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KINETICS OF THE REDUCTION OF NITRITE ION
BY SULFUR DIOXIDE IN AQUEOUS SOLUTION

Steven Bartley Oblath
(Ph.D. thesis)

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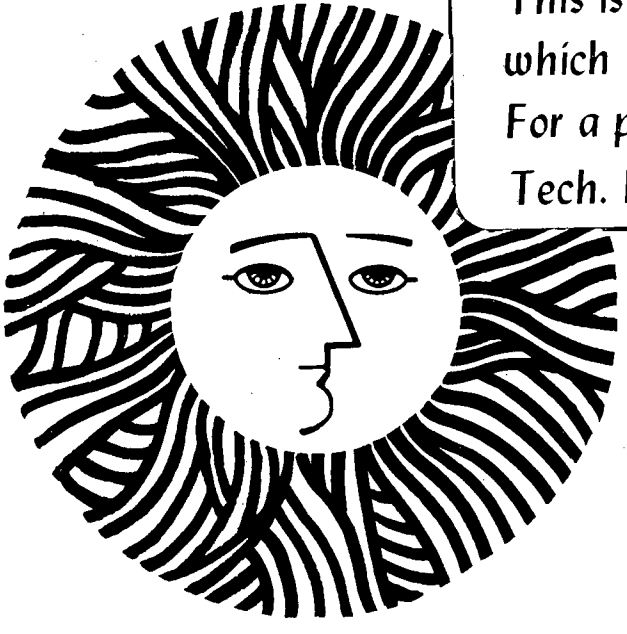

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University of California
Berkeley, California

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TABLE OF CONTENTS

I. INTRODUCTION. 1

A. History of Air Pollution. 1

B. Gas Phase Reactions of NO_x and SO_2. 3

C. Interactions of SO_2 and NO_x 5

D. Solution Reactions Between Nitrite and Bisulfite Ions . 7

E. Objectives. 14

F. A Note on Nomenclature. 15

II. EXPERIMENTAL. 16

A. General Experimental Setup. 16

B. Reagents. 16

C. Spectrophotometric Methods. 18

D. Iodometric Methods of Analysis. 22

E. Other Methods of Analysis 25

F. Nitrite/Bisulfite Studies 27

G. Nitrite/Hydroxylamine-N-Sulfonate Studies 29

III. RESULTS 31

A. Kinetics of Hydroxylamine Disulfonate Formation 31

B. Stoichiometric and Mass Balance Studies 52

C. Formation of Nitrous Oxide. 55

D. Kinetics of Nitrite Ion Reactions with Hydroxylamine Monosulfonate 60

IV. DISUCSSION. 73

A. Mechanism for the Formation of Hydroxylamine Disulfonate 73

B. Mechanism for the Formation of Nitrous Oxide. 79

C. Mechanism for the Reaction of Hydroxylamine Monosulfonate with Nitrite Ion. 81

D. Buffer Effects. 86

E. Confirmation of Results 89

V. SUMMARY AND CONCLUSIONS 92

APPENDIX A: Sample Data 99

1. Mass Balance. 99

2. Rate Determination. 100

3. Stoichiometric Determination. 101

APPENDIX B. Error Analysis and Calculational Methods. 102

APPENDIX C. Abstract of "Kinetics of the Formation of Hydroxylamine Disulfonate by Reaction of Nitrite with Sulfites," J. Phys. Chem., 1981, 85,: 1017-1021 . . 110

ACKNOWLEDGEMENTS 111

REFERENCES AND FOOTNOTES 112

KINETICS OF THE REDUCTION OF NITRITE ION BY SULFUR DIOXIDE IN AQUEOUS SOLUTION

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ABSTRACT

Reactions between nitrite and bisulfite ions in aqueous solutions were studied in which sulfur (IV) species are oxidized to sulfate ions and nitrogen (III) species are reduced. The dependence on temperature, ionic strength, acidity, and solution composition was determined. The actual products formed depend primarily on the concentration of bisulfite ion. The importance of these reactions to atmospheric aerosol formation processes is discussed.

Under most conditions, the nitrogen product is hydroxylamine-N, N-disulfonate. Two processes are responsible for its formation. The first process (when the bisulfite concentration is greater than 0.1 M) is first order in nitrite ion, second order in bisulfite ion, and independent of acidity and temperature. It has a strong dependence on the ionic strength. The second and dominant process contributes to the product formation under all conditions and is first order in nitrite, bisulfite, and hydrogen ions. This process is independent of ionic strength and has a 12 kcal/mole activation energy. Both processes are insensitive to the choice of buffer. Whenever the hydrogen ion concentration is nearly equal to that of the bisulfite ion, nitrous oxide is also a product.

A mechanism is proposed to account for these results. It consists of a direct reaction of nitrite ion with metabisulfite ion to form

hydroxylamine disulfonate, in parallel with a reaction between nitrous acid and bisulfite ion to form nitrososulfonic acid. This rapidly adds a bisulfite ion to form hydroxylamine disulfonate or undergoes hydrolysis to form nitrous oxide. Other possible mechanisms are also presented.

The reaction between nitrite ion and hydroxylamine-N-sulfonate to produce nitrous oxide was also investigated. The reaction is first order in nitrite ion, second order in hydrogen ion, and between zero and first order in hydroxylamine monosulfonate, depending on the concentration. There is a dependence on the buffer type and concentration and an 8 kcal/mole activation energy. A mechanism is proposed. The rate is too slow to account for the nitrous oxide produced in the hydroxylamine disulfonate formation.

I. INTRODUCTION

Nitrite ion and bisulfite ion both have extensively studied chemistries. The interaction of the two species is not a new field, having first been investigated over a century ago. What is it that drives chemists to look at the interactions once again? In the present case, it is the abundance of SO_2 and NO_x (NO and NO_2) as urban air pollutants and the equilibria between the ions and gases in the presence of water. In the search for answers to problems in air pollution, potential reaction pathways involving these species (including ionic ones) must be understood and evaluated. Because the kinetics of reactions between nitrite and bisulfite ions was not sufficiently understood, questions in the field of atmospheric aerosol formation could not be answered. The work described herein serves to increase this understanding of the ionic reactions as they contribute to the aerosol field. A brief digression into the background of air pollution is given first to clarify the rationale for the study.

A. History of Air Pollution

The study of air pollution as a science is considered to have begun in the 1950's when Haagen-Smit identified some of the processes responsible for the formation of photochemical smog.[1] Pollution of the atmosphere by humans has been going on for quite a bit longer, at least since the beginning of combustion of fossil fuels. As early as the 14th century, records show that air pollution in the form of combustion soot was a problem in London.[2] These early problems were

alleviated by converting from soft to hard coal and later by improvements in combustion technology. Cleaner fuels such as oil and gas also helped control the problems. The increased use of combustion eventually caught up with the early controls, and in 1930 an air pollution episode in Belgium may have killed 60 people[2] - the result of a week-long stagnation of the atmosphere. In 1948 in Denora, Pennsylvania, and again in 1952 in London, other major episodes resulted in deaths.[2] These events, fortunately rare, prompted studies in the field of air pollution. The Los Angeles basin in southern California had not had a major episode, but the almost daily occurrence of visibility-reducing pollution made it a natural place for early studies. It was there that Haagen-Smit made his discoveries about photochemical smog.[1]

The pollution episodes mentioned were caused by stagnation which resulted in unusually high levels of urban pollutants, among them CO, NO, NO_2, SO_2, and hydrocarbons. These gases, as well as finely-divided particles, are the result of combustion processes. They are known as primary pollutants. Other species such as ozone, organic nitrates (PAN), and sulfate aerosols are the results of processes occurring in the atmosphere and are called secondary pollutants. Processes which form ozone and organic nitrates are now understood to be photochemical in nature. Studies in the thirty years since Haagen-Smit have shown that nonphotochemical processes also exist. Winter pollution episodes in the northern latitudes are an example because there is insufficient ultraviolet radiation in these areas to explain

the pollution in terms of photochemistry. Although not fully understood, these reactions are termed "dark reactions." A great deal of emphasis has recently been placed on studying those dark reactions which result in the formation of sulfate aerosols. The intent of this study is to determine the possible role of nitrite ion in the non-photochemical production of sulfate species. It should be stated that the photochemical studies described below presented the ideas leading to the study of this ionic mechanism.

Carbon dioxide, while considered a pollutant in terms of the greenhouse effect, is not treated in this thesis.

B. Gas Phase Reactions in NO_x and SO_2

The oxides of nitrogen (NO_x) are known to undergo a number of reactions in the atmosphere until eventually removed by adsorption on surfaces or washout by rainfall. The most simple of them is the oxidation of nitric oxide (the principal product of nitrogen in high temperature combustion) to nitrogen dioxide:

$$NO + O_2 \longrightarrow NO_3$$

$$NO_3 + NO \longrightarrow 2\ NO_2$$

The rate of this reaction at ambient atmospheric concentrations of NO (less than 1 ppm) is too slow to be of importance in air pollution chemistry. The reactions which are believed to control the atmospheric chemistry of the nitrogen oxides are known as the NO_2 photolytic cycle:[1]

$$NO_2 + h\nu \rightleftarrows NO + O$$

$$O + O_2 \rightleftarrows O_3$$

$$O_3 + NO \rightleftarrows NO_2 + O_2$$

Although these reactions form a null cycle after reaching equilibrium, the rate of attainment is fast enough to control the atmospheric concentrations. In a real situation there are a number of other reactions, mostly involving hydrocarbons, which alter the equilibria by involving the intermediates of the cycle.

The oxidation of sulfur dioxide to sulfur trioxide or particulate sulfates also takes place in a polluted atmosphere until removed by washout.[2] Again the dark reaction with oxygen is too slow to be important. The photochemically assisted oxidaton is also slow.

$$2\ SO_2 + O_2 \rightleftarrows 2\ SO_3 \quad \text{(dark or light assisted)}$$

Reactions which involve the same net equation but take place on the surface of dry particles are also believed to be slow. Two important oxidation pathways are known. The first involves the catalytic oxidation of SO_2 in aerosol droplets. Iron and manganese oxides are the usually cited catalysts; however, graphitic soot particles seem to be a far more efficient catalyst.[3] The other important pathway involves the oxidation of SO_2 in the presence of oxides of nitrogen, a process which was originally believed to be photochemical and is still being investigated.

C. Interactions of SO_2 and NO_x

An enhancement in the rate of production of sulfate aerosols is observed in the presence of NO_2 under photochemical conditions.[4] The reaction of O_3, O, and NO_3 species with sulfur dioxide have all been suggested as the reason for this enhancement, by means of the following reactions:

$$O_3 + SO_2 \longrightarrow SO_3 + O_2$$

$$O + SO_2 \longrightarrow SO_3$$

$$NO_3 + SO_2 \longrightarrow NO_2 + SO_3$$

The rates of these reactions have recently been shown to be too slow to account for the observed effects.[5] Similar reactions with NO_2, N_2O_3, and related species can be visualized but are also too slow. The key to enhancement appears to be the role of water vapor (or liquid water) and the formation of the hydroxyl radical (OH).

Hydroyxl radicals can be formed from the photolytic cleavage of nitrous acid with ultraviolet radiation. The nitrous acid is in turn formed from the reaction of NO and NO_2 with water:

$$H_2O + NO + NO_2 \longrightarrow 2\ HONO$$

$$HONO + h\nu \longrightarrow HO + NO$$

The hydroxyl radical then combines with sulfur dioxide, forming an unstable radical product ($HOSO_2$) which can further react with O_2 followed by NO or NO_2 to produce sulfate through a rather complex set of reactions:[5]

$$HO + SO_2 \longrightarrow HOSO_2$$

Because OH radicals are present as a result of hydrocarbon reactions by other mechanisms, and $HOSO_2$ radicals can be converted to sulfate in the absence of NO_x, it is not clear that this is the actual mechanism which is taking place. Water vapor is necessary for the enhancement, and the sulfate aerosols are prone to deliquesce at low relative humidities to form droplets.[6] This suggests that non-photochemical reactions could be involved. From consideration of what is known about the prodution of sulfuric acid by the lead chamber process[7] and the nonphotochemical winter episodes, a "dark" interaction is not unexpected.

The idea of droplet mechanisms suggests that ionic reactions between nitrous acid and sulfurous acid (or hydrated SO_2) could be occurring. Only careful determination of the kinetics of these reactions will allow the mechanism to be counted or discounted as an actual atmospheric process. Since this study began, several researchers have shown that interactions of NO_x and SO_2 to enhance sulfate production do take place in aerosols which are not being irradiated.[8,9] Further demonstration that ionic solution reactions

can occur at low concentrations comes from experiments where NO_2 was bubbled through dilute solutions of sulfurous acid.[10] The possibility of nitrate ion reactions has been discounted because these reactions are only observed at high concentrations. At moderate concentrations the reactions have slowed enough so they are immeasurable, and at low concentrations it is expected that there would be no reaction as well.

D. Solution Reactions Between Nitrite and Bisulfite Ions

The solution reactions between nitrite ion and bisulfite or sulfite ions have been studied since 1845 when Fremy noted the formation of a variety of salts from mixtures of potassium nitrite, hydroxide ion, and sulfurous acid. The 135 years of study since then have produced much useful information; but since the system has become of interest to atmospheric chemistry only very recently, much of the needed information has yet to be determined. Atmospheric concentrations of NO_x and SO_2 are almost always less than one part per million (ppm) so knowledge of the reactions at very low concentrations is needed. Once the correct mechanisms are understood, extrapolation will allow this concentration range to be evaluated. Extreme care must be used in this type of extrapolation as other reactions tend to enter the mechanism as inteferences.[11] The earlier studies, while a convenient starting point, were concerned with the kinetics of the synthetic processes and were all done at moderate or high concentrations. The results are of little use to atmospheric chemists.

One of the earliest studies, as already noted, was Fremy's work on the synthesis of many of the amine- and hydroxylamine-sulfonates and their derivatives. Divers and Haga continued this work and came up with a systematic classification of the many derivatives.[12] Most of this work dealt with the salts rather than the solutions of these compounds. It was in 1904 that Raschig, considering the possible reactions involved in the lead chamber process, came up with a reaction scheme which could explain the entire synthesis.[13] This scheme has been shown to be correct for the most part and is shown in an updated form in Figure 1. For clarity the sulfate species which is formed in each of the hydrolysis steps has been omitted. The one species in this scheme which has never been identified—nitrososulfonic acid—has been placed in quotation marks. There are several other reactions which can be considered part of this system; but since they play no role under the conditions in this study, they have not been included. In each case they are minor processes unrelated to the general scheme.

Early studies of the entire reaction scheme showed that the formation of amine trisulfonate and its hydrolysis products were favored at high concentrations of sulfur species or at higher temperatures (above 50°C) or both. Slightly basic solutions also favor these products by slowing or stopping the acid-catalyzed hydrolysis steps. It is clear from this that at the low concentrations and weakly acidic solutions which characterize the aerosol droplet reactions, the rates of formation of nitrososulfonic acid, hydroxylamine-N,N-disulfonate, hydroxylamine-N-sulfonate, and nitrous oxide will be the most

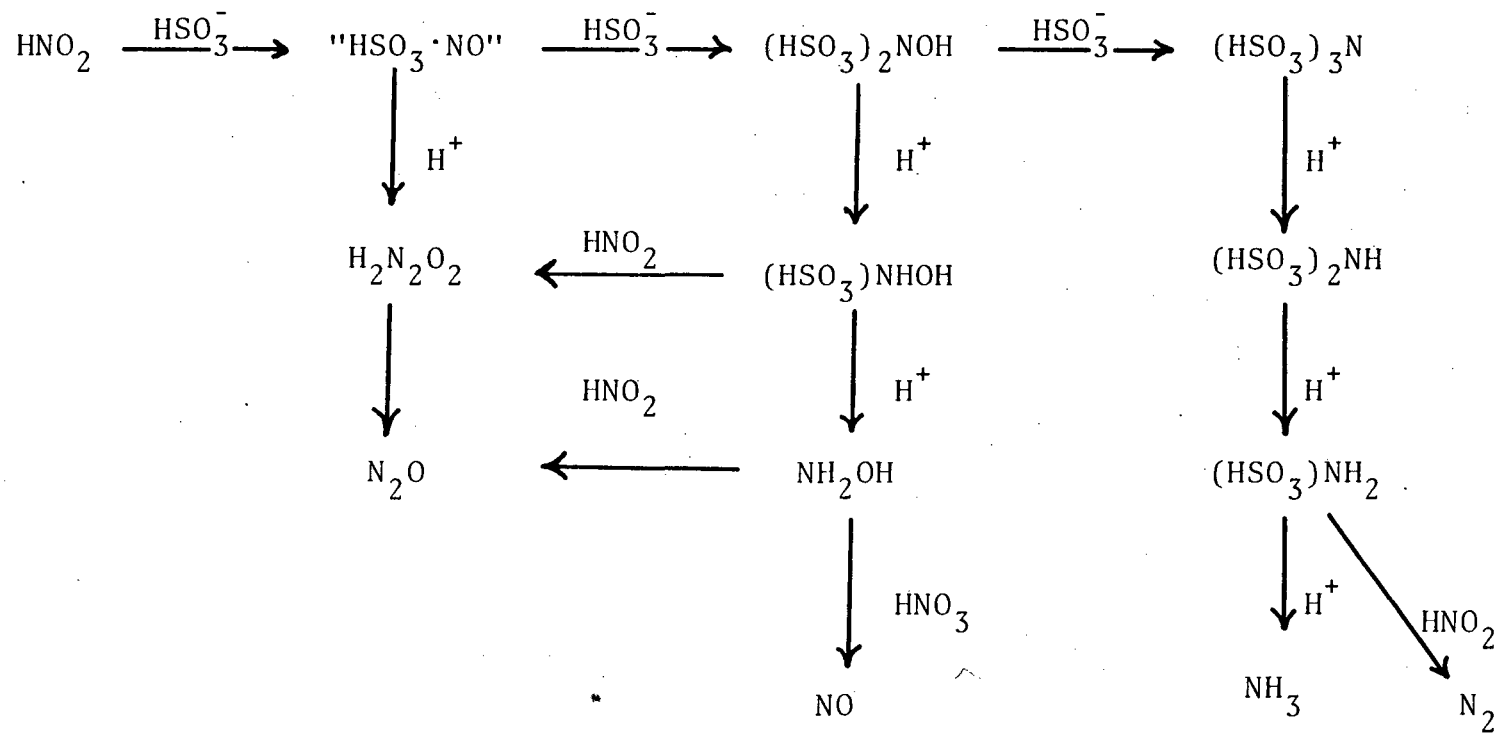

Figure 1. Raschig reaction scheme for nitrite and bisulfite ions.

important. These formation reactions are among the least well characterized reactions in the entire scheme.

The hydrolysis reaction taking hydroxylamine disulfonate to the monosulfonate is probably the best characterized of any of these reactions.[14] It is acid catalyzed and has a rate law of the form

$$\text{Rate} = (k[H^+] + k')\,[\text{disulfonate}] \quad .$$

This reaction proceeds readily at room temperatures and concentrations of the disulfonate on the order of 10^{-2} M. In the absence of acid, the reaction proceeds rather slowly. The hydrolysis reaction of hydroxylamine monosulfonate is believed to follow a similar rate law but is observed only at temperatures well above 50°C. Because of this slow rate, the reaction is not important to atmospheric chemistry.

In addition to hydrolysis, both hydroxylamine di- and monosulfonates undergo sulfonation reactions (not shown in Figure 1).[15] For disulfonate, both amine trisulfonate and amine disulfonate are formed. The hydroxylamine monosulfonate reacts to form amine di- and monosulfonates. For both of the hydroxylamine sulfonates, the rate law is of the form

$$\text{Rate} = k[HSO_3^-][\text{sulfonate}] \quad .$$

The rates of these reactions are relatively slow except at relatively high (greater than 10^{-1} M) concentrations. Hydrolysis reactions of

the amine sulfonates are known but shall be ignored as they do not enter into the formation of atmospheric aerosols. In all four of these reactions of hydroxylamine sulfonates, there is no reason to believe that their rate laws will not be correct when extrapolated to much lower concentrations. The proposed mechanisms suggest that side reactions should not interfere.

