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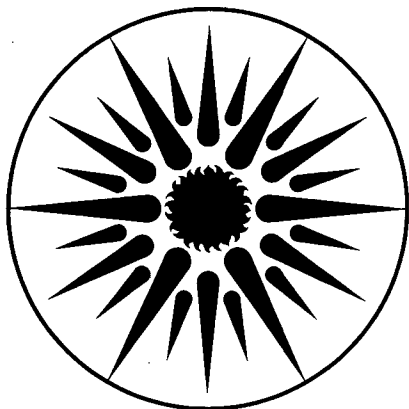
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D. Littlejohn and S.G. Chang

November 1984

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REACTION OF FERROUS NITROSYL CHELATES WITH SULFITE AND BISULFITE IONS⁺

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Abstract

The behavior of the reaction of ferrous nitrosyl chelate complexes with sulfite and bisulfite ions has been investigated and a mechanism capable of explaining the observations is reported. The three key features of the mechanism are: the reaction of nitric oxide with sulfite ion to form the compound $(\text{NO})_2\text{SO}_3^{2-}$; the oxidation of Fe(II)(L) by $(\text{NO})_2\text{SO}_3^{2-}$ to form Fe(III)(L) ; and the formation of $\text{HON}(\text{SO}_3^-)_2$ by the reaction of HSO_3^- with NOSO_3^- . The reaction products that have been observed are: Fe(III) , N_2O , N_2 , SO_4^{2-} , $\text{S}_2\text{O}_6^{2-}$, and $\text{HON}(\text{SO}_3^-)_2$. The reaction rate expression for the Fe(NTA)NO and Fe(EDTA)NO complexes can be expressed as:

$$\frac{d[\text{Fe(II)(L)NO}]}{dt} = k_1 [\text{HSO}_3^-] + k_2 [\text{SO}_3^{2-}] [\text{Fe(II)(L)NO}].$$

For L=NTA at 25°C and pH 3 to 8, $k_1 = 1.2 \times 10^{-5} \text{sec}^{-1}$ and $k_2 = 0.13 \text{M}^{-1} \text{sec}^{-1}$ for $10^{-4} \text{M} < [\text{Fe(II)(NTA)NO}] < 10^{-3} \text{M}$ and $10^{-2} \text{M} < [\text{S(IV)}] < 10^{-1} \text{M}$. For L=EDTA at 25°C and pH 4 to 8, $k_1 = 5.6 \times 10^{-5} \text{sec}^{-1}$ and $k_2 = 0.175 \text{M}^{-1} \text{sec}^{-1}$. For EDTA at 55°C and pH 4 to 8, $k_1 = 9.0 \times 10^{-5} \text{sec}^{-1}$ and $k_2 = 0.60 \text{M}^{-1} \text{sec}^{-1}$. These values for EDTA are valid for $10^{-4} \text{M} < [\text{Fe(II)(EDTA)NO}] < 10^{-3} \text{M}$ and $10^{-3} \text{M} < [\text{S(IV)}] < 10^{-1} \text{M}$.

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Introduction

A number of studies, (1-5), have been made of the reaction of ferrous nitrosyl chelates with sulfite (SO_3^{2-}) and bisulfite (HSO_3^-) ion in recent years. The studies published have generally been limited to ferrous nitrosyl complexes with ethylenediaminetetraacetic acid (EDTA) as a chelate. The motivation for these studies has been the development of a technique for the simultaneous desulfurization and denitrification of flue gases. Reports of the reaction have indicated that it is complicated, and have not provided a complete understanding of the reaction process. There are contradictions in the literature as to what the reaction products are, as well as the kinetic behavior. Teramoto et al. (1978)¹ measured the uptake of diluted nitric oxide gas by a $Fe(II)(EDTA) + Na_2SO_3$ solution in a flow system and reported that sulfamate, disulfamate and dithionate had been observed as products. Sada et al. (1980)² did similar experiments using a $Fe(II)(EDTA) + MgSO_3$ slurry and found that the consumption of $Fe(II)(EDTA)NO$ complex by SO_3^{2-} is much slower than the formation of the complex, but did not mention any reaction products. Their results indicated the reaction was more rapid at lower pH conditions. Both of these studies could have had problems of the reaction of nitric oxide (NO) with SO_3^{2-} affecting their results. Miyadera et al. (1982)³ investigated the rate of reaction of $Fe(II)(EDTA)NO$ with SO_3^{2-} and HSO_3^- . At pH 6.94, they obtained a rate equation of:

$$\frac{-d[Fe(II)(EDTA)NO]}{dt} = k[NO(aq)][SO_3^{2-}]$$

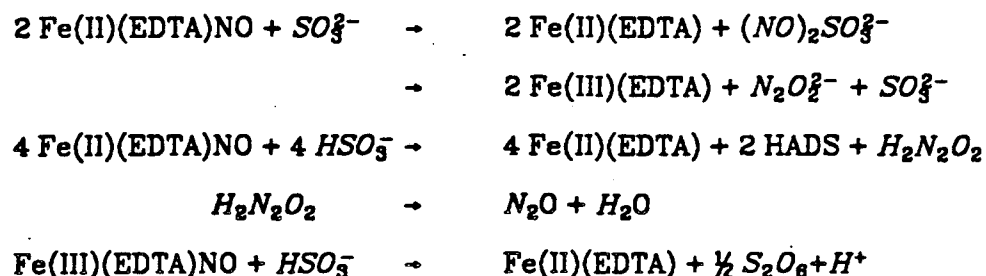
They observed a slower reaction rate at lower pH and expressed the pH dependence as:

$$\frac{-d[Fe(II)(EDTA)NO]}{dt} = (k_1[HSO_3^-] + k_2[SO_3^{2-}])[Fe(II)(EDTA)NO]$$

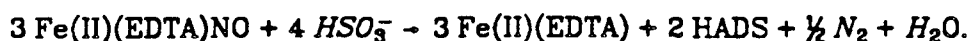
where $k_1 = 4.02 \times 10^{-4} \text{ m}^3/(\text{mol min})$ and $k_2 = 6.22 \times 10^{-3} \text{ m}^3/(\text{mol min})$ at 25°C .

They found that roughly half of the $Fe(II)$ was oxidized to $Fe(III)$. Their experiments were done with only one set of reactant conditions and over a limited pH range. Sada et al. (1984)⁵ made a study of the reaction products of this reaction and

observed N_2O , $S_2O_8^{2-}$, Fe(III), hydroxylamine disulfonate (HADS) and other nitrogen-sulfur compounds. A complicated wet analytical technique was used to determine the concentrations of the nitrogen-sulfur compounds. They also used a system where diluted NO gas was continuously flowed into a Fe(II)(EDTA) + Na_2SO_3 solution. They proposed that the reaction proceeds by the following steps:



Narita et al. (1984)⁵ investigated the production of HADS by the reaction of Fe(II)(EDTA)NO + HSO_3^- . Again, diluted NO was continually passed through a Fe(II)(EDTA) + Na_2SO_3 solution. They observed HADS, N_2 , $S_2O_8^{2-}$ and other nitrogen-sulfur compounds. They attributed N_2O and SO_4^{2-} formation to the reaction of unbound NO with SO_3^{2-} . They proposed that the reaction occurs by:



It appears that no measurements of N_2 production were made.

We have studied the reaction using several different chelates bound to the Fe(II) ion. Studies of the kinetics of the reaction and of the reaction products were made over a pH range of 2 to 10. The observed reaction products are Fe(III), SO_4^{2-} , $S_2O_8^{2-}$, N_2O , N_2 and HADS. The HADS can further react to produce other nitrogen-sulfur compounds such as hydroxylamine monosulfonate (HAMS), aminetrisulfonate (ATS) and aminedisulfonate (ADS), as shown in Fig. 1⁶. The product distribution is affected by the solution pH and the reactant concentrations. The rate of reaction was also affected by pH and reactant concentrations.

Experimental

PREPARATION OF REACTION MIXTURES

Solutions of the ferrous nitrosyl complexed were prepared on a vacuum line to avoid oxidation of the ferrous ion and nitric oxide. The ligands used in these studies included ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA) and citric acid (cit). The chelates formed ferrous nitrosyl complexes with the following stoichiometry: Fe(II)(EDTA)NO , Fe(II)(NTA)NO , Fe(II)(IDA)NO , Fe(II)(cit)NO . Some work was also done with the hydrated ferrous nitrosyl complex, $\text{Fe(II)(H}_2\text{O)}_6\text{NO}$. After the solution containing the ligand was degassed, ferrous ammonium sulfate was added under an Ar or SF_6 atmosphere. The solution was adjusted to the desired pH and further degassed. Nitric oxide (Matheson, C.P.) was distilled three times, with the first and last portion of the distillate being discarded. The purified nitric oxide was stored at liquid nitrogen temperature until use. The nitric oxide was added to the bulb containing the solution while the solution was vigorously stirred. The concentration of the nitrosyl complex was checked spectrophotometrically. The visible spectrum of Fe(II)(NTA)NO , shown in Fig. 2, is typical of spectra of ferrous nitrosyl complexes. Other complexes show similar structure.⁷

KINETIC STUDIES

The kinetics of the disappearance of the ferrous nitrosyl complex was monitored by observing one of the visible absorption bands of the complex with a Cary 219 spectrophotometer interfaced to an Apple II+ computer. Degassed solutions of reagent grade sodium sulfite (Na_2SO_3) and/or sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) were added to the spectrophotometer cell and the cell was evacuated. The solution containing the ferrous nitrosyl complex was added and the solutions were mixed and placed in the spectrophotometer for monitoring.

