literature⁵ and measured the absorption spectrum, shown in Fig. 1. The extinction coefficient determined at 258 nm was found to be in good agreement with Ackermann and Powell's value and was found to vary negligibly over the temperature range of 284K to 323K. NHAS was monitored in the wavelength range between 258 nm and 300 nm, where absorptions by other species would not interfere. The 5 cm cell was used except in cases where the NHAS absorption was too strong, in which case the 1 cm cell was used.

To ensure that the reactants would be properly mixed by the mixer, it was checked by observing the reaction of Fe(II)(NTA) with NO. The Fe(II)(NTA) + NO reaction has a rate constant on the order of $10^8 \text{ M}^{-1} \text{ sec}^{-1}$ ⁶, and the mixed solution should react completely before entering the cell if the reactants are well mixed. This was observed to be the case. Total flow rates of 0.5 ml/sec to 11.5 ml/sec were used and the observation of the reacting solution varied from 0.25 to 9 seconds after mixing. The reaction was usually studied with one or the other of the reactants being in excess of the other. The NO concentration after mixing ranged from 0.3 to $1.7 \times 10^{-4} \text{ M}$ and the $\text{SO}_3^{2-}/\text{HSO}_3^-$ concentration after mixing ranged from 1.2×10^{-5} to $5.0 \times 10^{-3} \text{ M}$.

The reaction was studied in two ways. In continuous-flow measurements, the flow rates of the reactants were stabilized and a spectrum of the reaction mixture was taken from 350 nm to 230 nm. In stopped-flow measurements, the flow rates of the reactants were stabilized and one wavelength where NHAS alone absorbed was monitored. The flow of the reactants was stopped abruptly and the change in NHAS concentration vs

time was monitored. The results of the experiments at high pH conditions were analyzed to obtain a rate constant for $\text{NO} + \text{SO}_3^{2-}$. This rate constant was then used to correct low and intermediate pH experiments to obtain the rate constant for $\text{NO} + \text{HSO}_3^-$. The hydrolysis rate for NHAS was obtained from the stopped-flow experiments at low pH and this was used to correct the low pH experiments for loss of the reaction product.

Results and Discussion

From the experiments in which the nitric oxide concentration was varied at constant sulfite concentration, it was found that the rate for NHAS production had first order dependence on nitric oxide concentration. Similarly, in experiments where SO_3^{2-} and HSO_3^- were varied with constant NO concentration, it was found that the rate for NHAS production had first order dependence on both SO_3^{2-} and HSO_3^- .

The pH of the mixed solution was varied from 4 to 10.5 to observe what influence the pH had on the rate. A plot of $\log k$ vs pH is shown in Fig. 2, where k is defined as

$$k = \frac{d[\text{NHAS}]/dt}{[\text{NO}](\text{[HSO}_3^-] + \text{[SO}_3^{2-}])}$$

Also plotted as dashed lines are log percent of the total S(IV) oxide as HSO_3^- and SO_3^{2-} . The experimental curves indicate that both sulfite and bisulfite ions react with NO. If the reaction occurred only between SO_3^{2-} and NO, the experimentally obtained curve would be expected to follow the dashed line for SO_3^{2-} , rather than leveling out at lower pHs. Runs were not done below pH 4 because the NHAS hydrolysis became quite rapid, and also because there was the possibility of interference from $\text{SO}_2 \cdot \text{H}_2\text{O}$, which has an absorption maximum near 280 nm.

We also studied the temperature dependence of the reaction by putting the reactant tanks in a thermostatted bath, passing the reactant solutions through a second thermostatted bath just prior to mixing, and regulating the temperature of the sample compartment. The curve of $\log k$ vs pH at 284K is also shown in Fig. 2. Only the reaction of NO with SO_3^{2-} was studied at 323K because of problems with the development of bub-

bles in the mixed solution which created unpredictable changes in the liquid volume between the mixer and the cell. This introduced uncertainty in the reaction time between mixing and viewing. The problem was greater at the slow flow rates that would have been needed to study the $\text{NO} + \text{HSO}_3^-$ reaction. The formation of the product can be expressed as

$$\frac{d[\text{NHAS}]}{dt} = k_a[\text{NO}][\text{HSO}_3^-] + k_b[\text{NO}][\text{SO}_3^{2-}]$$

The values for k_a and k_b are listed in Table 1.