The reaction between nitrous acid or nitrite ion and hydroxylamine-N-sulfonate to form N_2O has been observed[16] but little kinetic information was noted. It was believed that the reaction was independent of the monosulfonate concentration, but this should not hold if one goes to lower concentration levels. A second order dependence was reported for hydrogen ion. The reaction is shown on the scheme as proceeding through the hyponitrous acid intermediate, although there is some doubt as to whether this is really what happens. Under the conditions of acidity at which the reaction has been observed, any $H_2N_2O_2$ formed would very rapidly decompose to nitrous oxide.[17]

The rate of production of hydroxylamine-N,N-disulfonate from nitrite and bisulfite ions has been studied several times, but the results were somewhat inconclusive. In each study the reaction of interest was:

$$NO_2^- + 2\ HSO_3^- \longrightarrow HON(SO_3)_2^{2-} + OH^- \quad .$$

The first study showed that the reaction proceeded most rapidly under weakly acidic conditions.[18] No other information was given. Then in 1956 Seel and Degener[19] reported a detailed study of the reaction and proposed the following rate law:

$$\text{Rate} = k_1[H^+][NO_2^-][HSO_3^-] + k_2[H^+]^2[NO_2^-] \quad .$$

They explained this by a mechanism with two concurrent processes involving nitrososulfonic acid and nitrosyl ion (NO^+) as the two intermediates. In 1959 Yamamoto and Kaneda[20] studied the same reaction under similar conditions. A similar two process rate law was reported except that the bisulfite independent term showed a marked dependence on the concentration of the buffer, here acetate-acetic acid. Finally, in 1961 the reaction was again investigated under higher concentrations and lower acidities and a quite different rate law was reported:[21]

$$\text{Rate} = \frac{k_3[NO_2^-][HSO_3^-]^2}{1 + k_4[SO_3^{2-}]} \quad .$$

No attempt was made to reconcile these results with the previous work. Although there is no stated dependence on the hydrogen ion concentration, the sulfite term in the denominator serves nearly the same purpose. This rate law was also explained in terms of nitrososulfonic acid formation. Values of all the reported constants are given in Table 1.

Clearly at least one of these mechanisms or rate laws is incorrect; and had sufficient results over a wide enough range of conditions been available, the conflict could have been resolved. The order with respect to bisulfite ion is vital to the evaluation of the reaction at atmospheric concentrations due to the low concentrations of bisulfite

Table 1. Previously determined rate constants

Rate Constant	Value	Temperature	Reference
k_1	9.0×10^2 l^2/mol^2-sec	5°C	19
	1.8×10^3 l^2/mol^2-sec	15°C	20
k_2	1.1×10^6 l^2/mol^2-sec	5°C	19
	1.0×10^6 l^2/mol^2-sec	15°C	20
k_3	2.4×10^{-2} l^2/mol^2-sec	25°C	21
k_4	1.8 l/mol	0°C	21

which result from ambient pollutant levels. In addition, any dependence on the buffer species must be known as the droplets would not be buffered by the sort of species used in these studies.

E. Objectives

With this background - in terms of both the reactions and the problems of air pollution - our investigation was begun. In its broadest terms, the objective was to study the kinetics of the initial reactions of nitrite ion in bisulfite solution at as low a concentration as feasible. Specifically, several things were being searched for. First was a determination of the kinetics of the formation of hydroxylamine-N,N-disulfonate. It was hoped this would resolve the discrepancies in the previously reported work. Second, evidence of the intermediate species (nitrososulfonic acid) was being searched for, as well as N_2O, its hydrolysis product. The final objective was to evaluate the rate of reaction of nitrite ion with hydroxylamine-N-sulfonate to conclusively show which pathway is responsible for the formation of nitrous oxide. This in turn could help determine whether or not an intermediate such as nitrososulfonic acid was indeed involved.

By determining these mechanisms and reaction rates the production of sulfate aerosols by this reaction scheme can be evaluated. Unfortunately the kinetics of the dissolution of NO_x into water to form nitrite ion is not well established, and the complete evaluation of the sequence must wait. The understanding of these mechanisms also provides a foundation for the interpretation of flue-gas scrubber systems which have recently been developed by Japanese workers.[22]

In these systems both NO_x and SO_2 are simultaneously removed and various hydroxylamine- and amine-sulfonates have been identified. With these goals in mind a fairly wide range of reaction conditions has been investigated, in order to give the results as wide an applicability as possible.

F. A Note on Nomenclature

It has already become clear that several words about nomenclature are necessary. By custom (in the air pollution field) the oxides of nitrogen, or NO_x, refer only to the species NO and NO_2. Nitrous oxide (N_2O) is not considered a part of NO_x. This convention will be used throughout this work. Similarly, I shall define nitrogen (III) or N(III) as the sum of NO_2^- and HONO, and sulfur (IV), or S(IV), as the sum of sulfurous acid (or hydrated SO_2), bisulfite ion, and sulfite ion. When one species in particular is being referred to, it will be called by its proper name.

Hydroxylamine-N,N-disulfonate ion will also be called hydroxylamine disulfonate although the former is the more exact name. These will be used interchangeably with the more common abbreviation HADS. Hydroxylamine-N-sulfonate will also be referred to as hydroxylamine monosulfonate and abbreviated HAMS. Both these species are polyprotic acids and can exist in several charge states. Unless one specific form is stated by indicating the charge of the ion, the name or abbreviation will stand for all the forms collectively. The charge state becomes important only in the discussion of the mechanisms. In all but very basic or very strongly acidic solutions, HADS exists as the dianion and HAMS as the singly charged anion.

II. EXPERIMENTAL

A. General Experimental Setup

The kinetics of the reactions between nitrite and bisulfite ions were studied by addition of a known amount of nitrite ion to a buffered solution of bisulfite ion. Nitrite ion was introduced by mixing two solutions or by addition of a small amount of solid sodium nitrite which immediately dissolves. Rates were measured by following changes in the concentrations of nitrite ion (spectrophotometrically) or sulfur species (iodometric titrations). The effects of ionic composition, temperature, acidity, and concentrations were investigated. These data, along with product analyses, allowed determination of the experimental rate law and provided suggestions for a proposed mechanism.

The reaction between nitrite ion and hydroxylamine-N-sulfonate (HAMS) was studied in an analogous fashion. Because a suitable analytic technique was not available, the HAMS concentration was not monitored, but was determined by addition of a known weight of pure salt. For this reason all these experiments were carried out under pseudo-first-order conditions. Specific details of the conditions for both reactions are given in a later section.

B. Reagents

All the reagents used in this study, with three exceptions, were of analytic reagent grade and were used as supplied. The exceptions were potassium hydroxylamine-N,N-disulfonate - $KON(SO_3K)_2$, potassium hydroxylamine-N-sulfonate - $HONHSO_3K$, and potassium nitrosodisulfonate -

$ON(SO_3K)_2$. Solutions of bisulfite ion were prepared from sodium metabisulfite ($Na_2S_2O_5$) to allow initial concentrations to be determined by addition of a known weight of the salt. Sodium bisulfite is available only as the metabisulfite salt with an unspecified amount of water, and an unspecified equivalent weight. All solutions were prepared using deionized water obtained from a Barnstead NANOpure system.

Potassium hydroxylamine-N,N-disulfonate (HADS) was prepared by the method of Rollefson and Oldershaw.[18] This consisted of bubbling SO_2 through an ice-cold solution of potassium nitrite and potassium acetate. The white solid which precipitated was collected, washed, and recrystallized in KOH solution.[23] The resulting pure crystals were dried and stored over P_2O_5 in a vacuum desiccator which was kept at 5°C. There was no sign of decomposition. Elemental analysis was performed by the Microchemical Laboratory at the University of California, Berkeley. Calculated for $K_3NS_2O_7$ $1.5 \cdot H_2O$ K:S:N:H = 35.1 : 19.1 : 4.2 : 0.9. Found: K:S:N:H = 35.3 : 18.8 : 4.3 : 0.7.

Potassium hydroxylamine-N-sulfonate (HAMS) was obtained by acid hydrolysis of the disulfonate species. The method is described by Seel and Degener[19] with the modifications noted below. The tribasic salt obtained above was used rather than the dibasic one. When the hydrolyzed solution (strongly acidic) was to be rapidly cooled and neutralized, excess base was added and the pH then adjusted with dilute nitric acid. Again a white crystalline solid was obtained and after

washing was stored in a vacuum desiccator over P_2O_5. When stored in a refrigerator (5°C), there was no sign of decomposition. Elemental analysis showed that the anhydrous salt was obtained. Calculated for KNH_2SO_4 K:S:N:H = 25.9 : 21.2 : 9.3 : 1.3. Found: K:S:N:H = 27.5 : 21.7 : 8.9 : 1.3. The excess potassium is probably due to $KHSO_4$ impurities. The yield of this method is lower when using the tribasic precursor; however, there was no need to dry and analyze the disulfonate prior to use. On the whole, I believe this to be the more efficient laboratory scale synthesis.

Potassium nitrosodisulfonate (Fremy's salt) can be obtained by the oxidation of hydroxylamine disulfonate. For this study it was prepared by the method of Moser and Howie[24] by addition of permanganate ion to a solution of freshly prepared hydroxylamine disulfonate. The crude orange crystals were recrystallized in concentrated potassium acetate. The nitrosodisulfonate salt is very soluble, even in an excess of potassium ions; to keep losses to a minimum, the mother liquors were recycled and the recrystallization done in small batches. This process was repeated until there was no futher increase in the molar absorptivity of the solution. The molar absorptivity at 545 nm (ϵ = 20.0 liter/mole-cm) agreed well with the literature value.[25] The compound was stored in a desiccator over CaO and $(NH_4)_2CO_3$ to provide an ammoniacal atmosphere. A slow decomposition was noted so only freshly recrystallized samples were used in this study.

C. Spectrophotometric Methods

Spectrophotometric methods were used to determine the concentrations of both the nitrite ion and hydroxylamine disulfonate. For the

former a direct absorption method was used. For the latter, an indirect method was used, based on the oxidation to nitrosodisulfonate and subsequent measurement. Although in theory this method could have been used for all species of interest, many had overlapping absorptions and only these two species had unique absorptions suitable for rapid analysis. The greatest advantage of this technique is that it is both rapid and noninterfering. This allows data to be collected over a wide variety of conditions.

The basis for this type of measurement is the Beer-Lambert Law, $A = \varepsilon cl$, where A is absorbance, ε is the molar absorptivity in liter/mole-cm, c is concentration in moles per liter, and l is path length in cm. The theory behind this technique is described elsewhere.[26] For a given spectrophotometer, the absorbance and concentration are directly proportional, provided ε remains constant as conditions are changed. Generally in dilute solutions or where nonreactive ions are present in high but fixed amounts, there is no deviation from theory. In the present study, no deviations from ideal behavior were noted, with the exception of nitrite ion in the most acidic buffers. During this study, measurements were carried out with a Beckman DU, Bausch and Lomb Spectronic 20, or Cary 219 visible spectrophotometer. Cell length was 1.0 cm with two exceptions. The Spectronic 20 uses 1.16-cm cells, and at the lowest concentrations 10-cm cells were used with the Cary. No differences were noted between identical experiments with different instruments.

For nitrite ion, absorbances were measured at 354 nm using a visible lamp. The absorbances measured were typically lower than the normally useful range of the Beer-Lambert Law (0.15-0.7); however, calibration curves in every case show good linearity with little scatter. A typical calibration curve for nitrite ion is shown in Figure 2. Sodium nitrite that had been dried in a desiccator was used to prepare all the calibration curves. The useful concentration range for this technique was found to be 5×10^{-4} to 5×10^{-2} moles per liter.

Nitrite ion does not follow the Beer-Lambert Law if one changes the pH of the solution. This is because HONO and NO_2^- both have absorbances at 354 nm, and the nitrous acid is the stronger absorber. However, this was not a problem because all the kinetic data were obtained in buffers which maintained a constant pH. Therefore, the value of ϵ was constant for each experiment. Fortunately all the measured rates were first-order in nitrite ion, and only the slope of a plot of log (concentration) vs. time contains useful kinetic information. Any change in the value of ϵ will correspond to a vertical displacment of the line but no change in slope. Although the absorbance measures the sum of nitrous acid and nitrite ion, the fraction present as nitrite ion may be computed from the equation:

$$pK_a = pH - \log \frac{[A^-]}{[HA]} \quad .$$

The value of pK_a for nitrous acid is 3.15 at 25°C and zero ionic strength.[27,30]

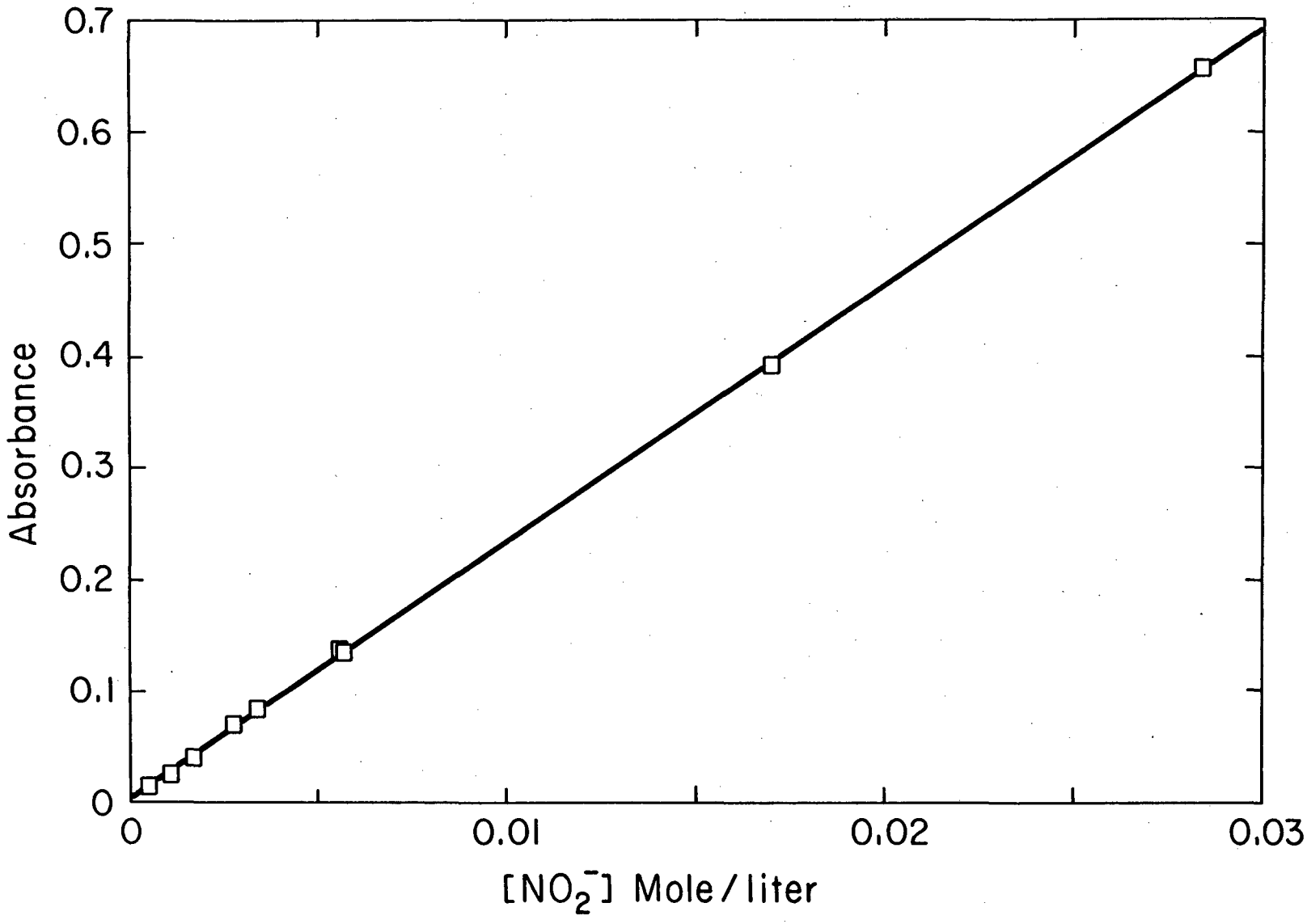

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Figure 2. Calibration curve for nitrite ion at 354 nm on Cary 219.

The concentration of hydroxylamine disulfonate was determined after oxidation to nitrosodisulfonate and measurement of the absorbance at 545 nm. The oxidation was carried out by taking a 5- or 10-ml aliquot of a solution containing HADS and quenching the reaction with 0.4 ml of 30 percent H_2O_2. This removes the bisulfite ions which would otherwise interfere by reacting with any nitrosodisulfonate formed. Silver nitrate (1.0 ml; 1.5 M) was then added, followed by 0.2 ml of 10 M NaOH solution. The silver oxide which is formed is the oxidizing species, and the nitrosodisulfonate formed can be detected spectrophotometrically after filtration. Upon correction for dilution, the conversion is quantitative provided the solution is not too basic (pH greater than 11) and there is not a great excess of peroxide. The net reaction involved is:

$$2\ HON(SO_3)_2^{2-} + Ag_2O \longrightarrow 2\ Ag + 2\ ON(SO_3)_2^{2-} + H_2O$$

Absorbances were measured using 1.16-cm cells with the Spectronic 20. A calibration curve was used to obtain concentrations of HADS after oxidation. Because of the time needed to obtain each data point and the number of possible interferences, this technique was used only to obtain a mass balance when HADS was the expected product. Typical experimental data for a mass balance experiment are shown in Appendix A-1.

D. Iodometric Methods of Analysis

The determination of sulfite and bisulfite species by iodometric methods is very common and particularly useful in this system. By

using an excess of iodine and backtitrating with thiosulfate solution, the concentration of the unreacted sulfur (IV) species may be determined, but more importantly the reaction is quenched at the start of the analysis. As a result the time scale remains well defined. The reactions were studied in weakly acidic solutions, which are nearly ideal for this method of analysis. However, there are certain limitations, none serious, which are more completely described elsewhere.[28] The reactions involved are:

$$H_2O + I_3^- + HSO_3^- \longrightarrow SO_4^{2-} + 3\ I^- + 3\ H^+$$

$$I_3^- + 2\ S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 3\ I^-$$

The actual analysis was carried out by quenching an aliquot of the reaction mixture of known size in 5- or 10-ml of triiodide solution. Starch was added as an indicator, and the excess triiodide titrated with standardized thiosulfate. Because the quantities of I_3^- and $S_2O_3^{2-}$ are known, the sulfur (IV) concentration can be calculated. If the pH has been measured, the actual calculations of sulfite and bisulfite ions can be calculated as well. Concentrations of analytic reagents were typically 10^{-2} or 10^{-3} M, but this varied depending on the concentration of S(IV) to be measured. Sulfur (IV) concentrations as low as 10^{-4} M could be detected. The thiosulfate was prepared in boiled water, and NaOH was added to control biological degradation.

The most serious problem with this technique is that nitrite ion can interfere with the measurement in both the following ways:

$$NO_2^- + 2\ OH^- + I_3^- \longrightarrow 3\ I^- + NO_3^- + H_2O$$

$$2\ HONO + 2\ H^+ + 3\ I^- \longrightarrow I_3^- + 2\ NO + 2\ H_2O$$

Fortunately at pH = 5.6, the interference from these two reactions is negligible although the reason is not completely understood.[19] Although NO_x species can also catalyze the oxidation of iodide ion by oxygen, no evidence of this process was observed. For this reason all the titrations were performed in a triiodide solution mixed with a concentrated (1 M) acetate buffer at pH = 5.6. Standards doped with nitrite ion showed that there was no interference by nitrite ion when present at less than the 10^{-2} M level.

Some of the products formed are also possible sources of interference. Other work on analytic schemes for these products show that hydroxylamine disulfonate does react with triiodide ion but only in basic solutions.[29] Use of the acetate buffer eliminates this reaction. Hydroxylamine-N-sulfonate, nitrous oxide, and amine trisulfonate are the other products which might be formed under these conditions. These are neither expected to be produced on the time scale and at the acidities of the experiments for which this method was used, nor are there any interferences should small amounts of them form.

E. Other Methods of Analysis

Two other chemical species were analyzed for during the course of this investigation. The first of these was dissolved oxygen, which was measured with a Yellow Springs Instruments Model 57 dissolved oxygen meter. In most experiments the solution was at equilibrium with the ambient atmosphere. To determine if dissolved oxygen was involved in the reaction, a number of experiments was performed after purging the solution with nitrogen for at least 5 minutes prior to preparing the solutions. The solutions were then kept under a nitrogen atmosphere. Measurement at the end of the experiment showed that greater than 95 percent of the oxygen had been removed by purging.

The other species measured was nitrous oxide. Analysis was performed in experiments where N_2O was suspected of being one of the products formed. This was accomplished by carrying out reactions in stoppered flasks and injecting the gas above the solution into a gas chromatograph (Varian Aerograph Model 700). A Porapak Q column (7 ft, 100-120 mesh) was used at 45°C with a thermal conductivitiy detector. Helium was used as the carrier gas at a flow rate of 32 ml/min. Air, CO_2, and N_2O peaks were observed; water vapor remained on the column until periodic heating removed it. Qualitative nitrous oxide samples were prepared by reaction of nitrite ion with hydroxylamine and collection of the gaseous products. These measurements were performed only once at the end of each experiment because the thermal conductivity detector is not sufficiently sensitive for time-resolved studies. The 10- to 15-minute sampling time also severely restricts

the time resolution. Time-resolved studies of N_2O could also be complicated if the mass transfer from solution to gas phase is slower than the rate of production.