REACTION PRODUCT DETERMINATION

Reagent grade sodium sulfite and/or sodium metabisulfite was added to the ferrous nitrosyl complex after the nitric oxide over the solution was replaced with Ar or SF_6 . The gas over the solution was again removed and replaced with more Ar or SF_6 .

Gaseous products were analyzed by periodic withdrawal of gas samples with a syringe and injection into an Aerograph A700 gas chromatograph with a 10 ft. x 1/8 in. Porapak Q column. SF_6 was used over most solutions to allow determination of N_2 generated by the reaction mixtures. Occasionally, gas samples were withdrawn and run on an A.E.I. MS12 mass spectrometer to check the results obtained by gas chromatography.

Ferrous ion concentrations were determined by the 1,10 phenanthroline method. Small amounts of the reaction mixture were periodically withdrawn for testing. Test solutions were acidified to pH \sim 2.5 to avoid interference from the ligands used in the reaction mixtures.

One method used for HADS determination was oxidation of HADS to nitrosodisulfonate, a colored compound with an absorption maximum at 545 nm⁸. A sample of the reaction mixture was treated with hydrogen peroxide to oxidize the sulfite and bisulfite ions. Sodium hydroxide and silver nitrate were then added to generate Ag_2O , which oxidizes HADS to nitrosodisulfonate. Nitrosodisulfonate concentrations were determined spectrophotometrically. This method has a lower detection limit than Raman spectroscopy.

Laser Raman spectroscopy was used to observe many of the species in solution. Use of Raman spectroscopy allows simultaneous determination of many species in solution⁹. The Raman shifts and relative molar intensities of anions potentially present in reaction mixtures are listed in Table 1. The major drawback of Raman spectroscopy is its need for a relatively high concentration of a compound for its determination. A Coherent Innova 90-5 argon ion laser was used as an excitation source. The 514.5 nm line was generally used in obtaining

spectra. A Spex 1403 double spectrometer was used with a Spex Datamate data acquisition system for collecting spectra. Samples were generally sealed in a 1mm id capillary tube for Raman spectroscopy. Quantitative measurements can be made by adding a known amount of an inert reference compound to the solution. By comparing the peak heights of the reference compound and the compounds of interest, one can obtain a measure of the relative concentrations.

Results and Discussion

KINETICS OF Fe(II)(L)NO + S(IV)

Solutions of ferrous nitrosyl chelates were mixed with Na_2SO_3 or $Na_2S_2O_5$ (collectively referred to as S(IV)) under oxygen-free conditions. The absorbance of the reaction mixture was observed with time at one of the absorption maxima of the Fe(II)(L)NO complex. Most runs were done at 25° C. The S(IV):Fe(II) ratio was varied, but the S(IV) was always in excess of Fe(II). The reaction was studied over a pH range of 2 to 10 and a Fe(II)(L)NO concentration range of $10^{-4}M$ to $> 10^{-2}M$. Problems with precipitation of the iron occurred at high pH when IDA and citrate were used as chelates. Consequently, most work was done with NTA and EDTA complexes. The Fe(II)(H_2O)₅NO, Fe(II)(cit)NO and Fe(II)(IDA)NO complexes do not bind NO as strongly as the Fe(II)(NTA)NO and Fe(II)(EDTA)NO complexes⁹. At low pH, the reaction rates of the former compounds were considerably faster than those containing NTA and EDTA. The reaction products generated were not highly affected by the chelate bound to the iron, however. The disappearance of Fe(II)(L)NO was found to be first order in S(IV) under all conditions, as shown in Fig. 3. At low pH (2 to 5), the rate was independent of the concentration of Fe(II)(L)NO. At pH > 7, the rate was found to have variable dependence on Fe(II)(L)NO concentration. At concentrations of about $10^{-4}M$, the rate appeared to be second order in Fe(II)(L)NO. This decreased to first order at about $10^{-3}M$ and was independent of Fe(II)(L)NO concentration above $10^{-2}M$. No ionic strength dependence was observed in the pH range of 6-7. A plot of dc/dt vs pH where $c = [Fe(II)(NTA)NO]$ is

shown in Fig. 4. A plot of $d(\frac{1}{c})/dt$ shows similar behavior. The rate expression we obtained for Fe(II)(NTA)NO and Fe(II)(EDTA)NO is:

$$\frac{d[\text{Fe(II)(L)NO}]}{dt} = k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}][\text{Fe(II)(L)NO}]$$

For L = NTA at 25° C and pH 3 to 8, $k_1 = 1.2 \times 10^{-5} \text{ sec}^{-1}$ and $k_2 = 0.13 \text{ M}^{-1} \text{ sec}^{-1}$ for $10^{-4} \text{ M} < [\text{Fe(II)(NTA)NO}] < 10^{-3} \text{ M}$ and $10^{-2} \text{ M} < [\text{S(IV)}] < 10^{-1} \text{ M}$. For L = EDTA at 25° C and pH 4 to 8, $k_1 = 5.6 \times 10^{-5} \text{ sec}^{-1}$ and $k_2 = 0.175 \text{ M}^{-1} \text{ sec}^{-1}$. For 55° C and pH 4 to 8, $k_1 = 9.0 \times 10^{-5} \text{ sec}^{-1}$ and $k_2 = 0.60 \text{ M}^{-1} \text{ sec}^{-1}$. These values are valid for $10^{-4} \text{ M} < [\text{Fe(II)(EDTA)NO}] < 10^{-3} \text{ M}$ and $10^{-3} \text{ M} < [\text{S(IV)}] < 10^{-1} \text{ M}$. The value obtained for k_2 with EDTA as a ligand is about 70% faster than that obtained by Miyadeva et al.³ The decrease in rate below pH 3 can be attributed to the decreasing fraction of S(IV) in the form of HSO_3^- . The increase in rate above pH 5 is due to an increasing fraction of the S(IV) as SO_3^{2-} . However, the rate should continue to increase until pH 9, where essentially all the S(IV) is in the form of SO_3^{2-} . The decrease in rate above pH 7 could be due to the formation of a complex between Fe(II)(L)NO and OH^- , which could have lower reactivity than Fe(II)(L)NO.

REACTION PRODUCTS

Upon addition of S(IV) to Fe(II)(L)NO solutions, the solution color changes from dark green to orange or red, suggesting the presence of Fe(III). This was confirmed by measuring the Fe(II) concentration with 1,10 phenanthroline at pH 2.5 where the ligand in the nitrosyl complex does not interfere. It was found that a substantial amount of Fe(II) is converted to Fe(III). Fig. 5 shows the amount of Fe(II) oxidized at pH ~ 8 as a function of $[\text{SO}_3^{2-}]:[\text{Fe(II)(NTA)NO}]$. Runs done at pH 4 show lower Fe(III) production than similar runs done at pH 8. The disappearance of Fe(II) was measured with time after the addition of S(IV) and was found to disappear more slowly than Fe(II)(NTA)NO, as shown in Fig. 6, suggesting that Fe(III) is not a direct reaction product of the reaction between Fe(II)(NTA)NO and S(IV). At all pH conditions studied, an increase in the pH of the solution is observed during the first few hours after mixing the reactants.

A substantial amount of S(IV) consumed appears to be converted to SO_4^{2-} , particularly at high pH conditions. This was determined by growth of the 981 cm^{-1} SO_4^{2-} peak in Raman spectra taken of the reaction mixtures. Another product is dithionate ion, $S_2O_8^{2-}$, which has also been reported by other workers^{1,4}. We have observed the 1092 cm^{-1} dithionate peak as a shoulder on the larger HADS peak in the Raman spectra taken, as shown in Fig. 7. Dithionate ion was observed only at low pH, suggesting formation by the reaction of ferric ion with bisulfite ion. Some of the S(IV) is converted into nitrogen-sulfur compounds such as HADS, HAMS, ATS, and ADS, particularly at low pH.