Table 1		
	k_a ($\text{M}^{-1} \text{sec}^{-1}$)	k_b ($\text{M}^{-1} \text{sec}^{-1}$)
284K	7.5 ± 2	220 ± 35
298K	32 ± 10	620 ± 100
323K	-	2000 ± 500

These values are plotted as $\log k$ vs $1/T$ in Fig. 3. For $\text{NO} + \text{SO}_3^{2-}$, a pre-exponential term of $A = 3.2 \times 10^{10} \text{ M}^{-1} \text{sec}^{-1}$ and an activation energy of $E_a = 10.6 \text{ kcal/mole}$ are obtained where $k = Ae^{-E_a/RT}$. For $\text{NO} + \text{HSO}_3^-$, a pre-exponential term of $2.6 \times 10^{14} \text{ M}^{-1} \text{sec}^{-1}$ and an activation energy of 17.6 kcal/mole are obtained.

It was necessary to correct runs done at low pH for the hydrolysis of the NHAS product. Fig. 4 shows the curve of absorption versus time for a typical stopped-flow experiment at pH 4.6. The flow was stopped at 4 seconds on the scale shown in the figure. The absorbance initially rises due to the continued reaction of NO with HSO_3^- and SO_3^{2-} . As the reactants are depleted, the hydrolysis of NHAS causes the absorbance to decrease. The decaying absorbance curves obtained from these experiments were used to determine the hydrolysis rate constant for NHAS as a function of pH. Short intervals of the decay curve were used to calculate values of the rate constant. Intervals of the curve

taken shortly after the flow was stopped yielded values which were low, due to the continuing formation of NHAS by $\text{NO} + \text{HSO}_3^-$ and SO_3^- . At longer times, the values became consistent when the NHAS formation reaction no longer occurred at a significant rate. These values were averaged to obtain the hydrolysis rate constant. This is shown in Fig. 5, along with results obtained at higher pH conditions by Ackermann⁷ and Seel and Winkler⁸. Seel used EDTA to bind any trace amounts of metal ions present in solution and obtained a lower hydrolysis rate constant than Ackermann, suggesting the hydrolysis may be catalyzed by metal ions. The NHAS product is not completely stable even at high pH conditions. Ackermann⁷ indicates that some decomposition exists even at pH 14. When doing absorption cross-section measurements at 323K with a pure NHAS solution at pH 11-12, it was noted that the concentration decreased at a rate of about 1% per minute. Ackermann and Powell⁵ found that NHAS would slowly oxidize in alkaline solutions when exposed to air, forming nitrite and sulfate ions.

The first order dependence of the rate on both NO and $\text{SO}_3^{2-}/\text{HSO}_3^-$ indicates the formation of an intermediate which rapidly reacts with a second NO to form the NHAS product. This is in agreement with what Terres and Lichti¹ and Nunes and Powell² have observed. The following reaction scheme can explain our observations:

The reaction scheme also applies to HSO_3^- . Nunes and Powell's work with the reaction of NO with SO_3^{2-} and SnCl_2 in the presence of Cu(I) led them to believe that NO exists in two forms in aqueous solution, which they refer to as dissolved NO and hydrolyzed NO . They indicate that the dissolved form reacts more slowly than the hydrolyzed form. They propose the following reaction scheme for $\text{NO} + \text{SO}_3^{2-}$:

For the reaction of dissolved NO with SO_3^{2-} (reaction (6)), Nunes and Powell obtained $-\text{d}[\text{NO}]/\text{dt} = \frac{1}{2} \text{d}[\text{NHAS}]/\text{dt} = 0.45[\text{NO}][\text{SO}_3^{2-}] \text{ sec}^{-1}$, which is about three orders of magnitude slower than the rate we have obtained. From their temperature dependence, we calculate a pre-exponential term of $4.9 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ and an activation energy of 8.2 kcal/mole for reaction (6). The activation energy is fairly close to the value we have obtained for reaction (2), 10.6 kcal/mole. They estimated that the rate constant for conversion of dissolved NO to hydrolyzed NO was about 0.14 sec^{-1} at 298K.