Acidities of the buffered reaction solutions were measured using a Beckman Model 4700 pH meter and a Corning semi-micro combination glass electrode (Ag/AgCl reference). Calibration of the instrument was obtained with Mallenckrodt BuffAR standard buffers. Because of differences in ionic composition of the buffers and the solutions, some drift was always present. Measured pH is therefore estimated to be no more accurate than ±0.02 units.

Acidities were controlled by the use of appropriate buffer solutions. The four buffers used were phthalate-biphthalate (pH range 4.1-6.0), tartrate-bitartrate (3.5-4.3), oxalate-bioxalate (3.0-4.0), and sulfite-bisulfite (6.0-7.0). On occasion a bisulfite-sulfurous acid (1.0-3.0) or acetate-acetic acid (4.5-6.0) buffer was used. Usually the buffers were prepared in bulk and portions used in each experiment as needed. This eliminated much of the scatter in the results. Acidities were measured when the buffers were prepared, as well as once during each experiment. In all cases the pH of the solution remained unchanged upon addition of the reactants.

Ionic strength (μ) of the reaction solutions was controlled only to the extent that the initial value was constant within each set of experiments. Attempts were made to keep the initial amount of 1:1 and 2:1 electrolytes constant as well. This was accomplished by the addition of sodium nitrate and sodium sulfate to the solutions if the

buffer were not of sufficiently high ionic strength. Generally the reactions were carried out at $\mu = 1.2$ unless ionic strength effects were being investigated. Because of the high concentrations of the buffer species and nonreactive salts, the ionic strength changed little over the course of the reaction. With the sulfite-bisulfite buffer, the ionic strength does vary, but the use of initial rates keeps this variation to a minimum.

The solution temperature was controlled as much as was practical. This was accomplished by keeping the solutions in constant tempeature baths. The Cary and Beckman spectrophotometer cell compartments were also kept at the same temprature as the bath. With the Spectronic 20, this was not possible. Sets of experiments were generally performed at 20 or 25°C, with variations not more than 0.2°C. In all cases the actual solution temperature was measured, rather than that of the bath. At either extreme for the temperature dependence studies, these values were not always equal (variations up to 1°C were noted).

F. Nitrite/Bisulfite Studies

Reactions between nitrite ion and bisulfite ion were studied under two different regimes. The majority of the experiments were carried out under pseudo-first-order reaction conditions, with nitrite ion as the measured and limiting reactant. All the kinetic information came from first-order rate studies during the initial reaction period. The underlying factor in choosing the initial reaction period is that various reactions between the products and nitrite or bisulfite ions can take place. The use of the initial period keeps these

interferences to a minimum. Also, any back-reactions are minimal during this period. A smaller number of experiments were carried out under nearly stoichiometric conditions. These enable the reaction products and mass balance to be determined. No rate information came from these experiments. Besides monitoring the loss of nitrite ion, these studies involved the simultaneous measurement of sulfur (IV) or other species.

Reaction rates were measured by following the loss of nitrite ion to determine the order of reaction with respect to nitrite, bisulfite, and hydrogen ions. This was done by varying the concentration of the ion of interest while holding all the other parameters constant. Typical concentrations for nitrite ion were 0.5 to 5.0 millimolar with bisulfite ion concentrations at least 10 times in excess of nitrite ion. This assured the reaction took place under pseudo-first-order reaction conditions. Acidity was maintained by buffers with pH in the range of 3.2 to 7.0. In more acidic solution, the reaction is too fast to measure by the present techniques, and in basic solutions the reaction is slow enough that air oxidation of sulfite ion interferes. Experiments were typically performed at 20°C and $\mu = 1.2$. Typical data are shown in Appendix A-2.

Temperature dependence studies were performed at otherwise constant conditions to determine the activation parameters. The temperature range was 15 to 30°C. Ionic strength dependence was investigated in a similar manner with μ being varied from 0.2 to 1.5 M. Nitrate and sulfate salts were both used. The role which the buffer species plays

was investigated by changing the concentration of only the buffer. Experiments performed in two different buffers at otherwise identical conditions were also used to investigate the role of the buffer.

Stoichiometry of the reaction was investigated by simultaneously measuring the concentrations of nitrite ion and sulfur (IV) species. Reactant concentrations were varied with acidity. At a pH less than 3, a known amount of nitrite ion was added to the mixture and allowed to completely react. The change in the sulfur (IV) concentration was then measured. Concentrations were in the 10^{-3} to 10^{-4} M range. At a pH greater than 3, both ions were measured as a function of time. Concentrations were in the range of 10^{-2} M with a slightly greater than stoichiometric amount of sulfur (IV). In either case the stoichiometric ratio ($\Delta S/\Delta N$) is easily calculated. Typical data are shown in Appendix A-3.

The products were analyzed for according to the value of the stoichiometric ratio. When $\Delta S/\Delta N$ was less than 2.0, nitrous oxide was looked for by gas chromatography. At $\Delta S/\Delta N$ values of 2.0 or greater, a mass balance between nitrite ion and hydroxylamine disulfonate was investigated.

G. Nitrite/Hydroxylamine-N-Sulfonate Studies

Reactions between hydroxylamine-N-sulfonate and nitrite ions were carried out in an analogous fashion to those for nitrite ion with bisulfite, described in the preceding section. Concentrations of HAMS, determined by addition of a known amount of the pure potassium salt, were in the range of 0.01 to 0.5 M. Nitrite ion was present at

the 10^{-2} or 10^{-3} M level. Because the reaction is much more dependent on the acidity, pH was maintained between 3.8 and 5.0. Outside this range the reaction is again either too fast to measure or slow enough that other reactions interfere with the experiments. Initial rates of nitrite ion loss were again employed. In this case it is the formation of bubbles of the gaseous products on the cell windows, rather than the interfering reactions, which led to the use of initial rates.

Mass balance and stoichiometric studies were not carried out, as suitable techniques could not be found. Nitrous oxide was determined to be the product by use of gas chromatography. Ionic strength studies were carried out in the range of 0.2 to 1.5 M using sulfate, nitrate, or dihydrogen phosphate salts. Temperature dependence was investigated in the range of 10 to 40°C.

III. RESULTS

A. Kinetics of Hydroxylamine Disulfonate Formation

All the results determining the kinetics of formation of hydroxylamine-N,N-disulfonate were obtained by monitoring the nitrite ion concentration as a function of time. The direct relation between the measured absorbance and actual concentration of nitrite ion, which makes the spectrophotometric method both fast and accurate, allowed the order of the reaction with respect to nitrite ion to be readily determined by the shape of its decay curve. In light of the previous studies, first-order dependence was expected, and a large excess of bisulfite ion was used to prevent any changes in the shape. A decay curve obtained under these conditions is shown in Figure 3. The semilogarithmic plot shows a first-order dependence on nitrite ion. Those data points which are at the lowest concentrations show an increase in scatter but were obtained from extremely low absorbance readings and therefore have larger error bars. Typically the reaction conditions are not quite this ideal and more usual results are shown in Figure 4. The decay curves are not obtained over such a wide concentration range but still show a first-order dependence. The parallel curves at different initial concentrations confirm this behavior. Slight departure from linearity is seen at longer times and is the result of a breakdown of the pseudo-first-order conditions caused by too small an excess of bisulfite ion. Here the initial slope was used to determine the rate. Over the entire range of pH studied (3.0 to 7.2), only first-order dependence on nitrite was observed.

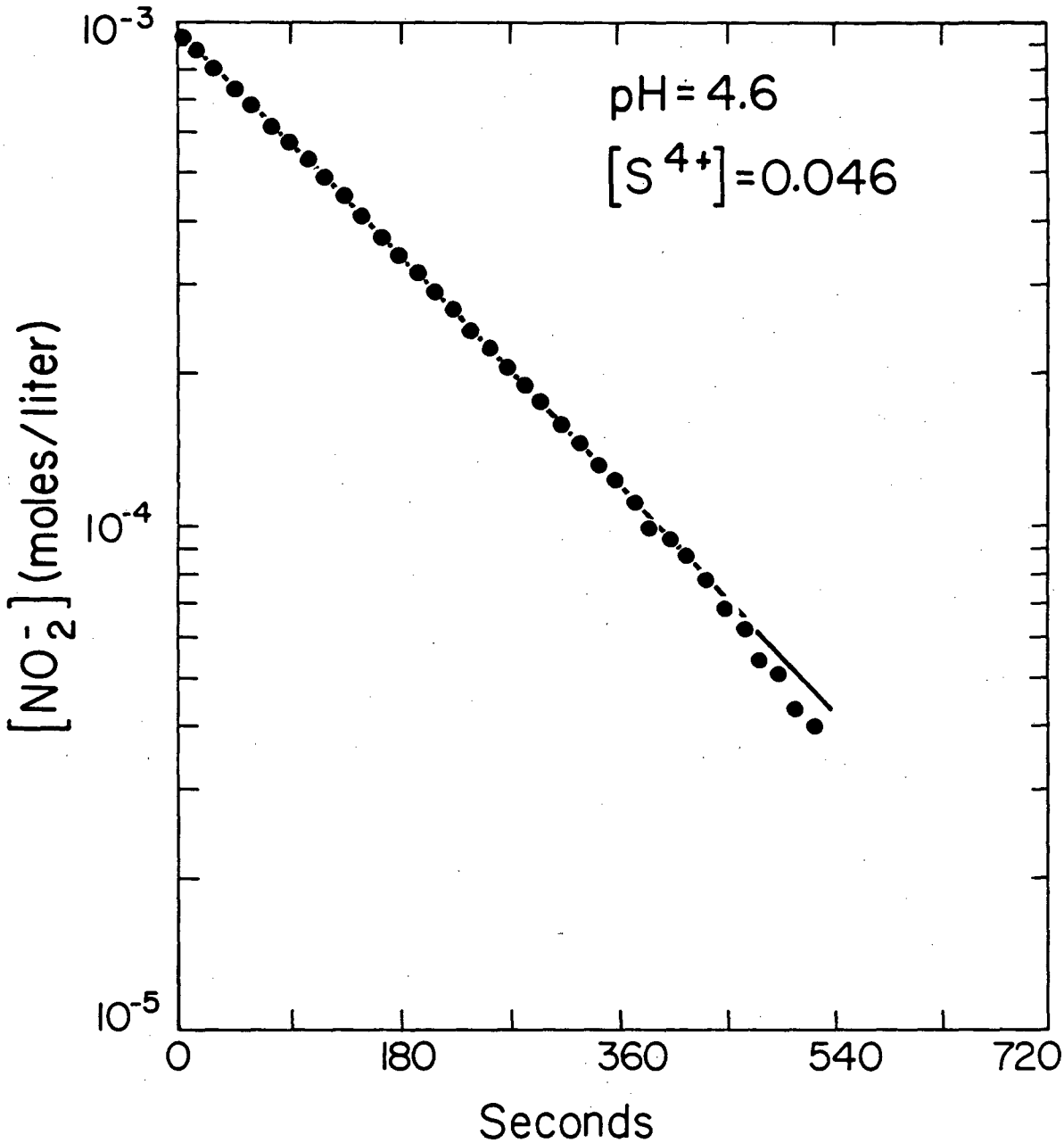

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Figure 3. Nitrite ion decay curve recorded on Cary 219 using 10 cm cells for nitrite ion-bisulfite ion reaction. The concentration of sulfur (IV) species is in moles per liter.

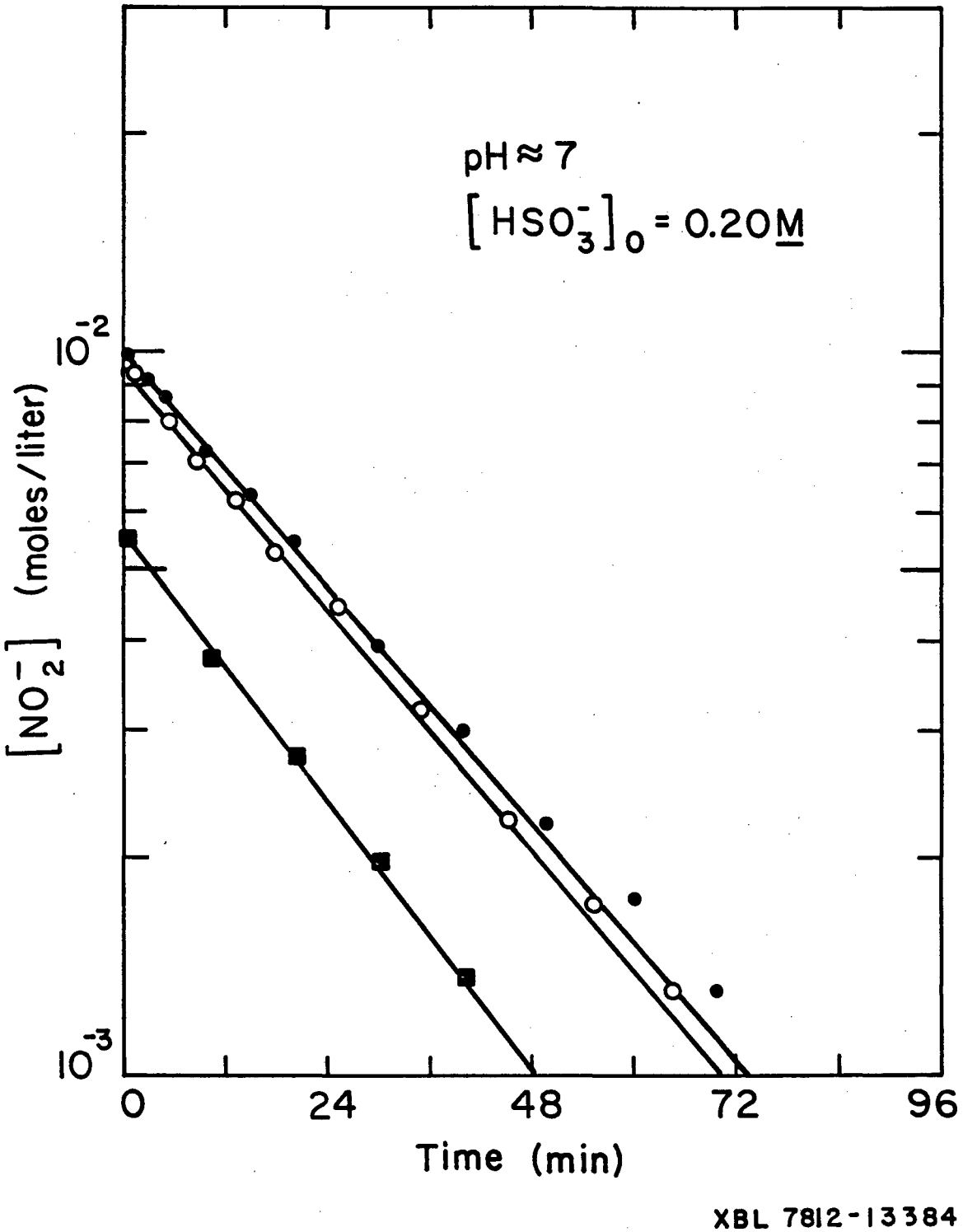

Figure 4. Nitrite ion decay curves recorded on Spectronic 20 using 1 cm cells for nitrite ion-bisulfite ion reaction.

This first-order dependence has consequences which greatly simplify many aspects of the study. First, it allows a linear least-squares fit to the data in order to obtain an initial slope, which eliminates much of the bias of the experimenter in interpreting the data. More importantly, it makes it unnecessary to measure the exact time between the addition of the nitrite ion to the reaction mixture and measurement of the first data point. This is true only if sufficient bisulfite ion is present to insure pseudo-first-order conditions. Because the time required to obtain a uniform mixture in some of these experiments is substantial compared to the time between successive data points, this was an important consideration. Finally, the exact initial nitrite ion concentration did not need to be known, which allowed addition of a few crystals of salt rather than a measured amount of a prepared standard. This decreased the mixing time considerably and resulted in increased accuracy.

Determining the order of reaction with respect to bisulfite ion was not as straightforward. Initial studies were carried out at pH of 4.5 and 5.5 where bisulfite ion is essentially the only sulfur (IV) species present. All conditions were kept constant with the exception of bisulfite concentration. The rate law was expected to be of the form

$$\text{Rate} = V[NO_2^-]\,[HSO_3^-]^n \quad ,$$

where V contains the rate constant, hydrogen ion dependence, and any other parameters. The order with respect to bisulfite ion can then be obtained from a plot of $\log(\text{rate}/[NO_2^-])$ vs. $\log[HSO_3^-]$. The

results for these two pH's are shown in Figure 5 and the order with respect to bisulfite ion is one. The difference in rates at the different acidities is due to a dependence on hydrogen ion which will be discussed later.

In less acidic solutions, the amount of bisulfite ion must be increased in order to minimize the percentage of sulfur (IV) species lost by air oxidation which otherwise would result in a breakdown of pseudo-first-order conditions. When this was done, there was a steady increase in the observed order from 1.0 to about 1.8 at a pH of 6.6. Addition of phthalate or acetate ions showed that this was not due to the change in buffer species which were used. This effect complicates the treatment of the data at higher concentrations. The change in order from lower to higher value with increasing bisulfite ion concentration can only be consistent with two concurrent processes for the formation of HADS. The consecutive addition of reactant molecules in several steps often results in a change in order with increasing concentration, but would give a change in the opposite direction. A check of the reaction stoichiometric (see next section) showed there had been no change in the net reaction.

At pH = 7 the magnitude of the rate due to the process which is first-order with respect to bisulfite ion can be estimated from the results obtained at lower pH. This calculated value accounts for up to 50 percent of the measured rate. If one instead assumes that the entire rate at pH = 7 is due to a process second-order in bisulfite ion and calculates the expected rate at pH = 5.5 (also lower bisulfite

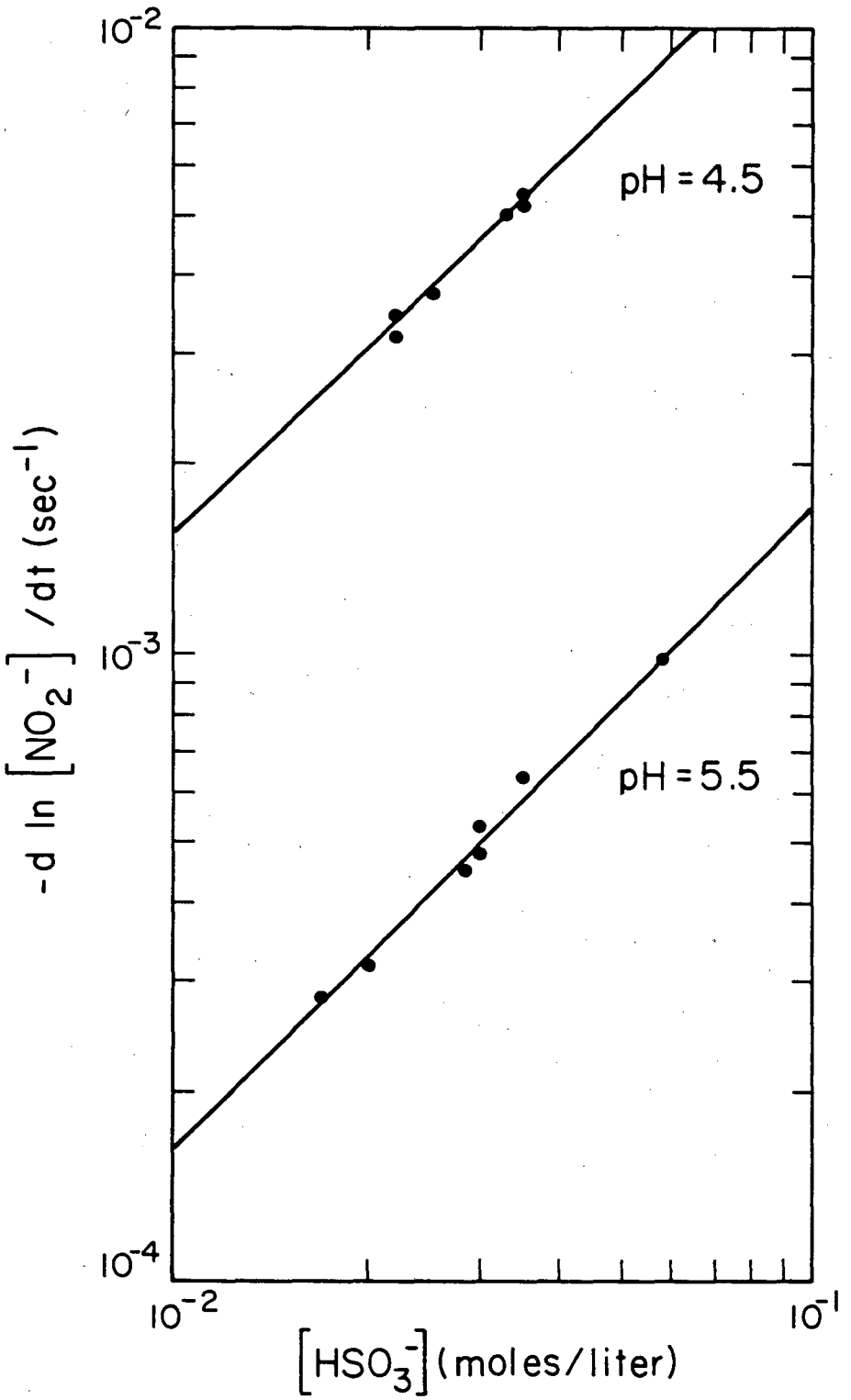

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Figure 5. Dependence of nitrite ion-bisulfite ion reaction rate on the bisulfite ion concentration.

concentration), it is small (<5 percent) compared to the measured value. Similar results are obtained if the rate laws of Seel and coworkers[19,21] are used to estimate the rates. The conclusion is that the first-order contribution must be subtracted from the measured rate prior to analyzing the data for a higher-order term. These corrected rate data, plotted against $[HSO_3^-]$ on a log-log plot, are shown in Figure 6; and the reaction is found to be second-order in bisulfite ion. Once the rate is specified as second-order in bisulfite ion there is no explicit dependence on either sulfite ion concentration or pH in the rate law. The data in Figure 6 were obtained from experiments where the pH varied from 6.5 to 7.2. Some of the scatter in these values is probably due to slight errors in the value of the rate constant for the process first-order in bisulfite ion, which was used to correct the data. The rate constant for the process which is second-order in bisulfite ion may be calculated by fitting these data to a second-order rate law; however, more accurate values shall be reported after a discussion of the temperature and ionic strength dependences.