It was found that a large amount of the nitrogen from the NO bound to Fe(II)(L) was converted into N_2O and N_2 , particularly at high pH. Fig. 8a shows the effect of $(SO_3^{2-}) : (Fe(II)(NTA)NO)$ on the conversion of NO to N_2O and N_2 . N_2O production is unaffected by the ratio above 2:1, whereas N_2 production increases up to a ratio of $\sim 8:1$. Fig 8b illustrates the effect of Fe(II)(NTA)NO concentration on N_2O production decreases with concentration and N_2 production increases with concentration. Fig. 8c shows the influence of pH on N_2O and N_2 production with a $(S(IV)):(Fe(II)(NTA)NO)$ ratio of 10:1. Both N_2O and N_2 production increase with pH. N_2O was always produced in excess of N_2 and no N_2 was observed at low pH conditions. The threshold for N_2 generation is $pH \sim 6$.

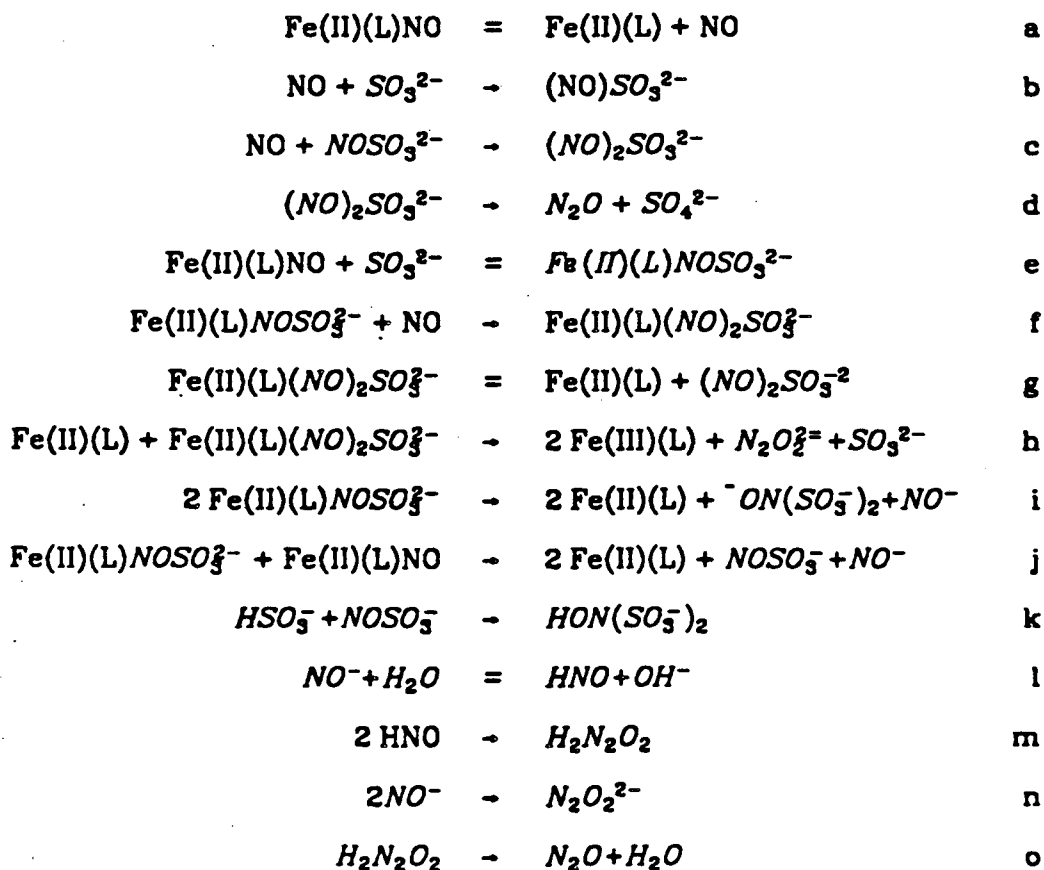
Essentially none of the nitrogen remains as NO in solution. The nitrogen is converted into N_2O , N_2 and nitrogen-sulfur compounds. At low pH, some of the nitrogen may exist as $H_2N_2O_2$, which decomposes slowly to N_2O . A weak peak at $\sim 1480\text{ cm}^{-1}$ is observed in Raman spectra of low pH reaction mixtures, and could be due to $H_2N_2O_2$. At high pH, some of the nitrogen may occur as $(NO)_2SO_3^{2-}$, which under these conditions is fairly stable against decomposition to N_2O and SO_4^{2-} .

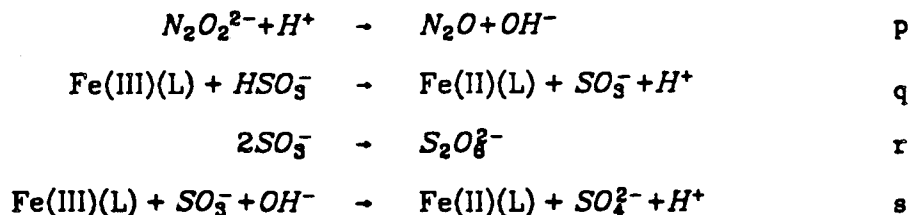
The N_2O and N_2 produced by the reaction appear to evolve at roughly the same rate. Their appearance is presumably controlled by diffusion out of solution and not by the rate of production. They appear to build up slightly more

slowly than Fe(III), presumably because of the delay in diffusion out of solution. Because of the techniques used in nitrogen-sulfur compound determination, as well as their chemical behavior, it is difficult to determine the rate of production for these species.

MECHANISM

From the reaction products observed and their behavior, it appears that the reaction between Fe(II)(L)NO and S(IV) is quite complicated. Some insight can be obtained from studies of NO + SO₃²⁻ and Fe(II)(L)NO. Also, some constraints can be obtained from the need for a balance between compounds being oxidized (Fe(II), S(IV), N(II)) and the compound being reduced (N(II)). The mechanism we have developed is listed below. In most cases, SO₃²⁻ and HSO₃⁻ can be used interchangeably and only SO₃²⁻ is listed. HSO₃⁻ is written where this is not the case.





The NO - S(IV) reaction in the presence of Fe(II) could proceed by a number of pathways. Free NO will exist in equilibrium with Fe(II)(L)NO, as shown in reaction a). Reactions b) and c) were developed by Nunes and Powell¹¹ to explain the kinetic behavior of the reaction of NO with SO_3^{2-} . We have found this rate to be pH dependent. Reaction d) is given by Ackermann and Powell¹⁰ as the decomposition of $(NO)_2SO_3^{2-}$ in the absence of O_2 . Reactions e) through g) are alternate pathways for the formation of $(NO)_2SO_3^{2-}$ in the presence of Fe(II)(L).

Preliminary experiments in our laboratory show that Fe(II)(L) will react with $(NO)_2SO_3^{2-}$ to produce Fe(III)(L), N_2O , SO_4^{2-} , and some Fe(II)(L)NO. This can be explained by reactions g), h), and p).

Reaction e) has been mentioned by Teramoto et al¹ and by Sada et al.². It is particularly likely to happen at low pH where the reaction of Fe(II)(L)NO + HSO_3^- occurs slowly. The complex formed by reaction e) could react with a second complex or with Fe(II)(L)NO to produce HADS as shown by reactions i), j) and k). While the compound $NOSO_3^-$ has not been observed, it has been invoked a number of times to explain kinetic behavior observed in nitrogen oxide-sulfur oxide systems.¹⁶ The production of HADS by reaction k) has been discussed by Chang et al.⁶ and Oblath et al.¹⁶ The production of other nitrogen-sulfur compounds^{12,13,14} and N_2 are not included in this mechanism. Significant production of N_2 occurs only at very high pH and the amount produced is always less than that of N_2O . N_2 production may occur as a result of the decomposition of $(NO)_2SO_3^{2-}$ in the presence of Fe(II).

N_2 has been observed as a product of the autodecomposition of Fe(II)(acetate)(NO),¹⁵ and some of the observed N_2 could be produced by this process.

A number of studies have been done on hyponitrous acid and the nitroxyl radical¹⁵, and the occurrence of reactions 1) through p)¹⁶ are well established, although there is some uncertainty in the pK_a for HNO¹⁷. Huie and Peterson¹⁸ have reviewed the reactions of S(IV) with Fe(III). Several different mechanisms are discussed, and a S(V) intermediate is generally involved in production of dithionate ion ($S_2O_8^{2-}$). Reactions q), r), and s) are consistent with the mechanisms discussed in the review.