Using the above rate constants, we modeled the stopped-flow experiments done with $\text{NO} + \text{SO}_3^{2-}$ at 25 °C in an attempt to determine if our results could validate their hypothesis that there are two forms of NO in solution. Since the hydrolyzed NO would react more quickly than the dissolved NO, the rate of NHAS formation should slow down as the hydrolyzed NO is consumed in a stopped-flow experiment. From the comparison of the calculations and the observed NHAS curves, we estimate that $K_{\text{eq}} = [\text{NO (hydrolyzed)}]/[\text{NO (dissolved)}]$ is at least 10. There is considerable uncertainty in this value.

Since the NO is dissolved in solution well in advance of our experiments, there would be little evidence for two forms of NO in our experiments if the equilibrium constant is large. In an attempt to independently confirm the presence of two forms of NO in solution, Raman spectra were recorded of solutions of NO under approximately 34 bar pressure. The only NO peak observed was at 1873 cm^{-1} . This is slightly shifted from the gas phase peak of 1876 cm^{-1} , but the shift is similar to that observed for O_2 . It is less than the shift due to the formation of $(\text{NO})_2$ in the liquid ($\nu_{\text{NO}} = 1862 \text{ cm}^{-1}$)¹⁰ and much less than the shifts due to formation of ferrous chelate nitrosyls ($\nu_{\text{NO}} = 1750\text{-}1800 \text{ cm}^{-1}$, observed in this laboratory). It does not seem likely that the hydrolyzed NO compound that Nunes and Powell refer to would shift the Raman peak such a small amount. It

appears that the mixing system they used was not diffusion-limited, since the reaction rates were reported to be independent of stirrer amplitude and the rate they obtained for dissolution of CO_2 in a pH 9 buffer was in good agreement with literature values. They also obtained the same value for k_5 (forward) in both the $\text{NO} + \text{SO}_3^{2-}$ system and the $\text{NO} + \text{Sn(II)}$ system.

The only way we can reconcile their results with ours is to propose that the dissolution process for NO involves an intermediate which is formed directly from the gas phase and has a rate constant on the order of 0.1 sec^{-1} to form dissolved NO in aqueous solution. Without more information on the dissolution process, it is difficult to speculate about the chemistry associated with it.

It is uncertain whether NO reacts with dissolved sulfur dioxide. The possibility of interference from the UV absorption of $\text{SO}_2 \cdot \text{H}_2\text{O}$ and the rapid hydrolysis of NHAS prevented the investigation of this reaction by the method we used. At the highest pH used by Martin *et al.*⁴, the S(IV) should have been in the form of both $\text{SO}_2 \cdot \text{H}_2\text{O}$ and HSO_3^- . The HSO_3^- should have reacted with the NO, but the absorption decrease due to the loss of S(IV) may have been offset by the absorption increase due to NHAS. A better method to monitor the reaction may be to observe the decrease in pressure of NO over a solution of $\text{SO}_2 \cdot \text{H}_2\text{O}$. The reaction appears to be slow enough that diffusion should not be the limiting process if the solution is well stirred.

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FIGURE CAPTIONS

Fig. 1. UV absorption spectrum of NHAS (N-nitrosohydroxylamine-N-sulfonate).

Fig. 2. The pH dependence of the observed rate constant.

Fig. 3. Arrhenius plot for $\text{NO} + \text{SO}_3^{2-}$ and $\text{NO} + \text{HSO}_3^-$.

Fig. 4. UV absorption *vs* time at pH 4.6.

Fig. 5. The pH dependence of the NHAS hydrolysis rate.

Fig. 1

XBL 853-5939

Fig. 2

X8L853-5938

XBL 857-6393

Fig. 3

XBL858-6516

Fig. 4

Fig. 5

XBL 857-6394

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