The results of experiments to determine the order of the reaction with respect to hydrogen ion concentration also allow determination of the presence or absence of a bisulfite-independent term in the complete rate law. Whereas the process which was second-order in bisulfite ion has been shown to be independent of the hydrogen ion concentration, the process first-order in bisulfite ion has shown a marked dependence. The separation between curves in Figure 5 indicates that this is a

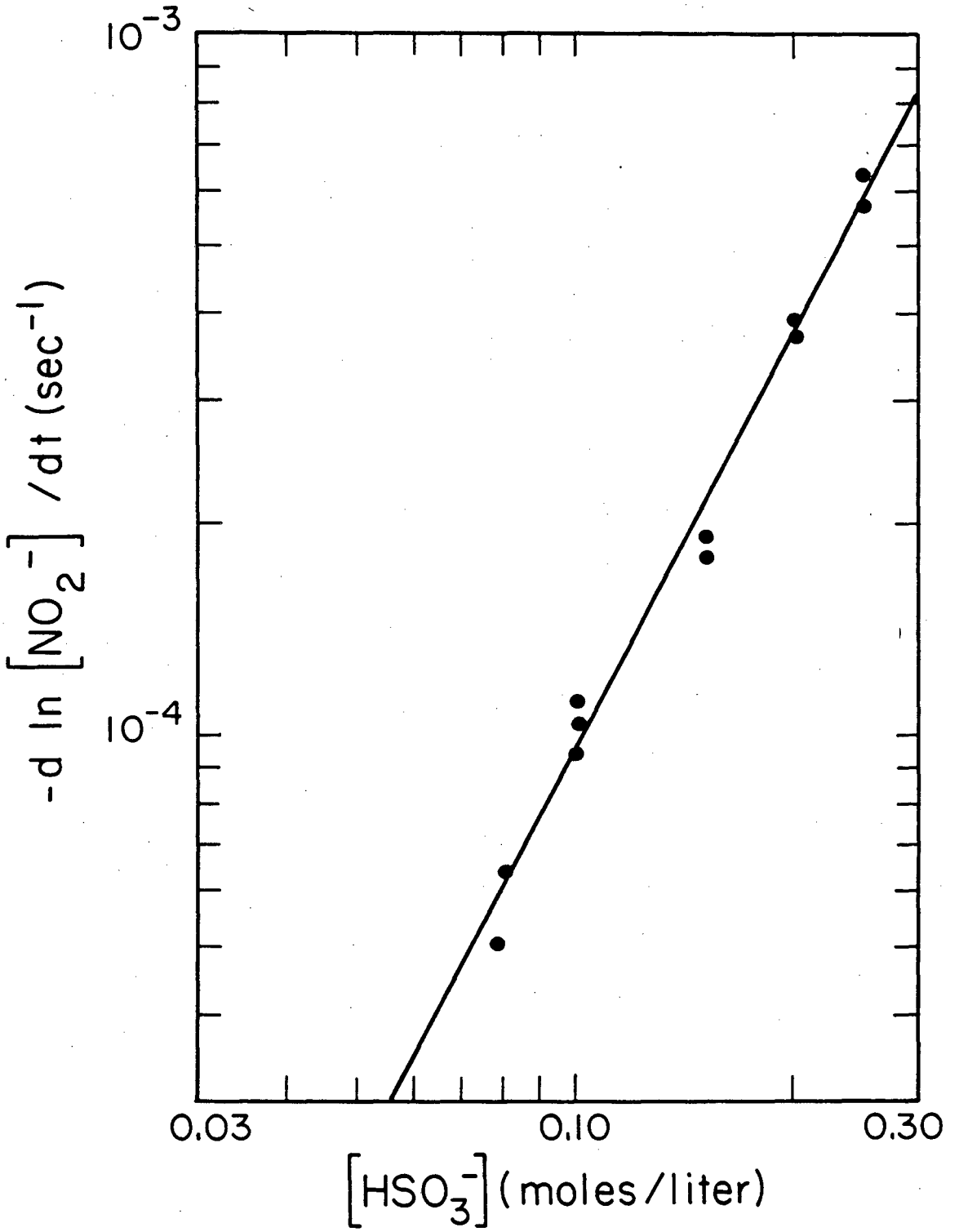

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Figure 6. Dependence of the reaction rate on bisulfite ion concentration after correction for the first-order process (see text for details). pH varied from 6.5 to 7.2 in these experiments.

first-order dependence on hydrogen ion. The process second-order in bisulfite ion does not contribute significantly to the rate below pH of 5.5, and no correction of the data is needed. This indicates that the rate law for this term has the form

$$\text{rate} = k[H^+]\,[NO_2^-]\,[HSO_3^-] \quad ,$$

which means a plot of rate/$[NO_2^-]$ vs. $[HSO_3^-]$ should show a straight line for any given pH. The slope should be equal to the rate constant times the hydrogen ion concentration and the intercept for such a curve, if nonzero, indicates that there is a term in the rate law which is independent of the bisulfite ion concentration. If the intercept increases with increasing acidity, this is an indication that the bisulfite-independent term is dependent on the hydrogen ion concentration.

A plot of the experimental results in this form confirms the first-order dependence on both hydrogen and bisulfite ions, as shown in Figure 7. Although the extrapolation is over a long range, statistical analysis shows that the intercepts all go through the origin (within experimental error), which eliminates a bisulfite-independent term from the complete rate law. Should any such process exist, it is of too small a magnitude to be of importance when compared to the other terms, under the conditions where HADS is the product. At pH of 3.9, 4.6, and 4.7, there appears to be a nonzero intercept. At pH of 3.9 there is simply a large standard deviation in the value of the intercept, due to scatter in the data. For the higher two pH's

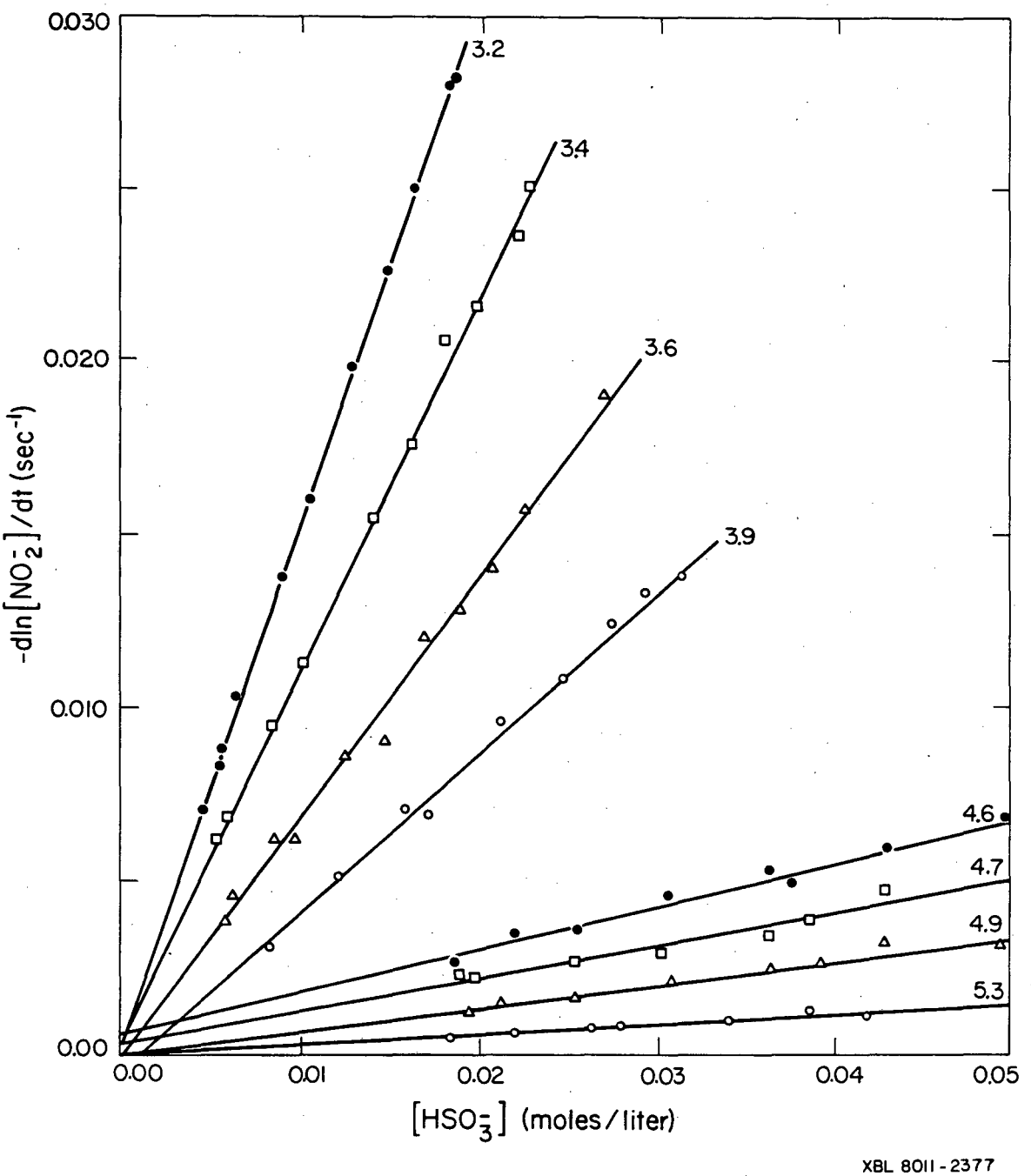


Figure 7. Reaction rate vs. bisulfite ion concentration. Numbers at the right of each line indicate the pH for that set of experiments.

the intercepts have been shown to be the result of losses of SO_2 at the higher concentrations of bisulfite ion, resulting in a slower rate and a skewing of the line. When reactions are performed in stoppered glassware rather than open flasks, these losses are no longer observed and the line does go through the origin. All experiments carried out at pH lower than 4.5 were performed in stoppered glassware. No mention was made in the previous studies as to whether the flasks were open or not, although the outgassing of SO_2 is more of a problem at higher acidities and may account for the bisulfite independent term which was observed.[19,20] The other possibility is that the acetate buffer used in the other investigations is the cause of the extra term, but this will be disucssed later. To check the first-order dependence on hydrogen ion, the slope of these curves were normalized by the acidity, and a first-order H^+ ion dependence is seen (see Table II).

An interesting artifact in the way these pH-dependence measurements were made provides another useful piece of information for determining the mechanism. At pH's less than 4.5, the absorbance by nitrous acid presents a problem, which was discussed briefly in the experimental section. The total nitrogen (III) concentration, not just nitrite ion, is determined in these measurements. The rate constants are determined from $d(\ln[NO_2^-])/dt$ or the equivalent direct experimental result $1/A(dA/dt)$, where A is the absorbance. However, when nitrous acid is also absorbing, the two quantities are not necessarily equivalent; and what is really determined is $1/[N(III)](d[N(III)]/dt)$. If HONO and NO_2^- both react with equal probability, the value of the rate

determined directly from the absorbance is equal to the desired quantity. This equal reaction probability implies that the slopes in Figure 7 divided by $[H^+]$ should all give the same value. However, if one of the two forms of N(III) is reacting and the other is not, an artifact develops which must be corrected. Assuming that nitrite ion is the reactive species, the entire change in N(III) concentration is due to nitrite ion and $d[NO_2^-]/dt = d[N(III)]/dt = dA/dt$. However, $1/A$ is no longer equal to $1/[NO_2^-]$, and a correction must be made for the fraction of NO_2^- in the total N(III). By use of the two boundary conditions,

$$[HONO] + [NO_2^-] = [N(III)]$$

$$[HONO]K_{eq} = [H^+]\,[NO_2^-] \quad ,$$

this correction may be determined. The value of K_{eq} must reflect any changes due to ionic strength.[30] Again, taking the slopes in Figure 7, dividing by the hydrogen ion concentration and multiplying by the correction term, $(1 + [H^+]/K_{eq})$, a rate constant which does not vary with pH should be found. If nitrous acid is the only reacting species, an identical correction is found, and the two rate constants differ only by the equilibrium constant for nitrous acid. The results of these calculations are found in Table II. These results clearly indicate that only one of the two species is reacting in this system. For the present, the rate is reported in terms of nitrite ion as that

Table II. Experimental Values of k_1.

All experiments at 22°C.

Units for k_1 are $liter^2/(mole^2 sec)$

K_{eq} for nitrous acid is 6.31×10^{-4} liter/mole at $\mu = 0.20$ M.

pH	k_1 = slope/[H^+]	K_1 = (slope/[H^+]) x (1 + [H^+]/K_{eq})
5.30	4.5×10^3	4.5×10^3
4.93	4.4×10^3	4.4×10^3
4.71	4.0×10^3	4.2×10^3
4.57	4.2×10^3	4.4×10^3
4.61	4.2×10^3	4.4×10^3
3.90	3.7×10^3	4.4×10^3
3.63	3.2×10^3	4.5×10^3
3.40	3.0×10^3	4.8×10^3
3.21	2.6×10^3	5.1×10^3

is the predominant species over the range of pH studied. Kinetic experiments are unable to determine which of the two species is reacting.

At this point another note on nomenclature is worthwhile. There are two terms in the complete rate law for the formation of HADS:

$$\text{Rate} = k_1[H^+]\,[NO_2^-]\,[HSO_3^-] + k_2[NO_2^-]\,[HSO_3^-]^2 \qquad (1)$$

Both these terms are third-order overall and are the result of several elementary reaction steps. To avoid cumbersome references to the two processes, they will be referred to only by their orders with respect to bisulfite ion, the first- and second-order process, respectively. This is not meant to refer to any specific reaction step or to the overall order, but is used solely as a bookkeeping device to simplify the later discussions.

Because of the necessity of carrying out experiments in closed cells to avoid the losses of sulfur dioxide under certain conditions, there was concern over the exclusion of oxygen from the reaction mixture, should it be involved in the reaction. At this point the possibility of radical reactions had not been completely eliminated. Reactions which were carried out under a nitrogen blanket after purging the system of oxygen showed that the exclusion of oxygen did not alter the rate. The experiments were performed at pH = 6.3 and bisulfite and nitrite ion concentrations of 0.37 and 0.02 M, respectively. These conditions were chosen so that both processes would contribute almost equally to the rate; and if either term were oxygen dependent, it would

most easily be observed. It is possible that the amount of dissolved O_2 present without purging was small enough compared to reactant concentrations that it did not affect the rate noticeably under these conditions. However, similar experiments at lower concentrations (ca. 10^{-3} M HSO_3^- at pH = 3) did not show any irregularities. If O_2 were reacting with bisulfite ion it would be slow at this pH. If dissolved oxygen were otherwise involved in the reaction, there should have been a disturbance, until the oxygen was depleted, with a different rate. No such disturbance was observed under any conditions, and the conclusion is that there is no oxygen induced reaction.

No dependence of reaction rate on choice of buffer could be detected. The pH range of oxalate, tartrate, and phthalate buffers overlap somewhat, and experiments which were performed in different buffers under otherwise identical conditions gave identical results. In addition, reducing or increasing the concentration of the buffer species by a factor of two, while maintaining the same pH had no observable effect on the rate. The only time at which anomalous results were obtained was during the use of biphthalate-phthalic acid buffers. Here a certain amount of bisulfite ion had to be added before the reaction would start, and the reaction occurred at slower than its expected rate. As the buffer concentration was decreased, this threshold also decreased. It appeared as if there was some impurity or that some of the bisulfite ion was being tied up in a phthalic acid complex, and was not available for reaction. No reference to any complex of this type has been noted in the literature.

The exact nature of this effect has not been determined, but none of the data obtained while using this buffer system were included in any analysis of the rate constants. Acetate ion, which was suspected of being responsible for a bisulfite-independent term in the rate law, was briefly investigated by performing several experiments in acetate rather than phthalate buffers. Identical rates were seen in both buffers for identical reaction conditions, so acetate buffers appear to be noninteracting.

The activation energies for both processes were investigated by varying the temperature of the solution while holding all other parameters constant. The reactions were carried out in phthalate buffers because the change in pH with increased temperature is less (for this system) than the error associated with pH measurement. The data have been treated in two different manners. First the values of the rate constants were fitted to an Arrhenius function:

$$k = A \exp(-E_a/RT) \quad ,$$

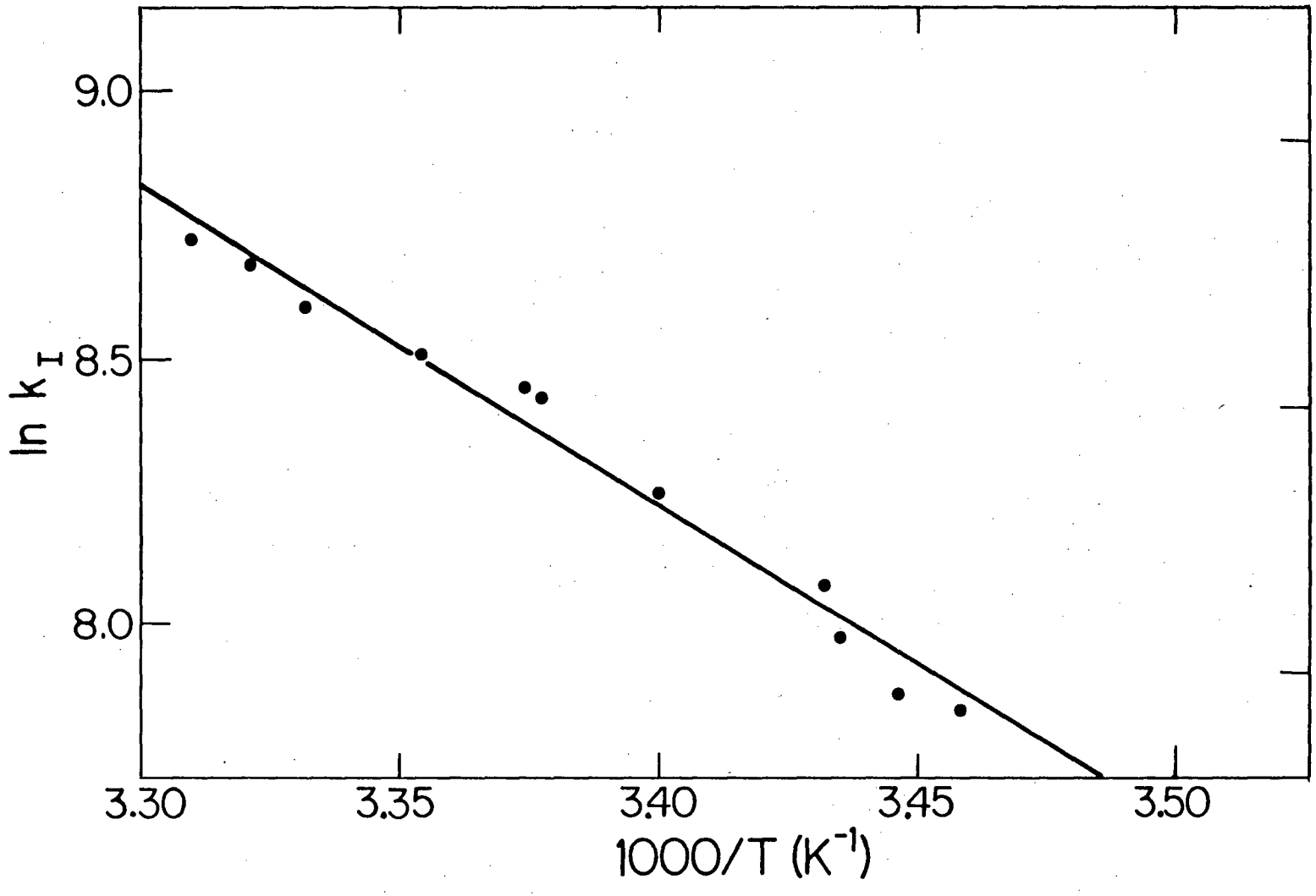
where E_a represents the activation energy. The data were then also fitted to a similar equation based on the activated complex theory for solution reactions:[31]

$$k = k_B T/h \exp(\Delta S^{\ddagger}/R) \exp(-\Delta H^{\ddagger}/RT) \quad ,$$

where k_B is Boltzmann's constant, h is Plank's constant, and $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ are the entropy and enthalpy of activation. As expected, E_a and

$\Delta H^{\ddagger}$ differ by RT over the present temperature range; however, $\Delta S^{\ddagger}$ can sometimes yield additional mechanistic information. The first-order process has an activation energy of 12 kcal/mole (Fig. 8). In addition, the value of $\Delta S^{\ddagger}$ is -3 cal/mole-kelvin. Values of $\Delta S^{\ddagger}$ near zero can be interpreted as indicating little change in solvation energy between reactants and activated complex.[32] However, no predictions can be made as to what reactions are occurring in the present process. For the second-order process, the enthalpy of activation is -1 kcal/mole. This negative value could either be the result of overcorrection of the measured rates before evaluating the second-order parameters or the presence of some dimerization equilibrium prior to the rate-determining step. The entropy of reaction is large and negative (-70 cal/mole-kelvin). The sign indicates that like ions are reacting; however, the magnitude is larger than expected for this type of reaction. Presumably the activated complex forms with an increase in charge density. Values of $\Delta S^{\ddagger}$ for similar reaction of bisulfite or nitrite ions are not reported in the literature, so a comparison is difficult.