The mechanism listed can help explain the kinetic behavior observed. The rate of ferrous nitrosyl disappearance appears to have second order dependence on Fe(II)(L)NO at low Fe(II)(L)NO concentrations and this decreases to zero order at high Fe(II)(L)NO concentrations. Plotting the second order rate, after correction for sulfite concentration, against Fe(II)(L)NO concentration gives an exponentially decreasing curve, as shown in Fig. 9. This indicates first order behavior, although plots of $d(1/[Fe(II)(L)NO])/dt$ vs. time are more linear than plots of $d(\ln [Fe(II)(L)NO])/dt$ vs. time. This ambiguity could be created by reactions e) and f). The relative rates of these reaction could create an apparent second order dependence and first order dependence at somewhat higher concentrations. At the highest concentrations we studied, these reactions no longer control the rate of reaction and reaction h) may become the rate-determining step. This would create the zero-order dependence on Fe(II)(L)NO that is observed at high concentrations. There is also competition between these reactions and reactions b), c) and d), which complicates the kinetics.

From the rate for $NO + SO_3^{2-}$ obtained by Nunes and Powell,¹¹ and the rates that we have obtained for $Fe(II)(L)NO + SO_3^{2-}$, we can calculate the relative amounts of N_2O produced by reactions a) - d) and by reactions e) - h). Using initial conditions of $1 \times 10^{-3} M$ Fe(II)(NTA)NO and $1 \times 10^{-2} M$ SO_3^{2-} at pH 8.5, the rate obtained for $d(Fe(II)(NTA)NO)/dt$ is $1.3 \times 10^{-6} M \text{ sec}^{-1}$. Using a value of $2 \times 10^{-6} M^{-1}$ for the equilibrium constant¹⁹ for $Fe(II)(NTA) + NO \rightleftharpoons Fe(II)(NTA)NO$, the concentration of unbound NO will be $4.5 \times 10^{-8} M$. From this, $d(NO)/dt$ is calculated as $0.7 \times 10^{-6} M \text{ sec}^{-1}$, which is just over half of the observed rate. Reactions

e) through h) are responsible for the rest of the observed rate. These reaction would be expected to produce Fe(III), and we observe that approximately half of the Fe(II) is converted to Fe(III) under these conditions. As the Fe(II)(NTA) concentration builds up, the amount of unbound NO will decrease, causing a decrease in the rate of $\text{NO} + \text{SO}_3^{2-}$ relative to the other process. This can explain why plots of $\ln [\text{Fe(II)(L)NO}]$ and $1/[\text{Fe(II)(L)NO}]$ vs. time show curvature in the reaction mixtures studied.

Ackermann and Powell¹⁰ have determined the decomposition rate of $(\text{NO})_2\text{SO}_3^{2-}$ as a function of pH, and note that heavy-metal ions could play a catalytic role in its decomposition. In the case of Fe(II), this could be attributed to reaction h). The observations that the rate of the $\text{NO} + \text{SO}_3^{2-}$ reaction is approximately half of the Fe(II) is converted to Fe(III) suggest that reaction h) is comparable in rate to reaction d) under these conditions.

At lower pH conditions where HSO_3^- is present, production of HADS by reactions i) - k) and $\text{S}_2\text{O}_8^{2-}$ by reactions q) and r) become significant. This is apparent from the Raman spectrum of a mixture 0.050 M Fe(II)(NTA)NO and 0.100 M HSO_3^- shown in Fig. 7. 0.105 M H_3BO_3 was added as a reference. The spectrum shows the 875 cm^{-1} H_3BO_3 peak, the strong 981 cm^{-1} SO_4^{2-} peak, weak peaks at $\sim 1052 \text{ cm}^{-1}$ for HSO_3^- and the merged HADS and $\text{S}_2\text{O}_8^{2-}$ peaks at 1083 and 1092 cm^{-1} . From the peak heights and the scattering efficiencies for the species present, the concentrations can be calculated. The spectrum is an average of 65 scans and took several hours to accumulate. The scans were begun a few hours after mixing the reactants to avoid problems with HADS hydrolysis. Some Fe(II)(NTA)NO appeared to be present at the beginning of the scans and the reaction was still in progress during data collection. Consequently, the concentrations obtained from the spectrum are averages for the period during which the scans were taken. The concentrations obtained are: 0.105 M SO_4^{2-} , 0.045 M HSO_3^- , 0.017 M HADS, and 0.006 M $\text{S}_2\text{O}_8^{2-}$. Most of the SO_4^{2-} is from the $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ used to prepare the solution. Very little conversion of Fe(II) to Fe(III) was observed, presumably

because it was converted back to Fe(II) during $S_2O_8^{2-}$ production. At the time of the scan the nitrogen not converted into HADS and N_2O (measured to be equivalent to about 0.008 M) existed as unreacted Fe(II)(NTA)NO and possible as nitrogen-based compounds in solution, such as $H_2N_2O_2$ and the Fe(II) complexes shown in the mechanism.

From the mechanism, it can be seen that the stoichiometry of the NO to S(IV) consumed in the reaction will be pH dependent. At high pH, the stoichiometry will depend on the rate of the process in reactions a) - d) relative to the process in reactions e) - h). If the two are approximately equal, then the stoichiometry should be N:S ~ 4:1. At lower pH, the situation is complicated by the production of HADS and $S_2O_8^{2-}$. In the mixture shown in Fig. 7, the stoichiometry would be expected to be close to 1:1.

The increase in pH observed after mixing the reactants can be attributed to OH^- formation by reactions 1) and p) and conversion of HSO_3^- to less acidic species, as in reaction k). More Fe(III) is observed at high pH because the removal processes in reaction q) and s) predominantly occur at low pH conditions.

The iron-nitrogen oxyanion-sulfur oxyanion chemistry in aqueous solutions is very complicated. Experiments that would help provide quantitative information would include the study of Fe(II)(L)NO autodecomposition at high pH conditions, NO + S(IV) kinetics over a range of pH conditions, Fe(II/III) - sulfur oxyanion complexes. The mechanism of the reaction of Fe(III) with HSO_3^- , the kinetics of the reaction of $(NO)_2SO_3^{2-}$ with Fe(II), complexation of various nitrogen-sulfur compounds to Fe(II) and Fe(III), and the effect of various ligands on the above reactions involving Fe(II) and Fe(III).

Conclusions

The reaction of ferrous nitrosyl chelates with sulfite and bisulfite ions has been investigated over a pH range of 2 to 10 at 25° C. A rate equation for the

disappearance of Fe(II)(EDTA)NO and Fe(II)(NTA)NO in the presence of sulfite and bisulfite ions has been determined. The range of reactant concentrations where this equation is valid has been established.

The major products of the reaction are Fe(III), SO_4^{2-} , N_2O , N_2 and HADS. HADS can further react to form other nitrogen-sulfur compounds. The relative amounts of the products formed are dependent on the reaction conditions. A mechanism that is capable of explaining the rate behavior and the observed product mixture has been developed. The mechanism provides an explanation of the complexity of this reaction system and helps explain the results obtained by others.

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We appreciate the support and encouragement of Earl Evans, Joseph Strakey, and John Williams.

Table 1

Species	Raman Shift (cm ⁻¹)	Relative Molar Intensity ^a
NO	1877	-
N ₂ O	1285	~0.18
NO ₂ ⁻	818	0.053
	1240	~0.025
	1331	0.125
NO ₃ ⁻	1050	0.95
N ₂ O ₂ ²⁻	692 ^b	weak ^b
	1115 ^b	weak ^b
	1383 ^b	strong ^b
SO ₃ ²⁻	987	0.12
HSO ₃ ⁻	1023	~0.10
	1055	~0.13
SO ₂ ·H ₂ O	1152	-
S ₂ O ₆ ²⁻	710	0.47
	1092	1.48
SO ₄ ²⁻	455	~0.07
	981	1.00
HSO ₄ ⁻	1050	0.05
(NO) ₂ SO ₃ ²⁻	932	0.19
	1051	0.31
	1130	0.51
HADS	700	0.13
	1084	1.43
HAMS	760	0.075
	1058	0.48
ATS	1097	1.80
ADS	1084	1.02

HA (pH 7)	1004	0.21
HA (pH 9)	918	0.09
SA (pH 3)	1049	0.41
H ₃ BO ₃	876	0.22

a. SO_4^{2-} 981 cm^{-1} = 1.000

b. J. E. Rauch and J. C. Decius, Spectrochim. Acta 22, 1963 (1966)