The results of the ionic strength studies are also difficult to interpret. Useful mechanistic information can be obtained from interpretation by Debye-Hückel theory but only in the limit of very low concentrations and ionic strengths.[31] The pseudo-first-order conditions, as well as the required buffer concentrations, raise ionic strengths to well above this limit. The results are still useful in an empirical sense, particularly in describing the processes involved



XBL 7911 - 13319

Figure 8. Arrhenius plot for the rate constant of the first-order process. K_I has units of liter^2/mole^2-sec.

in scrubber chemistry. These results also serve as further evidence that there are indeed two distinct processes for the formation of HADS. Results of the investigation of the dependence of the first-order process on ionic strength are shown in Table III. The scatter is due to variations in temperature from experiment to experiment (up to several degrees). The rate is independent of the ionic strength under these conditions. However, this may be due to the insensitivity of the activity coefficients in this range of ionic strength. The second-order process, again after correction for the first-order contribution, varies strongly with the ionic strength, as shown in Figure 9. The rate constant increases less rapidly than predicted by Debye-Hückle theory, although this is common at these higher ionic strengths. The magnitude of the effect is quite large, and its direction is consistent with the idea of forming an activated complex of higher charge than any of the individual reactants. This will be discussed later in relation to the proposed mechanism.

An experimentally determined rate law which describes all this data has already been given in Equation 1. The best values for the rate constants are:

$$k_1 = (3.8 \pm 0.2) \times 10^{-2} \exp(-6100/T) \quad \text{liter}^2/\text{mole}^2\text{-sec}$$

$$k_2 = (9.0 \pm 0.5) \times 10^{-4} \exp(2.1\ \mu^{1/2}) \quad \text{liter}^2/\text{mole}^2\text{-sec} \quad ,$$

Table III. Rate constant for the first-order process at various ionic strengths.

exp't No.	pH	μ (M)	k_1 ($M^{-2} \cdot sec^{-1}$)
a	4.63	0.2	4.3×10^3
b	4.62	0.2	4.3×10^3
c	4.45	0.6	3.5×10^3
d	4.36	0.9	3.5×10^3
e	4.31	1.3	4.0×10^3
f	4.50	0.2	4.8×10^3
g	4.50	1.2	4.7×10^3
h	4.50	1.2	3.8×10^3

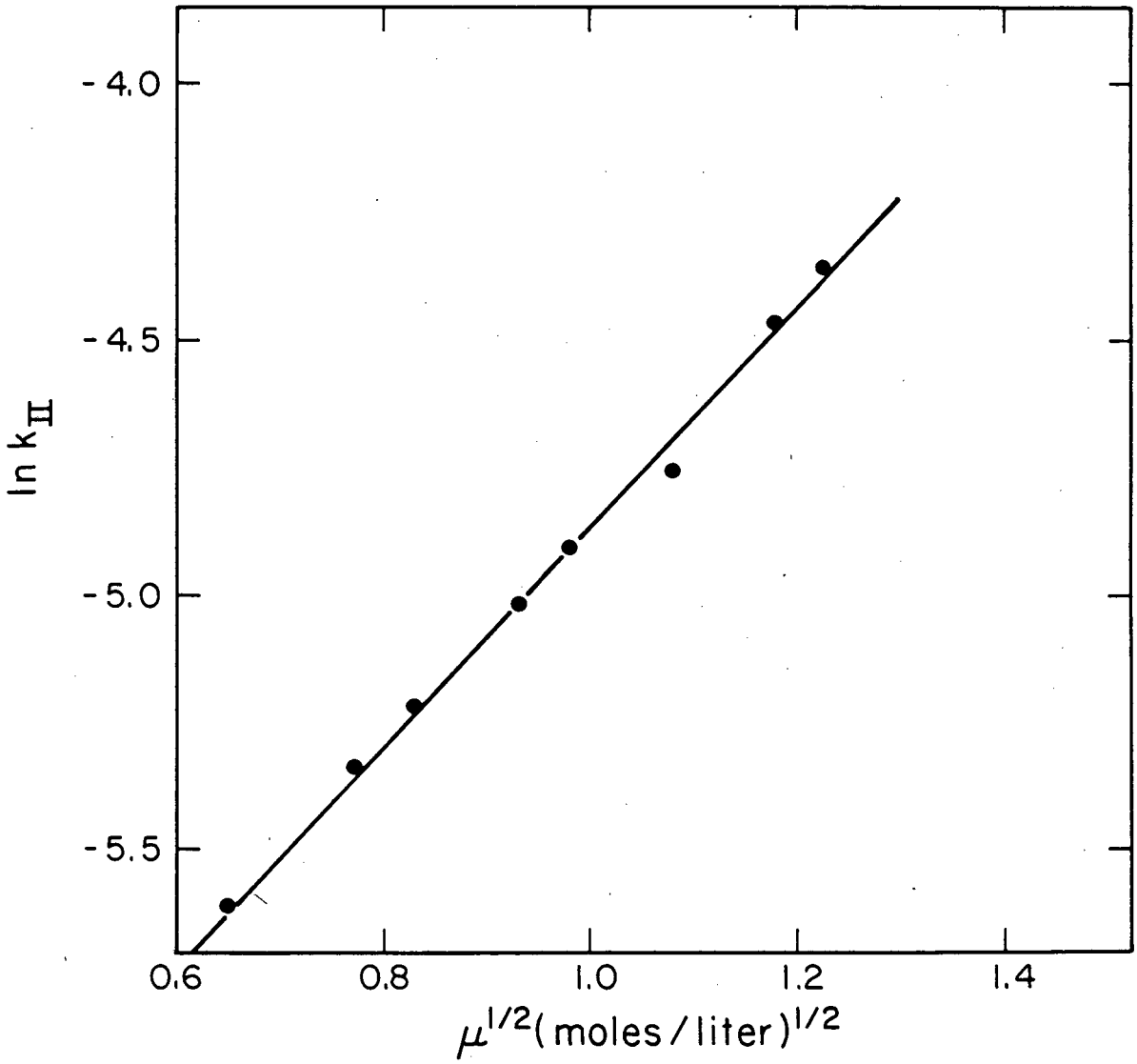


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Figure 9. Ionic strength dependence of the rate constant for the second-order process. k_{II} has units of liter^2/mole^2-sec.

where T is in kelvin and μ is in moles/liter. Errors are estimates based on a number of experiments performed under similar conditions (see Appendix B). At 295 K and $\mu = 1.2$ M, these values for k_1 and k_2 are 3.8×10^3 and 9.0×10^{-3} liter^2/mole^2-sec, respectively. Except at very low acidities (pH greater than 6.5) or high concentrations of bisulfite ion (greater than 0.1 M), the contribution to the rate by the second-order process is small compared to that of the first-order process.

B. Stoichiometric and Mass Balance Studies

Experiments were carried out to verify that the same net reaction had occurred under each set of experimental conditions. For all pH's greater than 3.2 which were investigated, the ratio of sulfur (IV) which reacted with nitrogen (III) or nitrite ion ($\Delta S/\Delta N$) was between 2.0 and 2.3. These ratios increased when measured after long reaction times. In the more acidic solutions, the increasing ratio is most probably due to loss of sulfur dioxide from the solution. At higher pH there are undoubtedly losses of sulfur (IV) species due to air oxidation, which will also increase the measured ratios. Over the entire region, the sulfonation of HADS is another source of error which will also increase the ratios. Because this sulfonation reaction is first-order in HADS, this becomes a major source of error only at long reaction times, when the HADS concentration has increased. Stoichiometric ratios were measured for experiments at pH as low as 1.0, and values less than 2.0 are obtained for $\Delta S/\Delta N$ in almost all experiments at pH less than 3. This indicates that another product is being

formed. These results are completely consistent with the Raschig scheme (Fig. 1) and are discussed fully in the next section.

While the stoichiometric ratio is a useful method for indicating a change in the product, it cannot determine whether HADS was actually formed over the entire region where $\Delta S/\Delta N = 2$. A mass balance between nitrite ion and HADS confirms the product which had been predicted by the $\Delta S/\Delta N$ ratio. Figure 10 shows the results of a mass balance experiment at pH of 6.3 under conditions where both the first- and second-order processes contribute equally to the rate. The combined errors from the two analytic techniques are great enough that one cannot rule out the possibility of other minor products being formed; however, greater than 95 percent of the reacted nitrite ion ends up as HADS under all the conditions in which this mass balance was investigated. After about 15 minutes one can begin to notice an apparent loss of nitrogen species. This is most likely due to loss of HADS by a sulfonation reaction, since the nitrite ion concentration continues to drop. Again, this is seen only after the concentration of HADS builds up to a level sufficient to result in a significant rate. Hydrolysis cannot account for the apparent loss as the rates are too slow at this acidity and HADS concentration. Solutions of nitrite ion are stable under these conditions (in the absence of bisulfite) with respect to other processes of removal. Because this effect is only noticeable after sufficient amounts of HADS have built up, the kinetic parameters which are determined from initial rate studies are not influenced.

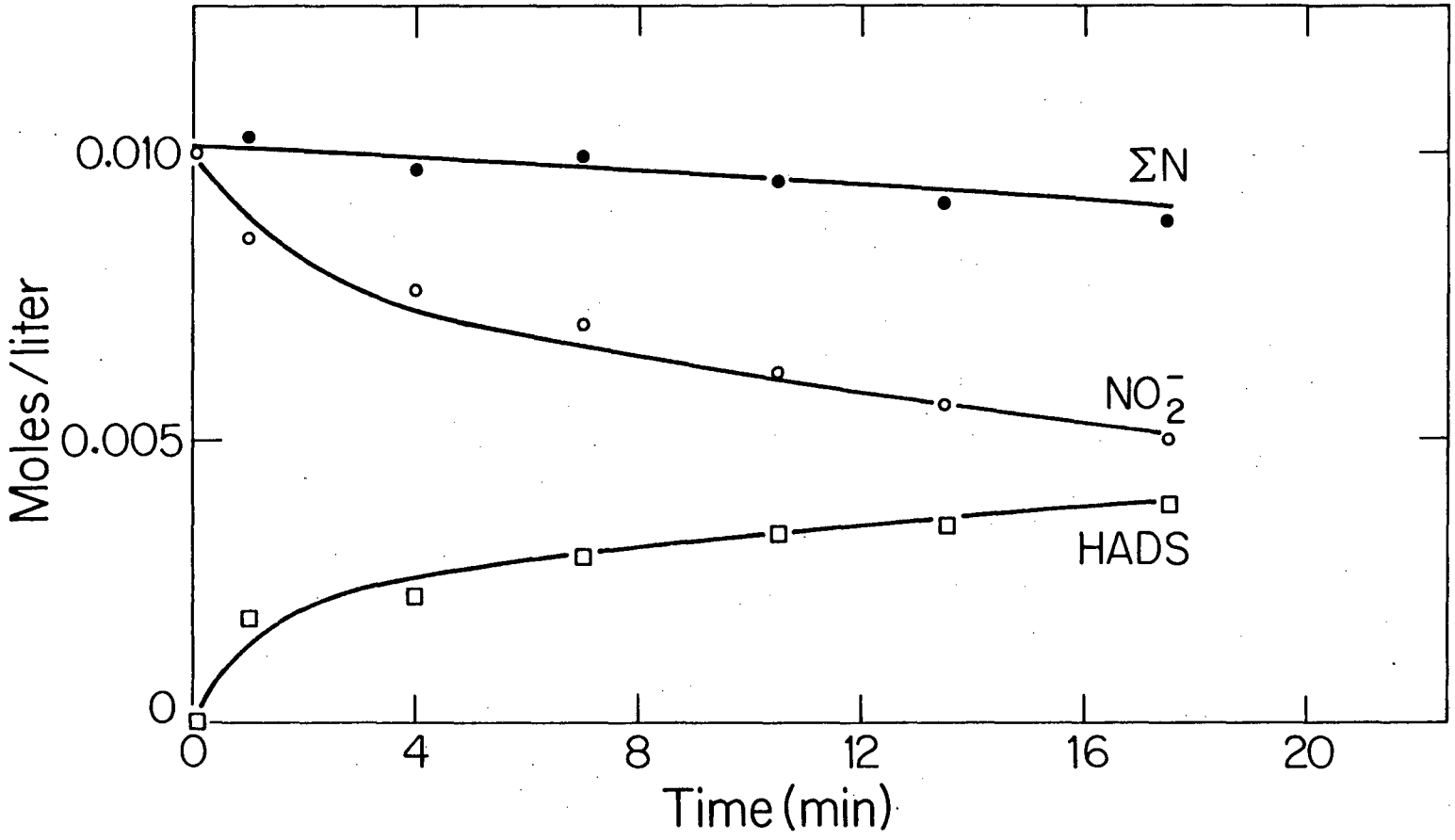

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Figure 10. Mass balance for the formation of HADS at pH = 6.3. ΣN refers to the sum of nitrite ion and HADS concentrations. The concentration of bisulfite ion is 0.200 M.

C. Formation of Nitrous Oxide

As noted previously, when the stoichiometric ratio was measured at pH less than 3, the resulting values of $\Delta S/\Delta N$ were less than 2.0. This is predicted by the Raschig scheme where N_2O (or hyponitrous acid) would be formed by the hydrolysis of some intermediate in the formation of HADS. If all the nitrite ion were converted to nitrous oxide, the observed value of $\Delta S/\Delta N$ would be 1.0. Experiments show a clear trend in the stoichiometric ratio from 2 to 1 as the pH decreased with a constant initial value of sulfur (IV) species. The results are shown in Figure 11 with most of the scatter again believed to be due to losses of SO_2 from acidic solutions. The same trend is observed at fixed hydrogen ion concentration as the sulfur (IV) concentration is reduced as shown in Figure 12. This indicates that there is a competition for the intermediate to undergo either hydrolysis or sulfonation. This is the first solid evidence that such an intermediate exists. Figures 11 and 12 should show sigmoid shaped curves, but there is sufficient scatter that a straight line has been used to show the trend.

In order to test the hypothesis that N_2O was formed, the gaseous products from a number of experiments where the stoichiometry was less than 2 sulfurs to 1 nitrogen were examined by gas chromatography. Analysis showed that nitrous oxide was the product; and although only semiquantitative results were obtained, significantly more N_2O was formed at lower values of the stoichiometric ratio. Typical results of these analyses are shown in Figure 13. Curve a shows the results

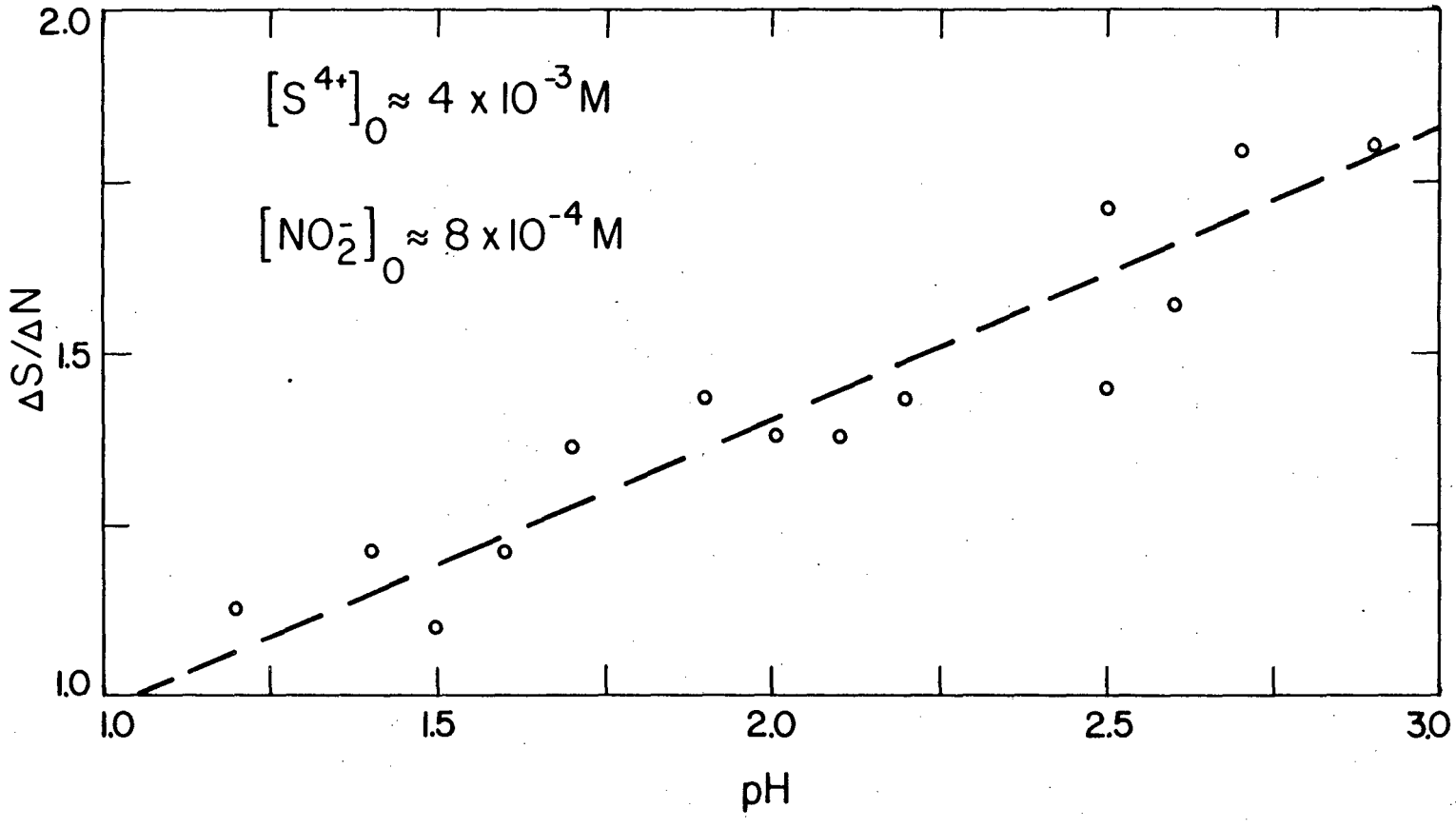

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Figure 11. Stoichiometric ratio as a function of pH at constant initial sulfur (IV) concentration.

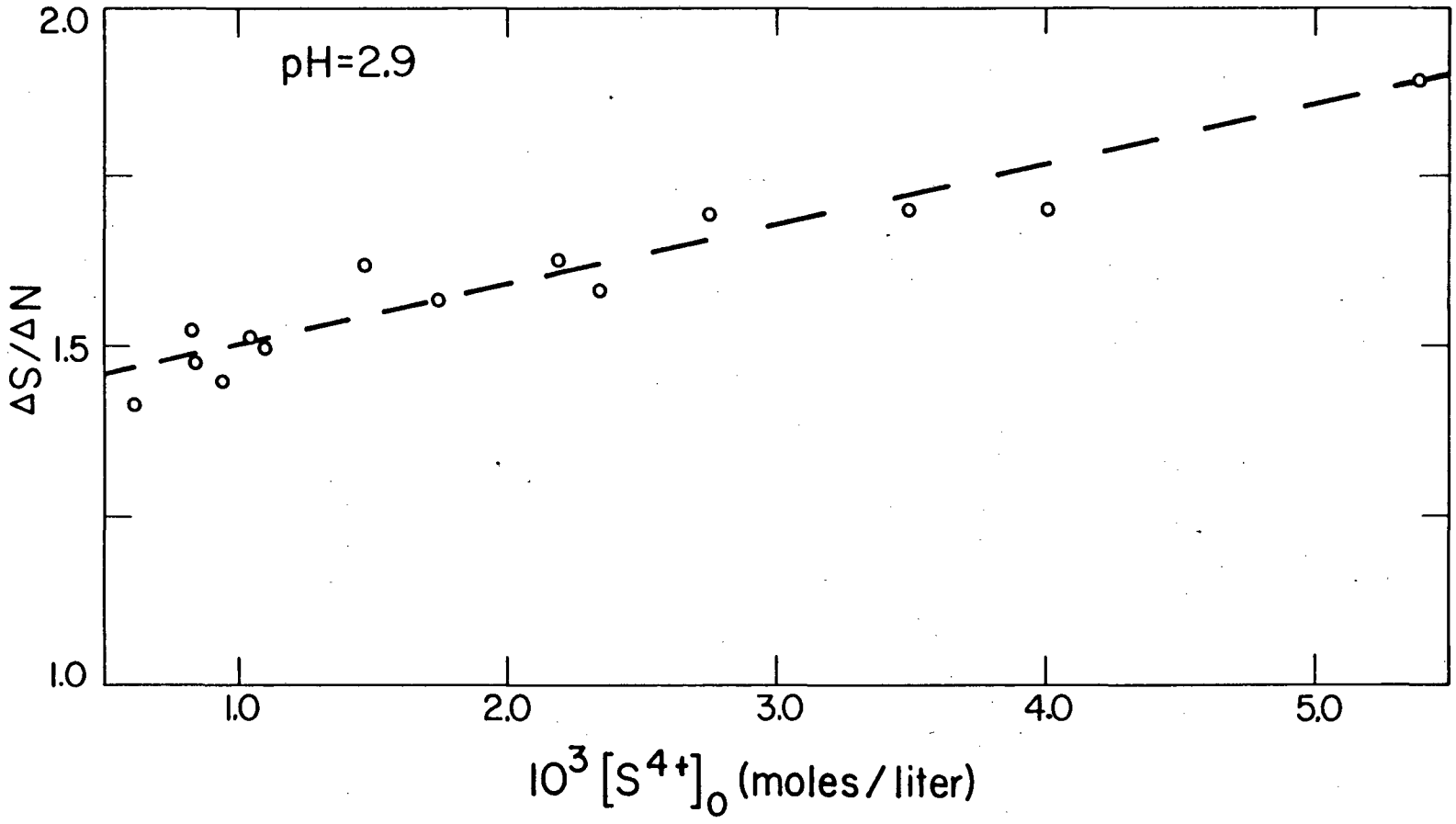

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Figure 12. Stoichiometric ratio as a function of Sulfur(IV) concentration at constant pH.

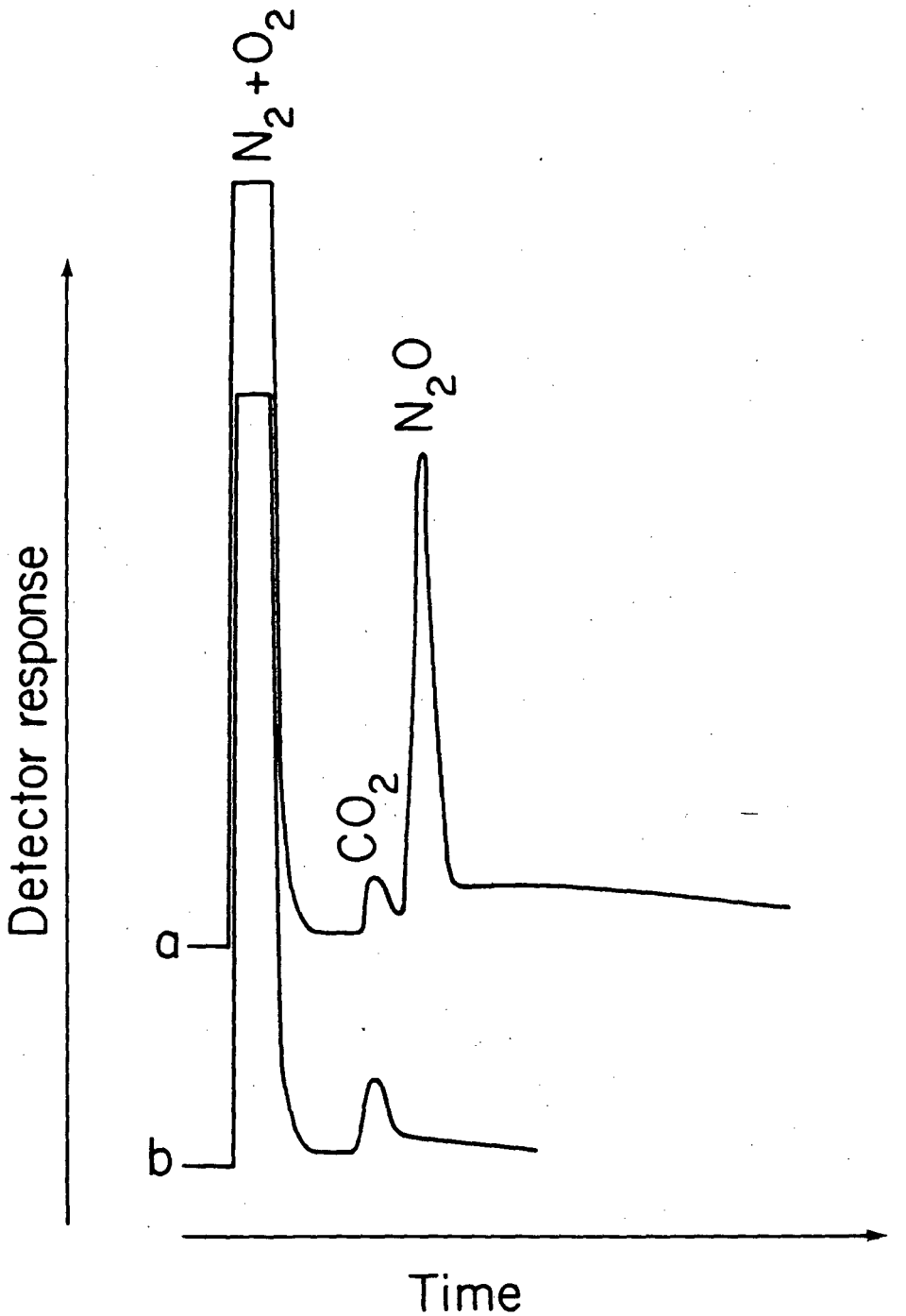

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Figure 13. Typical chromatograms. Curve a is for $\Delta S/\Delta N = 1.4$ and curve b is for $\Delta S/\Delta N = 2.0$.

when $\Delta S/\Delta N = 1.4$ and curve b is from an experiment where $\Delta S/\Delta N = 2.0$. The other possible mechanism which is known to produce nitrous oxide involves the formation of HADS, hydrolysis of this to HAMS and reaction of this with nitrite ion. The rate of hydrolysis is too slow for this to occur on the time scale in which the present experiments were completed (approximately 5 or 10 minutes). This forces one to rule out the indirect mechanism.

The nature of the competition for the intermediate allows one to determine the relative rate constants for sulfonation and hydrolysis, provided certain assumptions are made. Assuming first that HADS is produced by an elementary reaction between the intermediate and bisulfite ion, the fraction of the intermediate which reacts along this path can be expressed as $(\Delta S/\Delta N - 1)$. By further assuming that nitrous oxide is formed by the dimerization of NOH resulting from the hydrolysis of the intermediate (see discussion section), the fraction reacting through this pathway is $(2 - \Delta S/\Delta N)$. Since both reactions are being treated as elementary steps and there is a simple competition, the fractions are further related by the expression

$$k_s[S(IV)]/k_h[H^+] = (\Delta S/\Delta N - 1)/(2 - \Delta S/\Delta N) \quad ,$$

where k_s and k_h are the rate constants for sulfonation and hydrolysis of the intermediate. The value for the hydrogen ion was fixed by the buffer used in each experiment and presents no problem in the calculation. The concentration of the sulfur species changes

during the course of the reaction and consistent values must be used throughout the calculations. For the purpose of these calculations, the initial values of the sulfur (IV) concentration have been used; however, the results agree within experimental error if an average sulfur (IV) concentration is used. The results yield a value for k_s/k_h of 1.7 ± 0.5. Because both these reactions appear to be fast compared to the formation of the intermediate, it is not possible to determine the value of either one alone, and only the ratio can be reported.

D. Kinetics of Nitrite Ion Reactions with Hydroxylamine Monosulfonate

As previously stated the hydrolysis of hydroxylamine disulfonate to hydroxylamine monosulfonate is slow under most of the conditions of this study. This reaction does occur after long times, and the HAMS which results can react with nitrite ion or nitrous acid. This is shown in Figure 14. The time scale which is marked in seconds (abscissa) represents the time since the addition of nitrite ion to the solution (the reaction time). The times marked to the right of the curves represent how long the mixture was allowed to age prior to addition of the nitrite. The longer the solution ages, the more HAMS which is formed by hydrolysis and the greater the extent of the nitrite ion decay. This reaction between nitrite ion and HAMS results in the formation of nitrous oxide according to the net reaction

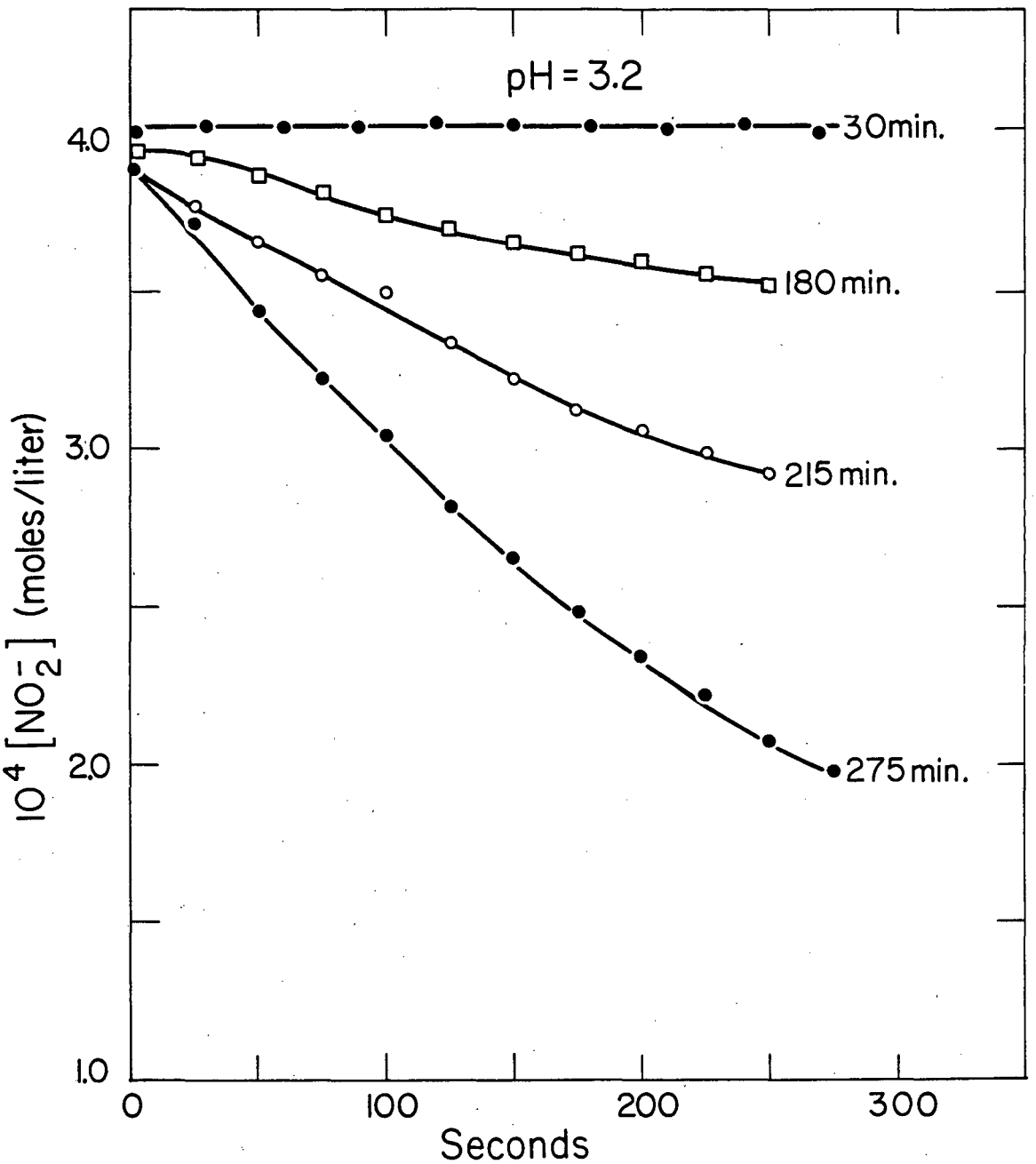

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Figure 14. Hydrolysis of HADS to HAMS. Time in minutes indicates the hydrolysis time, that in seconds the reaction time with nitrite ion. (See text for details). Nitrite ion is not the limiting reagent.

$$NO_2^- + HONHSO_3^- \rightleftarrows N_2O + SO_4^{2-} + H_2O \quad .$$

This mechanism for nitrous oxide formation has already been briefly described in the previous section. The kinetics which are reported in this section confirm that the conversion of HADS to N_2O by way of HAMS is too slow to account for the previous results. This further supports the conclusion that N_2O is also formed directly from the intermediate in HADS formation.

The dependence of the reaction of HAMS with nitrite ion was found to be first order with respect to nitrite ion by evaluating the shape of the nitrite ion concentration decay curve. There are fewer problems with maintaining pseudo-first-order reaction conditions because the stoichiometry for the reaction is one to one rather than two to one in the bisulfite reaction. Again, the correction for HONO absorbance must be made; however, the reaction was not investigated at pH less than 3.8 and insufficient evidence was available to determine whether NO_2^- or N(III) is the reactive species. At lower pH the reaction becomes too fast to measure accurately by the current techniques. The first-order dependence on nitrite ion allowed the use of the same techniques as in the bisulfite reactions.

Order of reaction with respect to HAMS was established by varying the concentration of this species at a constant pH. At the lower range of concentration, the reaction rate varied linearly with HAMS concentration indicating a first-order dependence. At higher concentrations there is less of an effect, and the reaction becomes nearly independent of the concentration of HAMS. A transition from higher to

lower order with respect to a reactant is fairly common in solution reactions and is indicative of a multistep mechanism where the reactant whose order changes is involved in the reaction after a reactive intermediate has been formed. At high concentrations this latter step becomes rapid, and the formation of the intermediate becomes rate determining. The mathematically determined rate law for the HAMS reaction would be of the form

$$\text{Rate} = k[\text{HAMS}]/(1 + k'[\text{HAMS}])$$

if a steady-state assumption is applied. By inverting both sides of the equation, the constants may be determined using a least-squares fit to the data. The results of this fit are shown in Figure 15 as a solid line. Unfortunately, the inversion of the equation makes the fit less sensitive to the high concentration points, as can be seen by a comparison of the fit to the actual points in that region. A better fit can be obtained by slight changes in the rate constants, particularly k'; however, the required change is small compared to the experimentally determined error (see Appendix B). A weighted least-squares fit could also be used. The values of these constants are reported at the end of this section. This change in order with respect to HAMS yields a great deal of mechanistic information and gives two regions in which all the other kinetic parameters must be evaluated.

The dependence of the reaction on hydrogen ion concentration was investigated by changing the pH values of the buffers used. These

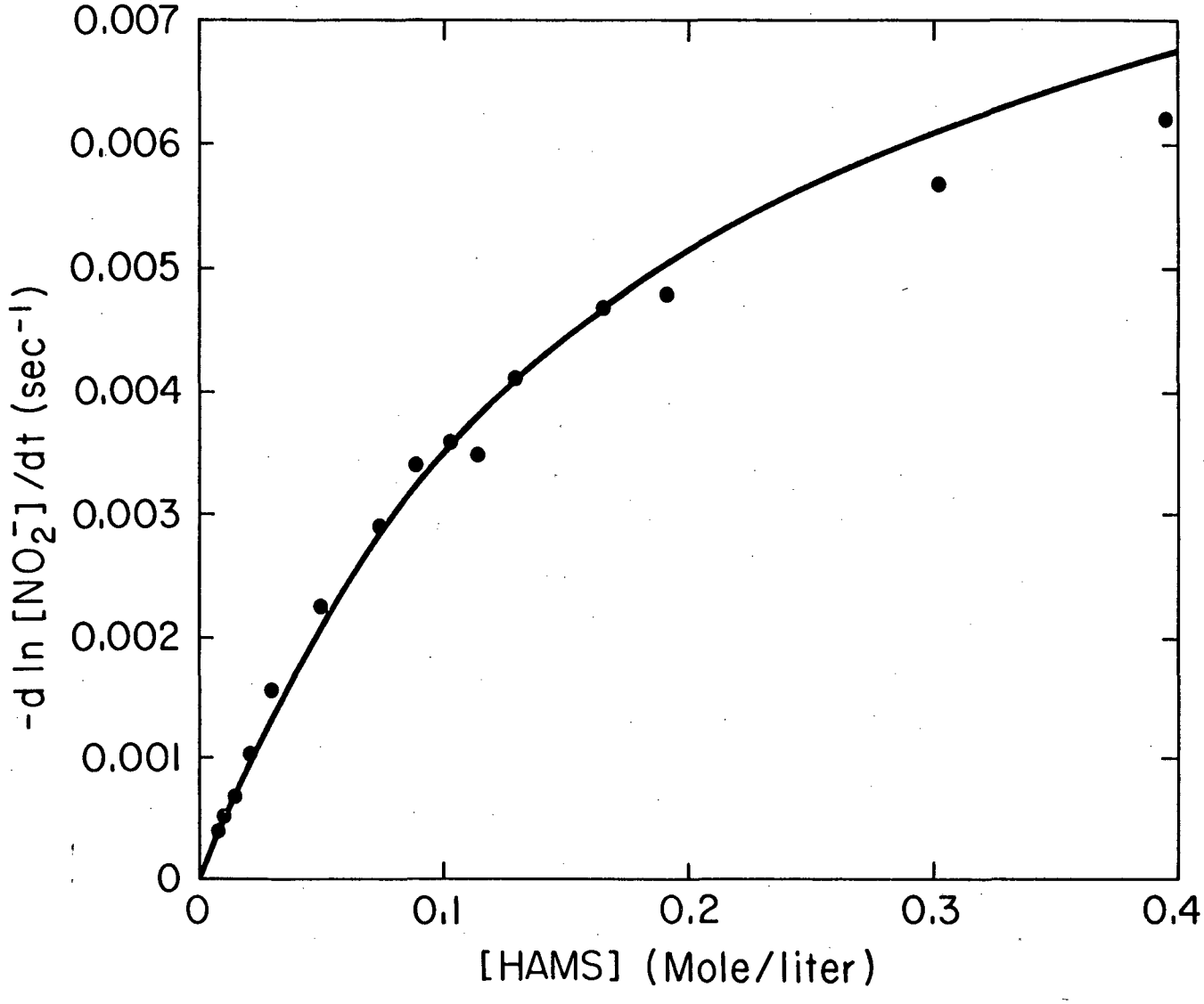

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Figure 15. Dependence of the HAMS-nitrite ion reaction rate on the HAMS concentration. (See text for explanation of the fitted curve.)

experiments were carried out in both the HAMS independent and dependent regimes. The order was determined from the slope of the best fit line on a plot of log(rate/[NO_2^-]) vs. pH, the results being shown for the HAMS-dependent regime in Figure 16. The slope is 1.9, which indicates a second-order dependence on H^+. The change in pH requires a change in the buffer concentration as well because the phthalate and biphthalate ions are not equally soluble. As will be discussed later, the rate of reaction is dependent on the buffer concentration, and correction of the rates for this effect accounts for the discrepancy between a slope of 1.9 and 2.0.