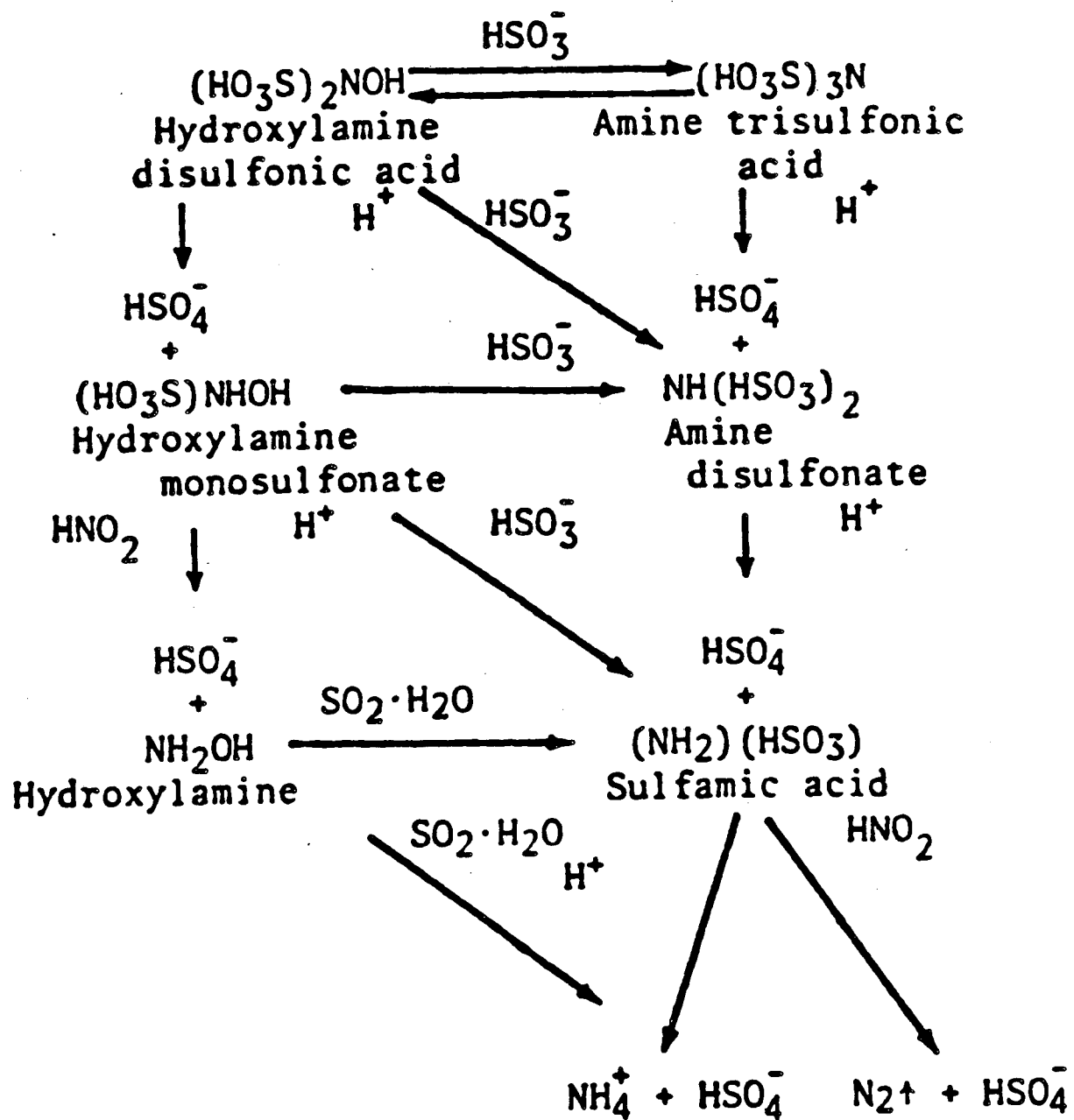
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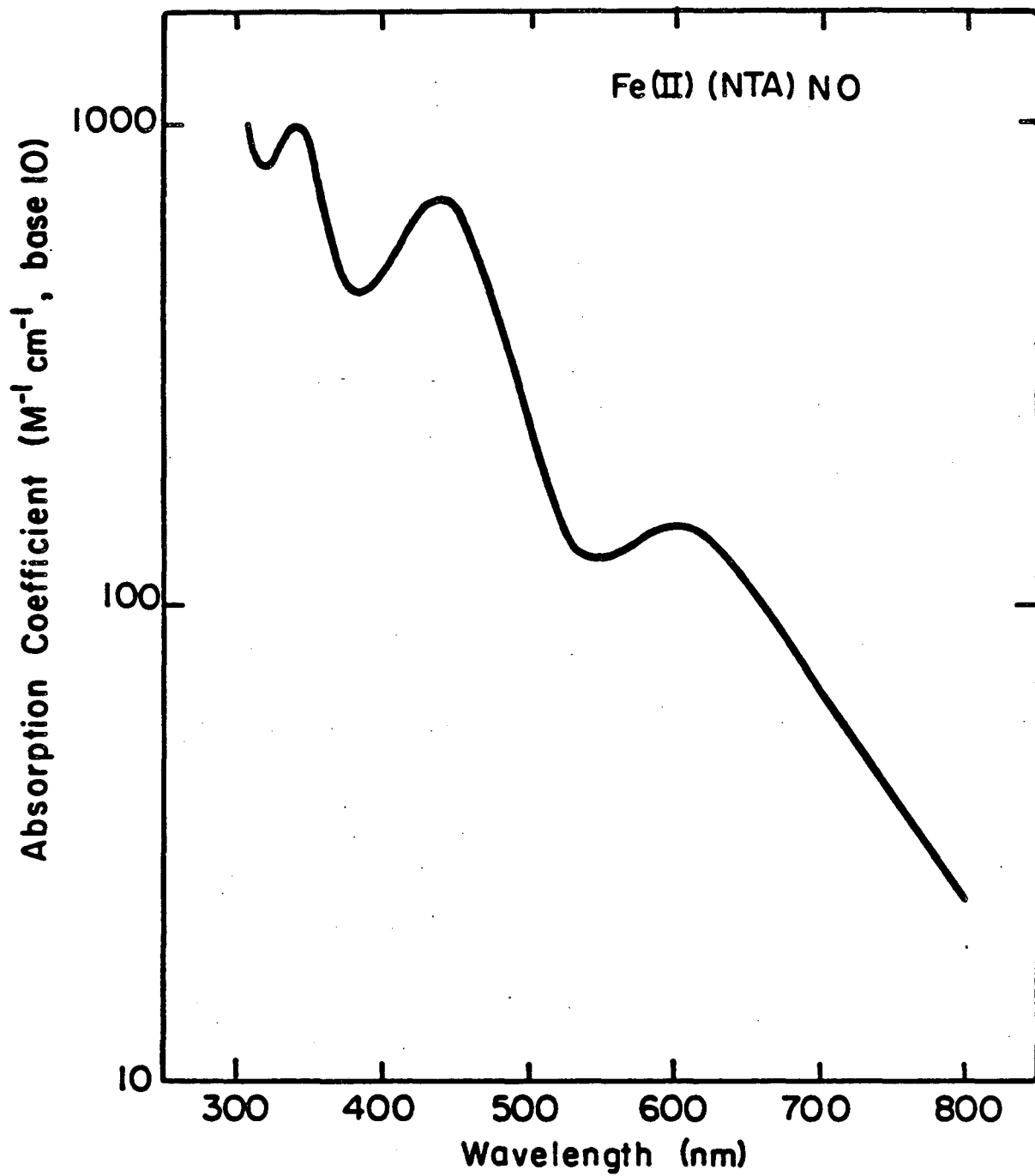
Figure Captions

- Figure 1 Reactions of nitrogen-sulfur compounds in aqueous solutions.
- Figure 2 Visible absorption spectrum of Fe(II)(NTA)NO .
- Figure 3 Rate dependence on S(IV) concentration.
- Figure 4 Rate dependence on pH.
- Figure 5 Fraction of Fe(II) oxidized as a function of $[\text{SO}_3^-]:[\text{Fe(II)(NTA)NO}]$.
- Figure 6 Reactant and product concentrations as a function of time after mixing.
- Figure 7 Raman spectrum of mixture of Fe(II)(NTA)NO and HSO_3^- .
- Figure 8 A) Effect of $[\text{SO}_3^-]:[\text{Fe(II)(NTA)NO}]$ on production of N_2O and N_2 .
B) Effect of Fe(II)(NTA)NO concentration on production of N_2O and N_2 .
C) Effect of pH on production of N_2O and N_2 .
- Figure 9 Second order rate as a function of Fe(II)(NTA)NO concentration.