Similar behavior is seen for the HAMS-independent regime where again the reaction is second order with respect to hydrogen ion. Since there is no change in order in H^+ ion along with the change in HAMS order, it is probable that the entire dependence on acidity is a result of the steps prior to the one in which HAMS finally becomes involved. This means that the reactive intermediate is composed of nitrite ion and hydrogen ions only, with the possible inclusion of a water molecule.

With the exception of the buffer species, no other compounds present in the reaction mixture had any effect on the measured rates. In the absence of buffer, the reaction still proceeds, which indicates that the buffer either reacts or is involved in some sort of catalytic enhancement of the rate. The rate law for the formation of N_2O from hydroxylamine monosulfonate and nitrite ions in the absence of buffer can be expressed as

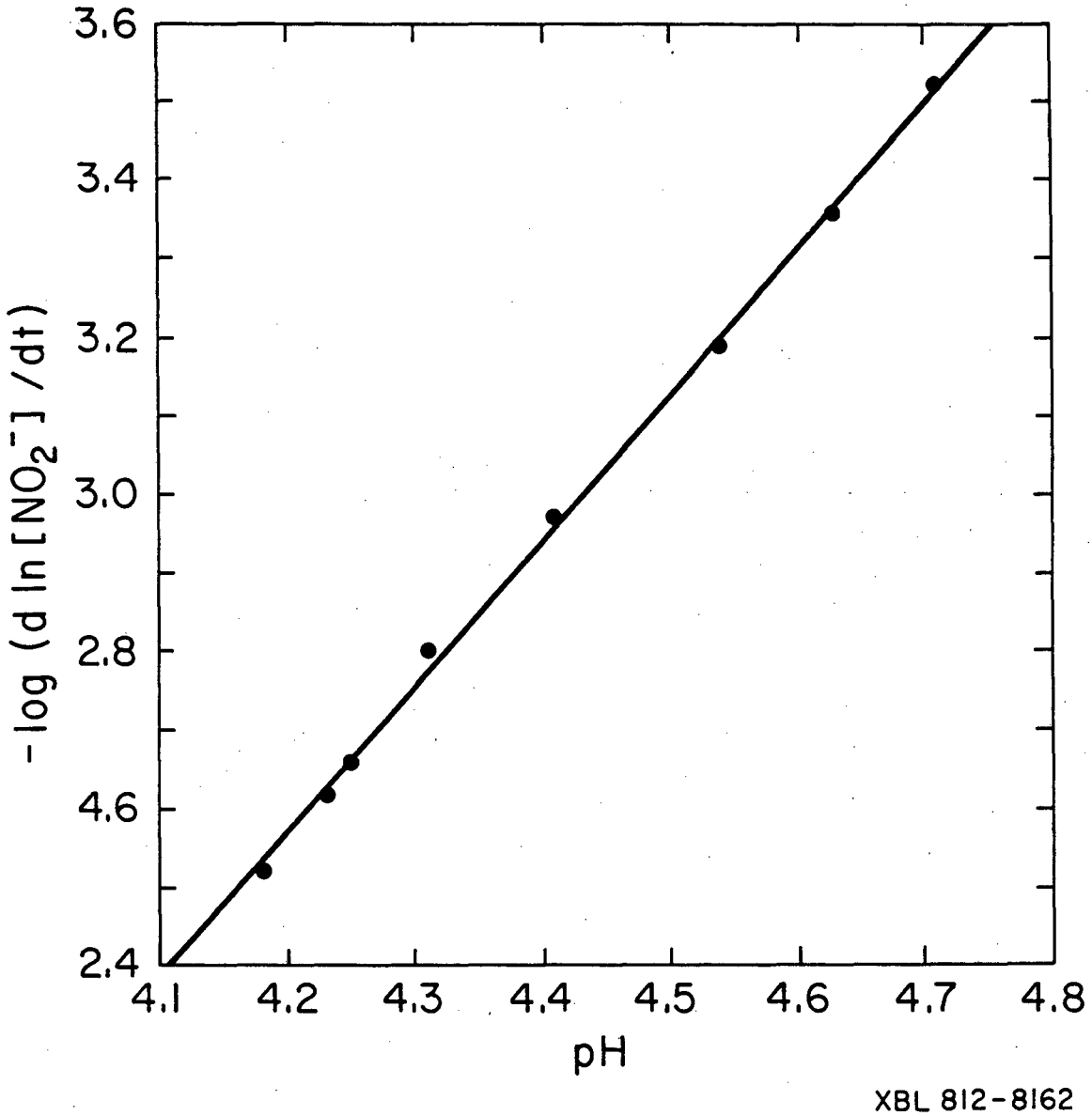

Figure 16. Dependence of the HAMS-nitrite ion reaction rate on pH ([HAMS] = 0.020 M, phthalate buffer system).

$$\text{Rate} = k_3[H^+]^2[NO_2^-][HAMS]/(1 + k_4[HAMS]) \qquad (2)$$

Values of the rate constants will be reported after a discussion of the effects of the temperature and buffer dependencies.

Studies to investigate the temperature dependence of this reaction yielded somewhat unexpected results. Activated complex theory was used to determine the enthalpies and entropies of activation for both the two regimes. For the HAMS-dependent regime, the enthalpy of activation is 7 kcal/mole and the entropy term is -2 cal/mole-kelvin. The data are plotted in Figure 17. The HAMS-independent regime yields values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 8 kcal/mole and -12 cal/mole-kelvin. Both values for the enthalpy of activation show that this reaction is less sensitive to temperature than the bisulfite-nitrite ion reactions. It is interesting that the values in the two regions agree so well, considering that different rate-determining steps are involved. None of these values can be interpreted directly because they are values for a complex rate constant with contributions from several reactions in the mechanism. The consequences of this difficulty will be considered in the discussion section after a mechanism has been proposed.

Ionic strength investigations lead to some confusing results. For both the HAMS regimes there was no change in rate when either sodium or potassium sulfate was used to adjust the ionic strength (μ between 0.20 and 1.50 M). Again it must be emphasized that the experiments cannot be performed at a concentration where Debye-Hückel theory is valid, and therefore the results are useful only in an empirical sense. No mechanistic information can be directly obtained from the results.

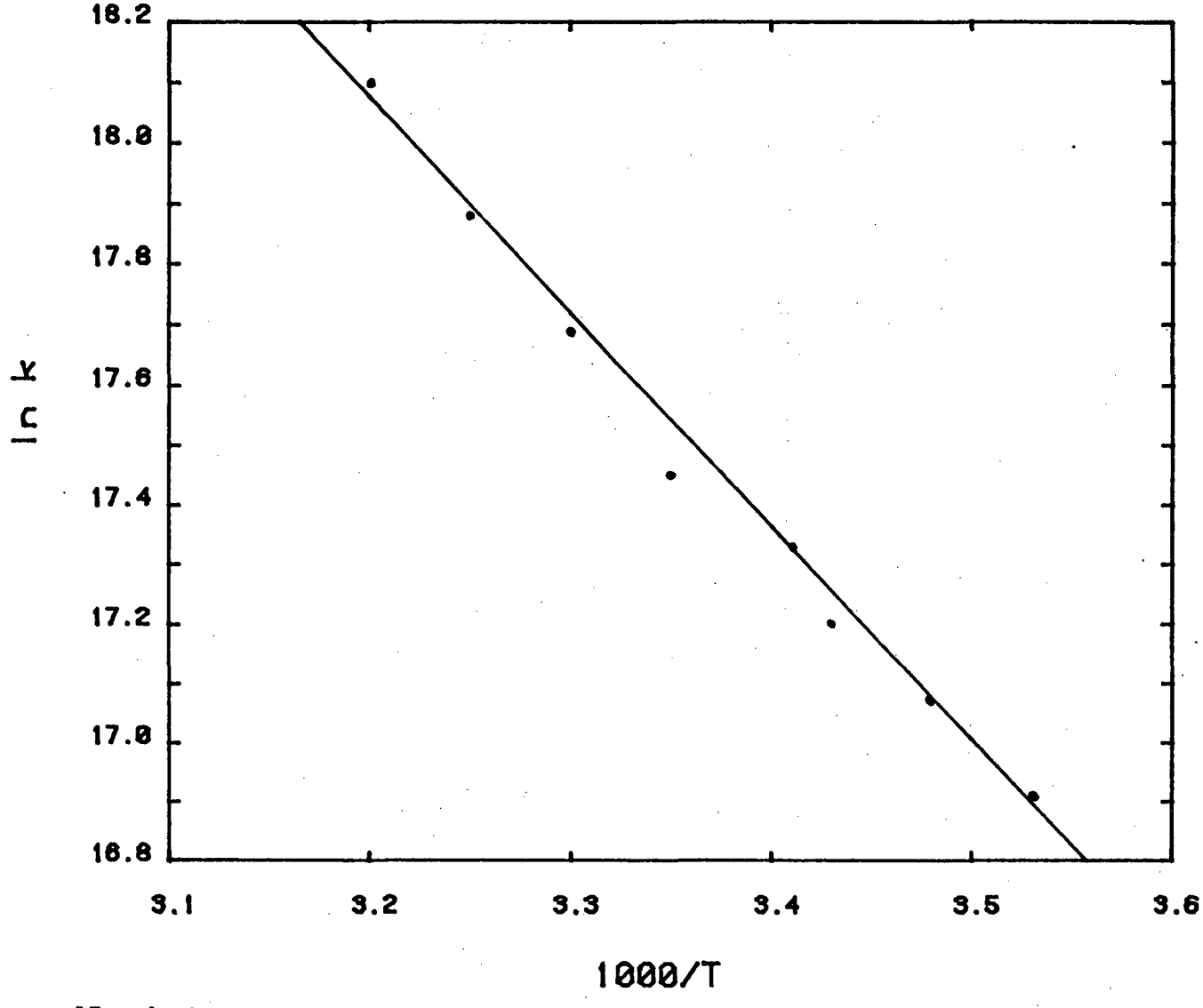

Figure 17. Arrhenius plot for the HAMS-nitrite ion reaction rate constant in the HAMS independent regime (temperature is in kelvin). XBL 812-8161

When dihydrogen phosphate is used to adjust the ionic strength, the rate increases with increasing value of μ (also increasing phosphate concentration). For several reasons this species appears to be acting as if it were a buffer. Most striking is that the concentration of phosphate seems to be the important quantity; addition of both sulfate and phosphate gives results as if only the phosphate was there. Reasons for this effect will be discussed along with the buffer effects. If nitrate salts are used to adjust the ionic strength, the reaction rate begins to slow down as the nitrate ion concentration is raised; and at higher concentrations nitrate ion has no effect. This is not presently understood; however, some speculation about this will be attempted in regard to the mechanism later. Perchlorate salts were not used because they react with acidic solution of nitrite ion.

All the previous results have indicated that some role is played by the buffer species, which was a phthalate system in almost every case. To elucidate this role, the buffer concentration was varied, keeping all the other parameters constant. Experiments were also performed in oxalate and tartrate buffers. In each buffer the increasing concentration brings with it an increase in rate as shown in Figure 18. The positive intercept indicates that the reaction proceeds in the absence of buffer, which eliminates it as a prerequisite for reaction to occur. The varying slopes indicate varying efficiencies for the different buffers as catalysts. This same type of behavior was already mentioned for phosphate ion and has been seen for acetate buffers in a previous study.[16]

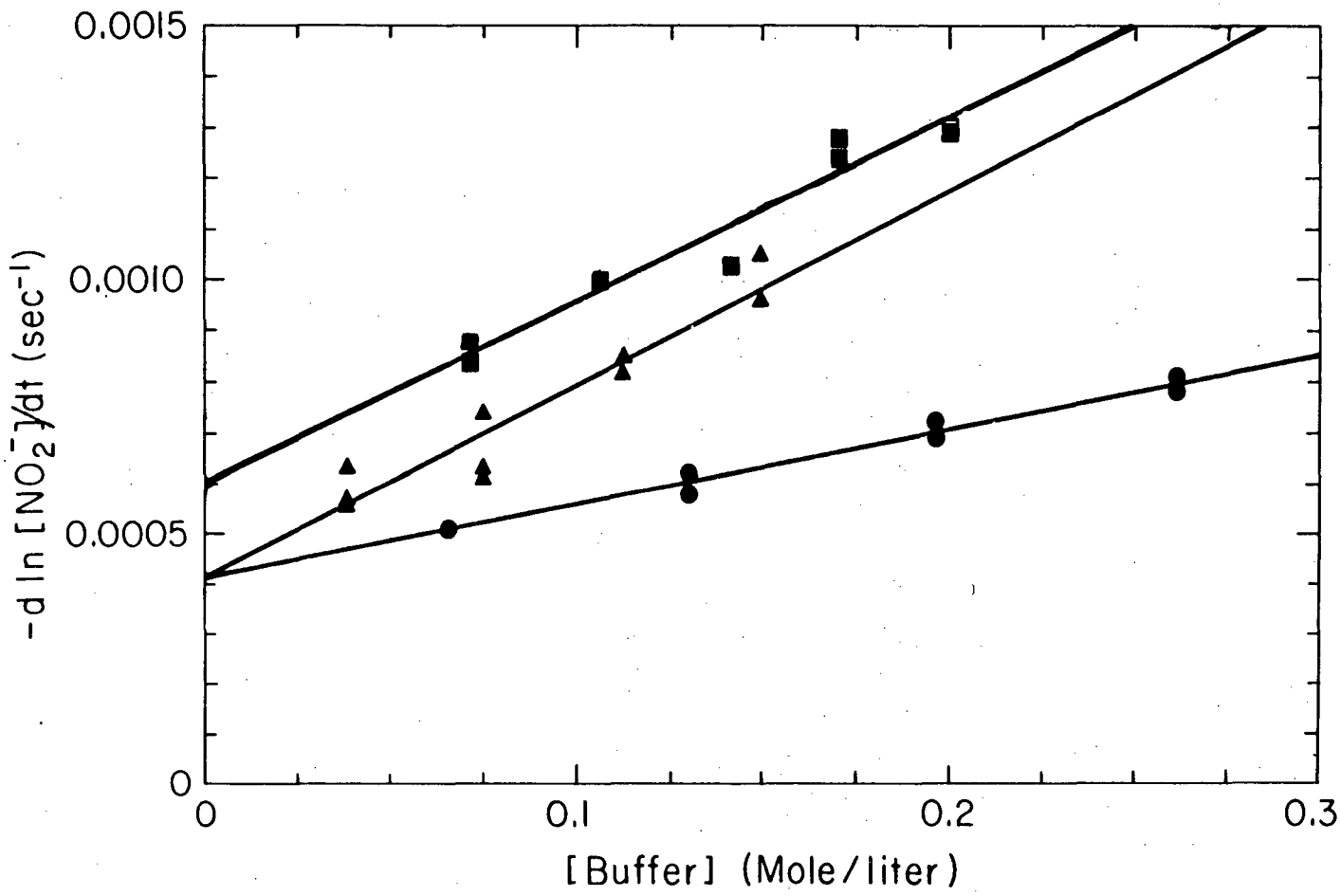

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Figure 18. Buffer dependence in the HAMS-nitrite ion reaction. □ indicate phthalate buffer, Δ indicate tartrate buffer, and ○ indicate oxalate buffer. See text for definition of buffer concentration. Ionic strength at 1.2 M.

There are two ways in which the aforementioned buffers could have acted as catalysts in this system. All the buffers are capable of acting as proton donors, which could mean the observed behavior was a general acid catalysis. In light of the second-order hydrogen ion dependence, this seems quite reasonable. However, the discrepancy between the H^+ ion dependence and the slope of the log-log plot in Figure 16 can be accounted for only if the entire buffer concentration is reacting or is acting as a catalyst. This implies that the second possibility for catalytic activity, the carboxylate functionality, is responsible. Both forms of each buffer used contain one $R\text{-}COO^-$ group. Presumably some different intermediate is formed by the reaction between hydrogen and nitrite ions in the presence of this functional group. The role of phosphate species is still unaccounted for unless it an also form a stabilized intermediate. Like the ionic strength effects, the buffer results only provide empirical information; however, some speculation regading this matter will also be given after the mechanism has been discussed.

The rate law for the uncatalyzed reaction has already been reported in Equation 2. The best values for the rate constants, in the absence of buffer speices and at 20°C, are:

$$k_3 = (1.5 \pm 0.3) \times 10^7 \text{ liter}^3/\text{mole}^3\text{-sec}$$

$$k_4 = 5.5 \pm 0.6 \text{ liter/mole} \quad ,$$

where the errors are given as the standard deviations. The total rate may then be expressed as:

$$\text{Total rate} = \text{uncatalyzed rate } (1 + k_{buffer}[\text{buffer}]) \quad .$$

The values of k_{buffer} expressed in this form are 8.0 ± 0.8, 3.1 ± 0.2, and 7.5 ± 0.7 for oxalate, tartrate, and phthalate buffers, respectively. The units are all in liter/mole, and the concentration of the buffer refers to the total concentration regardless of which form (acid or conjugate base) it is in.

IV. DISCUSSION

A. Mechanism for the Formation of Hydroxylamine Disulfonate

The mechanisms which may be proposed for a given solution reaction have one absolute boundary condition, namely that they predict the correct reaction kinetics when the rate expression is calculated. Implicit in this is the idea that the proposed elementary reactions must correspond to physically realistic events. It is usually considered unlikely that elementary reactions of termolecular or higher molecularity will take place unless one or more of the reactants is the solvent. For this reason the proposed mechanisms for this study will conform to uni- or bimolecular elementary steps, except when water is one of the reactants. All other restraints on the mechanism are the direct result of the experimental observations.

For the reactions which resulted in formation of hydroxylamine disulfonate, the mechanism has to be comprised of two separate processes which yield the same product. One of these, being referred to as the first-order process, has a transition state for the rate-determining step which consists of one nitrite ion, one hydrogen ion, and one bisulfite ion, plus or minus one or more water molecules. These species can be brought together through bimolecular collisions between nitrous acid and bisulfite ion or nitrite ion and sulfurous acid. The two are kinetically equivalent, which guarantees that the mechanism will be ambiguous. The second-order process must have two bisulfite ions and one nitrite ion (plus or minus a water molecule)

forming the transition state. In addition the observed concentration dependence tends to rule out the stepwise addition of the bisulfite ions to the nitrogen species for this second-order process. On this basis the following mechanism is proposed:

$$H^+ + NO_2^- \rightleftarrows HONO \qquad (A)$$

$$2\ HSO_3^- \rightleftarrows H_2O + S_2O_5^{2-} \qquad (B)$$

$$HONO + HSO_3^- \rightleftarrows ONSO_3^- + H_2O \qquad (C)$$

$$ONSO_3^- + HSO_3^- \rightleftarrows HON(SO_3)_2^{2-} \qquad (D)$$

$$S_2O_5^{2-} + NO_2^- \rightleftarrows ON(SO_3)_2^{3-} \qquad (E)$$

$$ON(SO_3)_2^{3-} + H^+ \rightleftarrows HON(SO_3)_2^{2-} \qquad (F)$$

Reactions C and D represent the first-order process, reactions E and F represent the second-order process, and reactions C and E are rate determining. The rate constants for the forward and backward reactions will henceforth be referred to as k_a and k_{-a}, with the corresponding equilibrium constant as K_A.

Protonation and deprotonation of nitrous acid in acidic solutions are sufficiently rapid to allow reaction step A to be treated as a fast equilibrium.[32] It is probably valid to treat reaction F as a rapid equilibrium as well, particularly since there is presently no way to differentiate experimentally between $HADS^{2-}$ and $HADS^{3-}$ ions. The dimerization of bisulfite ions to form metabisulfite ion (Eq. B) will

also be treated as a rapid equilbirium.[33] This is valid, considering that the dimerization need only be rapid compared to the reaction of metabisulfite ion with nitrite ion, which is observed to be moderately slow.