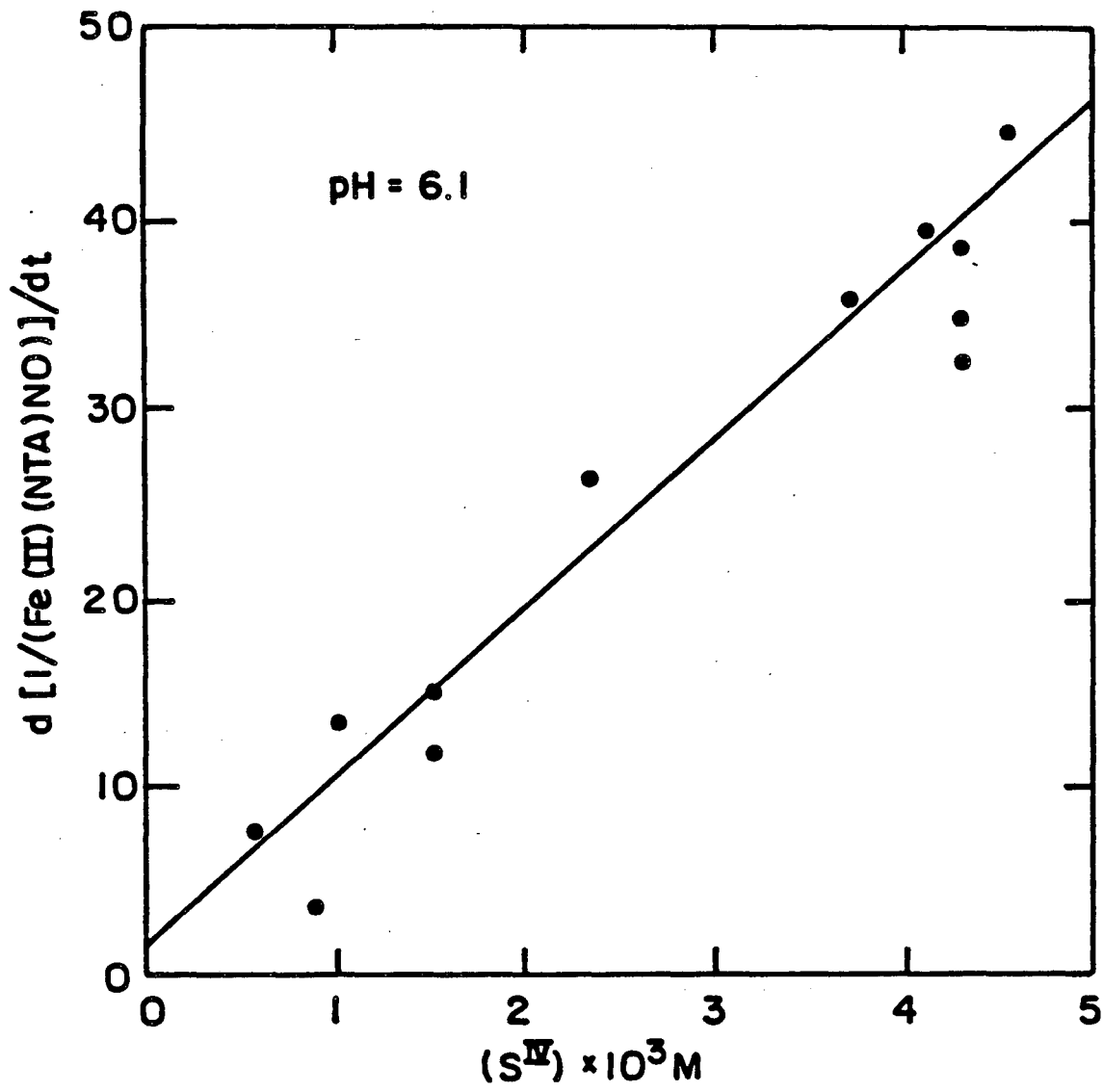
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Figure 1



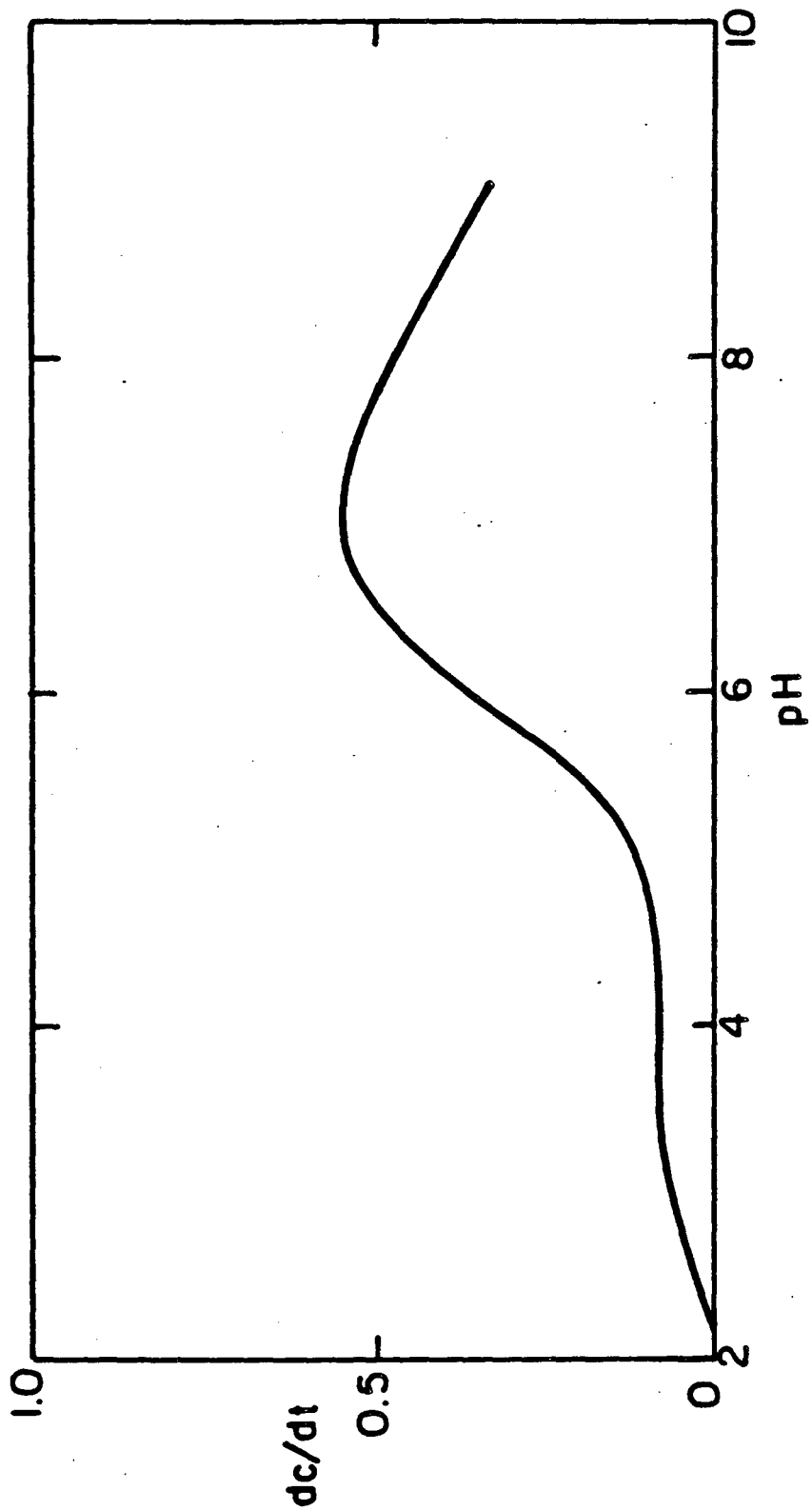
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Figure 2



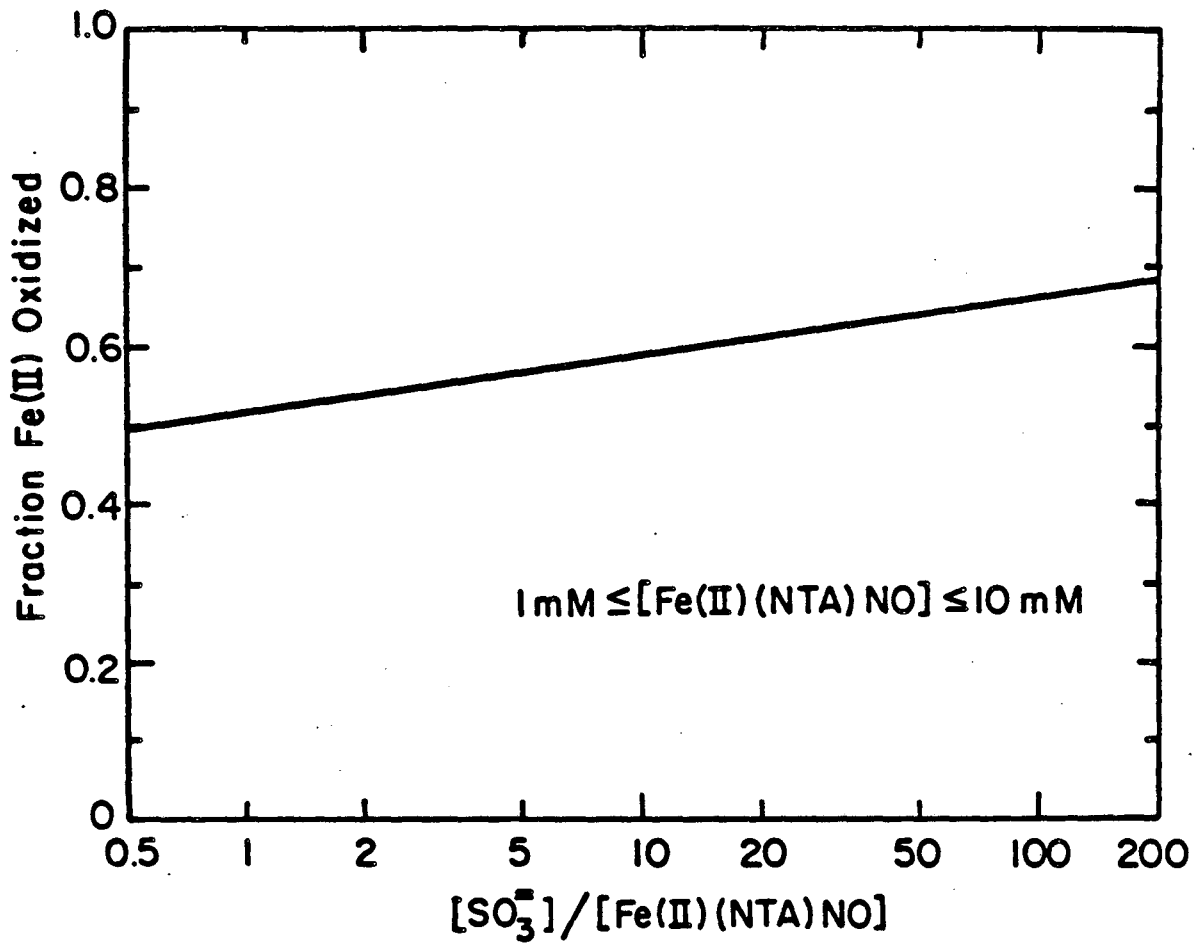
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Figure 3



XBL032-5298

Figure 4



XBL 846-7005

Figure 5

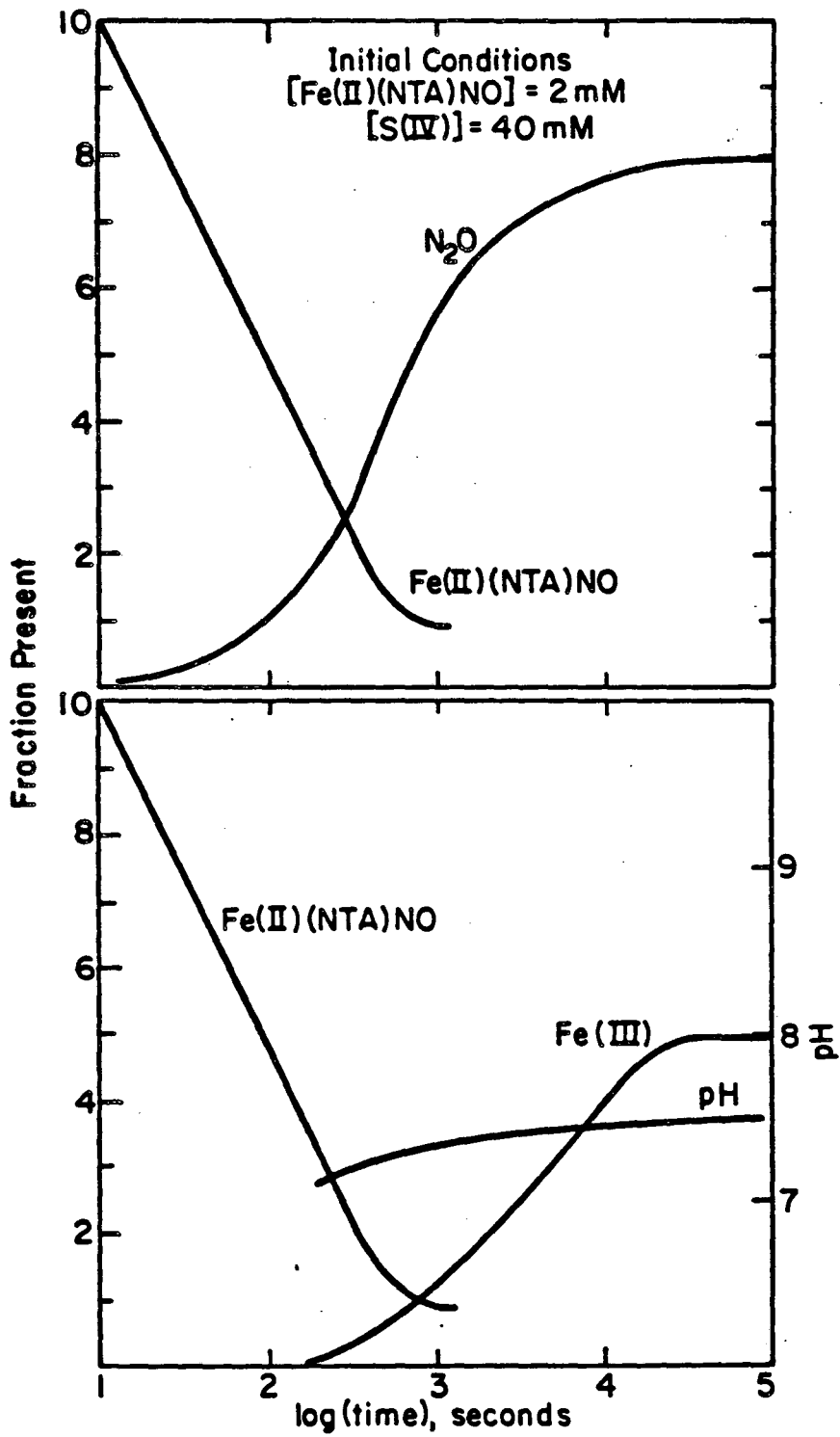
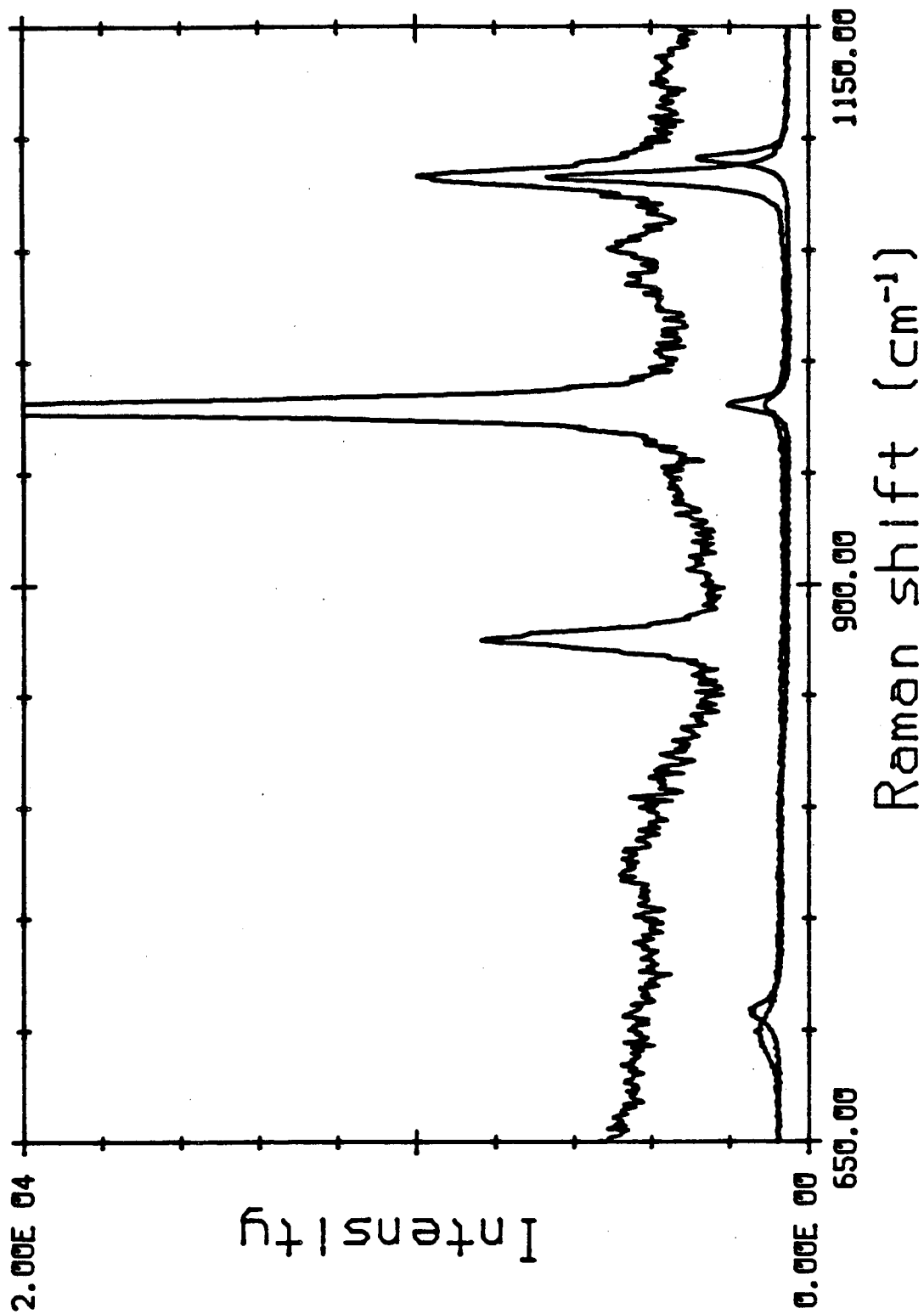


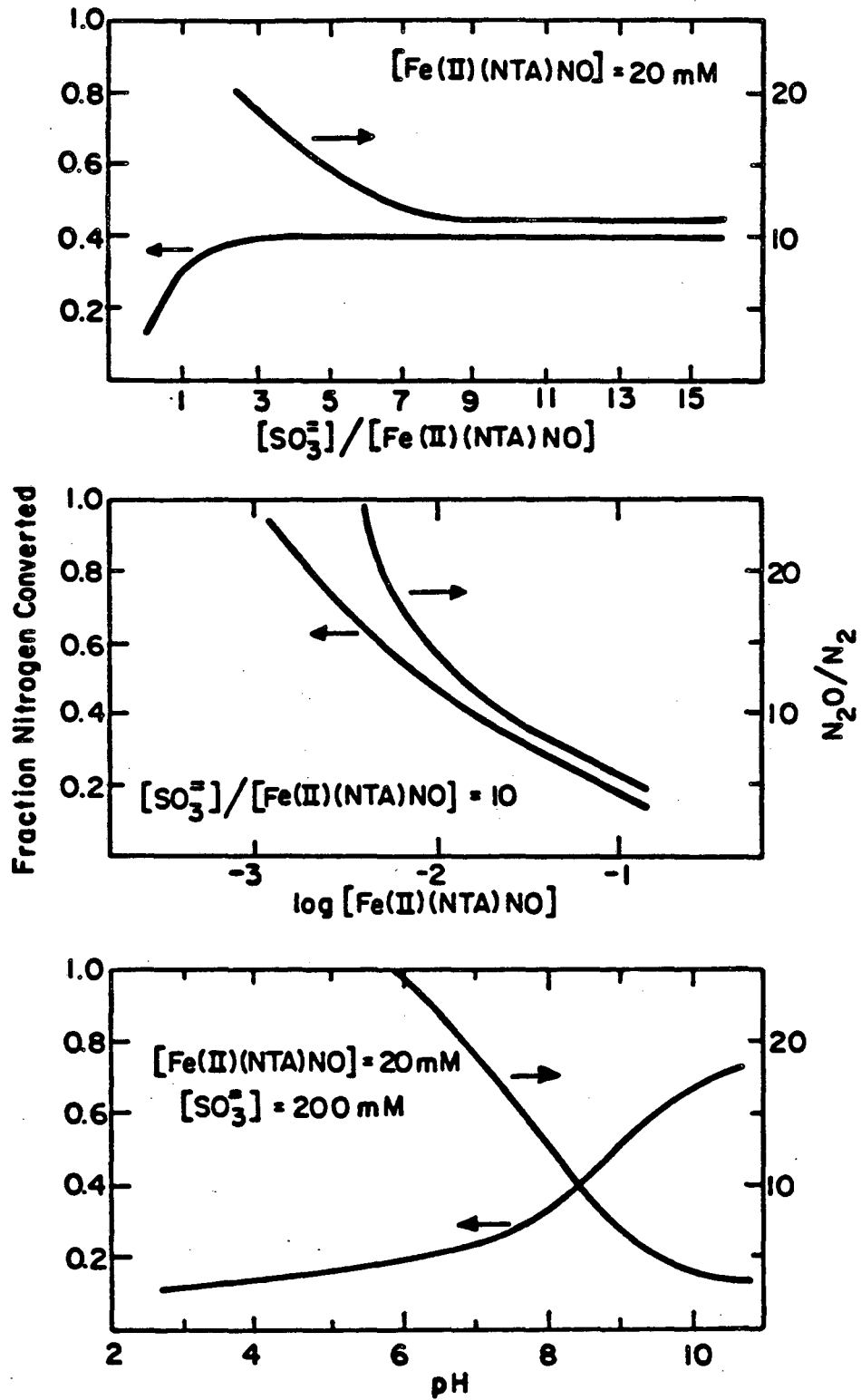
Figure 6

FE(II) (NTA)NO + H5O3-



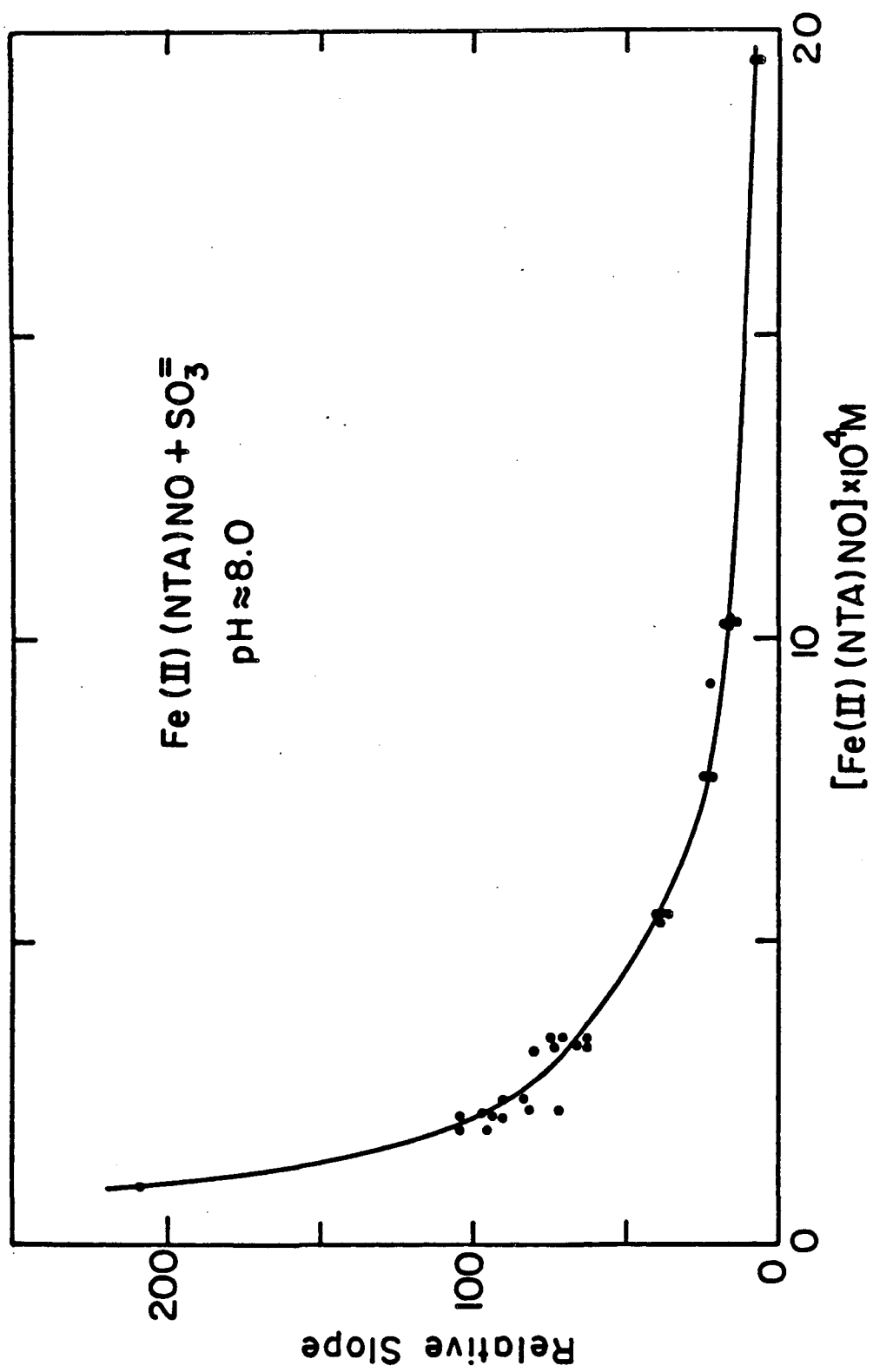
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Figure 7



XBL 846-7006

Figure 8



XBL823-5378

Figure 9

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