The rate law for this mechanism can be derived in several ways. Because the initial rate studies were used to determine the rate law, backreactions of steps D, E, and F can be ignored. In addition HADS salts are stable in solution and show no sign of decomposition into reactants, so the backreactions in steps D and E can be ignored even at long times (irreversible formation of HADS). If steps C and E are then taken as the rate-determining steps for the two processes, the rate law can be written by inspection of the mechanism as

$$\text{Rate} = -d[NO_2^-]/dt = k_c[HONO][HSO_3^-] + k_e[S_2O_5^{2-}][NO_2^-] \quad .$$

A full treatment under a steady-state approximation can be carried out and the same rate law results. This requires the additional assumption that $ONSO_3^-$ reacts to form products faster than it reverts to nitrite ion; the same condition as if step C were rate determining. After the inclusion of the fast equilibria into this rate expression, the result is identical in form to that which was observed (Eq. 1):

$$\text{Rate} = -d[NO_2^-]/dt = k_cK_A[H^+][NO_2^-][HSO_3^-] + k_3K_B[HSO_3^-]^2[NO_2^-] \quad .$$

In addition to providing the correct form of the rate expression, this mechanism can account for all the other results as well. The

ionic strength dependence was one of the most striking features of the observed results. Studies on the equilibrium between bisulfite and metabisulfite ions have shown a pronounced increase in K_B with increasing ionic strength.[33] This is consistent with the kinetic results of the present study because as μ is increased, so is the concentration of the $S_2O_5^{2-}$ ion. This means that for a fixed concentration of bisulfite ion, the measured rate will increase substantially. This change in K_B accounts for approximately 80 percent of the observed effect. The remaining 20 percent can be explained by electrostatic or solvation effects in forming the transition state from the two negative ions, nitrite and $S_2O_5^{2-}$. Very few quantitative data are available for the temperature dependence of K_B, other than that its value decreases with increasing temperature.[33] This is normal for dimerization-type equilibria and could account for the small negative activation energy which was observed.

In addition to both these facts supporting the involvement of metabisulfite ion, the species satisfies several more important prerequisites. It is the simplest species which consists of two bisulfite groups, has a weak S-S bond, and is present in a reasonable concentration (greater than 10^{-4} M). The weak S-S bond is important as a substantial bond energy would imply a greater activation barrier and a more positive activation energy than observed. The actual attack of the nitrogen species on the sulfur species is not straightforward, as considerable rearrangement is required. Most probable is a nitrogen

attack on one of the sulfur atoms, splitting the S-S bond, followed by a fast reaction of an unattached sulfur group with the nitrogen atom. This initial attack on the metabisulfite ion would have to be rate determining to give the correct kinetic results. Nitrogen-assisted bond cleavage leaves the second sulfur atom in close proximity for a second N-S bond formation reaction, which would be rapid. Another possiblity involves a concerted rearrangement which is considered less likely.

The first-order process in the proposed mechanism is not as easily justified. The ionic strength effect (or lack of it) is consistent with the proposed mechanism at these high ionic strengths. The mechanism also agrees with the observed value of the entropy of activation. However, reactions A and C could have been replaced by

$$H^+ + HSO_3^- \rightleftharpoons H_2SO_3 \qquad (G)$$

$$H_2SO_3 + NO_2^- \rightleftharpoons ONSO_3^- + H_2O \quad , \qquad (H)$$

and an identical form of the rate law would have been obtained. The only preference for the original choice lies in the basis that one of the oxygens on the nitrogen atom must act as a leaving group to form HADS. Of the two isomeric forms of bisulfite ion, one of them has a lone pair on the sulfur atom, which is at the top of a pyramidal structure. This can be used in a nucleophilic attack on the nitrogen atom. Sulfurous acid does not have a vacant lone pair on the sulfur atom and is less likely to be involved. The lone pair on nitrogen

could attack the sulfur atom, but it is unlikely that it would lose an OH group while attacking.

Another possible mechanism for the formation of the intermediate proceeds through the formation of NO^+ ion:

$$H^+ + HONO \rightleftharpoons NO^+ + H_2O$$

$$NO^+ + SO_3^{2-} \rightleftharpoons ONSO_3^- \quad ,$$

but this has been ruled out for two reasons. First is that the NO^+ is only formed at reasonable concentrations in more strongly acidic solutions where sulfite ion is present in very small concentrations. More importantly, formation of NO^+ (or a complex including NO^+) has been shown to exhibit strong enhancement in phthalate buffers,[34] and no effects such as these have been seen in the present reaction. It is more likely that if nitrosyl ion were involved in this sytstem, it is in the bisulfite-independent process that was observed by previous researchers in the field.[19,20] Although an early report[41] agreed with these researchers, further work in the present study finds no evidence for any process independent of bisulfite ion, and the final conclusion is that NO^+ is not involved in this set of reactions.

This six-step mechanism can be expanded to account for the various related reactions which are observed. Both sulfonation and hydrolysis of HADS are likely to occur; however, these reactions have been omitted because they are eliminated by initial rate studies and are involved only after the rate-determining steps. If included, they would not

affect the form of the rate law, which is derived for the rate of loss of nitrite ion. The intermediae ($ONSO_3^-$) is also available for hydrolysis to form N_2O (see next section). The proposed mechanism to produced HADS has no expected changes in order as one goes to lower and lower concentrations, other than the second-order process becoming negligible compared to the first-order one. Therefore, at ambient atmospheric concentrations, the proposed rate law for nitrite loss should hold true in its present form.

B. Mechanism for the Formation of Nitrous Oxide

Experimentally it was determined that HADS is not the sole product whenever there are comparable amounts of hydrogen and bisulfite ions. It was further shown that a competition exists between the two ions for the intermediate. This can be explained mechanisticalily by addition of one reaction to those previously proposed (Eq. A-F):

$$HONO + HSO_3^- \rightleftarrows ONSO_3^- + H_2O \qquad (C)$$

$$ONSO_3^- + HSO_3^- \rightleftarrows HON(SO_3)_2^{2-} \qquad (D)$$

$$ONSO_3^- + H_3O^+ \rightleftarrows HON + HSO_4^- + H^+ \qquad (I)$$

Equations C and D have been repeated here to clearly show the competition. Although the active intermediate is shown here in the deprotonated form, its acid form could equally well have been proposed with no change in the results. Whereas reaction D is most likely a nucleophilic attack by the sulfur atom lone pair on the nitrogen atom, reaction I is probably an attack by water on the sulfur atom in the

intermediate, with NO^+ or NOH as the leaving group. The protonated form of the intermediate is probably more susceptible to attack (NOH being the better leaving group), which would explain the acid catalysis (or effect of hydrogen ion) in the competition for $ONSO_3^-$. Reaction I may actually involve two steps, a protonation followed by an attack by a water molecule. Once formed the nitroxyl species (NOH) should rapidly dimerize and decompose to nitrous oxide.

It was pointed out in the previous section that reaction C was the rate-determining step and that reaction D was fast in comparison. The data also indicated that reactions D and I had very similar rate constants. Therefore, reaction I must also be rapid compared to C. This allows reaction I to be included in the overall mechanism with no change in the derived rate expression for nitrite ion loss, but with a change in products under very acidic conditions. This change in products will also occur when S(IV) concentrations drop to very low values. In aerosol droplets under ambient conditions, there will be H^+ ions from nitric and sulfuric acids formed by other processes which will most likely be in excess of the S(IV) species. This would indicate that N_2O would be the expected product. Reaction C as the rate-determining expression allows the same rate expression to be used as long as nitrite ion loss is used to measure the kinetics regardless of product. Once again, at the low concentrations there should be no change in the reaction order.

Any of the other possibilities for the formation of $ONSO_3^-$ would work equally well when reaction I is included in the mechanism.

There are only two requirements which are placed on the system by the observed phenomena. First is that the intermediate, if not $ONSO_3^-$, must have a basic site which when protonated assists in the hydrolysis step. Second, it probably must have a S-N-O backbone to allow formation of either HADS or NOH. These constraints still cannot distinguish between $ONSO_3^-$ and $ONSO_3H$, which leaves another ambiguity in any mechanism which may be proposed.

C. Mechanism for the Reaction of Hydroxylamine Monosulfonate with Nitrite Ion

The experimental observations of the reaction of nitrite ion with hydroxylamine monosulfonate have already indicated that it must be a multistep reaction with HAMS involved in the latter steps, after the hydrogen ions have been involved. Which step is rate-determining depends on the concentration of HAMS: but in the HAMS-independent limit, two hydrogen ions and one nitrite ion are involved in the transition state. There are a substantial number of reactions involving nitrite ion which show this type of behavior, among them to nitrosation of amines.[34] In these reactions the accepted mechanism involves the formation of NO^+ as the nitrosation agent. A similar mechanism for the present reaction, using NO^+ as the intermediate, would be:

$$H^+ + NO_2^- \rightleftarrows HONO \qquad (A)$$

$$HONO + H^+ \rightleftarrows NO^+ + H_2O \qquad (J)$$

$$NO^+ + HONHSO_3^- \longrightarrow NO\cdot HAMS \longrightarrow N_2O + HSO_4^- + H^+ \qquad (K)$$

A few comments about these reactions are in order. The reactions in step K are shown to imply that NO•HAMS reacts irreversibly to form nitrous oxide. That it is irreversible is easily shown by addition of N_2O to acidic sulfate solutions with no reaction occurring. It is not clear that the reaction of NO•HAMS to form products is rapid. If the decomposition of this to form products is rate determining rather than its formation being the rate-determining step, the same kinetics will be obtained. Because the rate of loss of nitrite ion was measured, the two different situations will be indistinguishable.

There is also some uncertainty as to how nitrous oxide is formed. If NO^+ attacks the nitrogen in HAMS in an electrophilic addition, there are two possibilities. First is a subsequent attack on the sulfur atom by a water molecule (solvent), which results in the formation of hyponitrous acid. Alternatively, the oxygen from the NO^+ species could migrate to the sulfur atom, and the nitrous oxide would be formed in a direct manner. Once again the present experiments cannot distinguish between the two possibilities, as a sufficiently sensitive analytic method for hyponitrous acid was not available.

Another equally plausible mechanism is obtained by replacing equations J and K with the following reactions:

$$H^+ + HONO \rightleftharpoons H_2NO_2^+$$

$$H_2NO_2^+ + HONHSO_3^- \rightleftharpoons H_2N_2O_2 + HSO_4^- + H^+ \quad .$$

The intermediate in this example is equivalent to a hydrated NO^+; and as expected, the results are kinetically indistinguishable from the previous case. Again a nitrogen-nitrogen bond is formed by an electrophilic addition, which is followed by or proceeds in concert with a transfer of hydroxyl (OH) group to the sulfur atom. Evidence points to NO^+ as the preferred intermediate because observed rates are in agreement with rates of production of NO^+ from polarographic[35] and isotope exchange studies,[36] but this cannot be considered conclusive.

The calculated rate expression can be derived by use of a steady-state approximation although reaction A is once again treated as an equilibrium:

$$\text{Rate} = -d[NO_2^-]/dt = \frac{K_A k_j k_k [H^+]^2 [NO_2^-][\text{HAMS}]}{(k_{-j} + k_k[\text{HAMS}])} \quad .$$

This is identical in form to the rate law for the unbuffered reaction which was reported in the last section (Eq. 2). As the HAMS concentration is increased, the expression becomes independent of this parameter as expected. It has been assumed in this derivation that the initial step in reaction K goes directly to the products. If NO•HAMS builds up in concentration, a more complex rate law which is of the same form results from the steady-state approximation. From the point of view of the kinetics it does not matter how NO^+ and HAMS ions react as long as that, or a subsequent, reaction is rate determining (and that the subsequent reaction does not involve other ions).

The temperature dependence which was noted in each regime is consistent with this mechanism. When HAMS is present in high concentration, the rate law reduces to

$$\text{Rate} = k_j K_A([H^+]^2[NO_2^-]) \quad .$$

The 7 kcal/mole activation energy which was observed is quite realistic. In the low concentration regime, the rate constant consists of

$$k = k_j K_A \ (k_k/k_{-j}) \quad ,$$

which has components from several steps. That the observed value is almost equal to the result of the other regime implies that the activation energies for the forward reaction K and the reverse reaction J are approximately equal. The entropy of activation in each regime is also a result of contributions from more than one elementary step and no mechanistic information can be derived from it other than that different rate constants are being measured in each regime (which was already established by the rate law).

The ionic strength effects which were observed can be explained in terms of this mechanism as well. Both limiting conditions exhibited the same effects. Sulfate salts had no effect which is once again probably due to the insensitivity of the activity coefficients of the salts at the high ionic strengths employed (0.2 to 1.5 M). Phosphate ions will once again be treated as a buffer effect rather than an ionic

strength phenomenon. Nitrate ion showed a reduction in the rate (by about 50 percent) which was not as severe at higher concentrations. The simplest explanation is that there is a nonlinear slowing of the rate as the ionic strength was increased with nitrate salt addition. Since no other salts show this behavior, a specific interaction by the NO_3^- ion is considered more likely. Nitrate ions must somehow react with either HAMS or H^+ ions to inhibit the rate of loss of nitrite ions. Reaction with HAMS is the most probable, although no evidence for products other than N_2O was observed. It is surprising that the rate decreases, because the following pathway is introduced:

$$NO^+ + NO_3^- \rightleftarrows 2\ NO_2\ (\text{or } N_2O_4)$$

$$2\ NO_2 + H_2O \rightleftarrows NO_3^- + 2\ H^+ + NO_2^- \quad .$$

These reactions, taken with the formation of nitrosyl ion (Eq. J), form a closed loop or null cycle. Prior to the introduction of nitrate ion, the NO^+ ion either reacted with hydroxyl ion to form nitrite ion or went on to form the products. These additional reactions introduce a second route for transformation of nitrite ion into NO^+, and should result in an increased rate of loss of nitrite ion. The principle of microscopic reversibility assures this even at the low concentrations which are under investigation, where the equilibrium between nitrate and nitrite ions and nitrogen dixoide lies very far to the ionic side.[37] Although there is little evidence of the ionization of N_2O_4 into NO^+ and NO_3^- ions in water, this ionization has

been detected in nearly anhydrous acids.[38] The gradual lessening of the observed effect at high concentration of nitrate ion may be partly due to this reaction cycle or changes in the values of the activity coefficients as the ionic strength increases. The chemistry of the dissolution of NO_x and its reactions in solution is an area of active research and more information regarding these reactions will hopefully be available in the near future.[39,40]

D. Buffer Effects

In discussing the production of hydroxylamine disulfonate, the hypothesis of the intermediate species' being formed from nitrosyl and sulfite ions was rejected because there was no observed buffer effect, which should have been present if NO^+ were involved. In the hydroxylamine monosulfonate reactions, a strong buffer effect was observed, which adds credence to the proposed mechanism which has NO^+ as the key. Again it must be stated that $H_2NO_2^+$ is another possibility, and the discussion which follows holds equally well for either species. In the one previous study of the HAMS-nitrite ion reaction, carried out in the HAMS-independent regime, an increasing rate was seen with increasing acetate concentration. There was no investigation into the source of the catalytic effect.[16] Work on the nitrosation of amines shows evidence that chloride, iodide, bromide, phthalate, and acetate ions all act as catalysts, and the reaction is believed to go through the NO^+ intermediate.[34] The present work shows the same type of buffer effect for phosphate,

phthalate, oxalate, and tartrate species. The nature of the enhancement by these buffers can be reduced to the question of what all these species have in common that can interact with NO^+ and why sulfate ions do not interact in this fashion.

The first explanation of the buffer phenomenon was attributed to a general acid catalysis of the reaction. Since hydrogen ion is needed to form NO^+ ion, it was believed that acetic acid or dihydrogen phosphate could act as proton donors, along with the H_3O^+. Sulfate would not be expected to act in this manner as there were almost no bisulfate ions present at the pH at which the reaction was under investigation. Biphthalate, bioxalate, and bitartrate ions can also act as proton donors. The halides do not agree with this theory because they are strong acids and cannot act as proton donors once in solution. All their contribution has to come through H_3O^+, which is the uncatalyzed portion of the reaction. These should act as sulfate did and show no effect; however, a catalytic effect has been seen for the halides.[34]

It has been suggested that the carboxylic acid or carboxylate functionality might exhibit a stabilizing effect on NO^+. This would serve to increase the concentration of the reactive intermediate if the complexes that were formed were weak enough to allow the complex to react in essentially the same manner as NO^+. This would explain the effect for the acetate, phthalate, tartrate, and oxalate buffers. Hughes and coworkers have shown that phthalate and acetate species form partially covalent complexes with nitrosyl ion.[34] The same sort of

behavior would be expected for all the species which contain a $R-COO^-$ functionality. In addition, the different R groups would give rise to different degrees of covalency and result in different catalytic efficiencies for the different species. This is completely consistent with the observations made during this investigation. Phosphate also forms a partially covalent complex with NO^+, although it is not clear if it is the dihydrogen phosphate ion or phosphoric acid which is responsible.[34] The nitrosyl halides are also known to be covalent, or at least partially covalent species, which would explain their behavior as well.[37] Sulfate ion is the one species used in this study which forms a completely ionic complex with nitrosyl ion - lead chamber crystals ($NOSO_4H$). In solution this would completely dissociate, and there would be no stabilization of the nitrosyl ion.

The other observed effect was that both the dianion and monohydrogen anion form of buffers containing carboxylic acids seemed to enhance the rate equally well in the HAMS-dependent regime. If only one NO^+ is stabilized by each buffer ion, which is the most probable situation at low NO^+ concentrations, then there would be little difference between the two forms because each of the two forms has at least one $R-COO^-$ functionality to stabilize the NO^+. Because the buffers do not exist in ambient aerosol particles or most of the scrubber systems where these reactions are considered important, the experiments were not designed to yield information on the actual catalytic species. Ionic charge considerations lead one to expect $R-COO^-$ as the active form. However, unless the complex is partially

covalent there is no reason to expect any complexation to be exhibited at the concentrations involved in this study.

This explanation of the buffer effect is also consistent with the nitrate ion observations. Both act on the reaction in such a way to open other pathways for the reaction to occur. These reactions are all parallel; and if all the species were present at the same time, the net effect would be a change in the steady-state concentration of the nitrosyl ion.

E. Confirmation of Results

Since the first report of these results was made available,[41] other laboratories have reported studies of these or related reactions under conditions more closely related to atmospheric situations. The two most relevant studies have dealt with the reactions of nitrous acid with bisulfite ion in sulfuric acid solutions as a model for the reactions which take place in sulfuric acid aerosols. The first study found a rate law for the loss of nitrite ion which was first order in nitrogen (III) species, first order in bisulfite ion, and half order in hydrogen ion.[42] Results of the present investigation, when converted to N(III) species (rather than nitrite ion) show between zero- and first-order dependence on hydrogen ion, the exact value depending on the pH range in question. In the pH range of 1.5 to 3 where the other study was performed, the form of the rate laws agree quite well. The rate constant which was reported is two to four times greater than the one determined in the present study. The second study was quite similar to the first[43] and although unpublished, the

results show a zero-order dependence on hydrogen ion. In all other respects, including the value of the rate constant and form of the rate law, the results agree with the first study. The solution in this study consisted of sulfuric acid (greater than 0.5 M in concentration). Both studies determined the product to be nitrous oxide which is what is predicted by the present investigation. All experimental conditions of the three studies were similar, with the exception that the two studies of other laboratories were made using ultraviolet rather than visible spectrophotometry. Because they could not establish that this did not increase the rate of reaction, it is believed to be the cause of the larger rate constants.

At the outset of this thesis several previous studies into the reactions of nitrite and bisulfite ion to form HADS were mentioned and the rate constants and rate laws were reported.[19-21] The rate laws are of the same form as the present study with two exceptions. First is that the bisulfite independent term is not seen when the reactions are carefully performed. Second is that the second-order process has been corrected for the first-order contribution before analysis which had not been done in any previous study. This leaves only one rate constant which can be directly compared after correction for temperature differences. It is found to agree with the present study to within ten percent. The rates for the second-order process, taken from the previous studies and correctly analyzed, yields a rate constant which also agrees to within ten percent.

These independent confirmations of the present results offer strong encouragement that the mechanisms are sufficiently well understood to allow extrapolation of the rate laws to conditions (particularly low concentration regimes) where experiments cannot be readily performed. The emphasis of the other two recent studies is empirical; while the results are in agreement with the proposed mechanisms described herein, they do not provide sufficient detail to offer additional support to the mechanisms or new ideas for other possibilities. The proposed mechanisms will therefore be considered valid as supported by the experimental observations until evidence is presented which supports other mechanisms.

V. SUMMARY AND CONCLUSIONS

The stated objectives of this investigation were focused at immediate and long-range levels. Three immediate objectives were: 1) determination of the kinetics of production of hydroxylamine disulfonate from nitrite and bisulfite ions; 2) a search for evidence of the existence of an intermediate (presumably nitrososulfonate ion) in HADS production which could undergo hydrolysis; and 3) determination of the kinetics of the reaction between hydroxylamine monosulfonate and nitrite ion. These objectives have been met. The longer range objective was to evaluate the contribution of these reactions to the formation of atmospheric aerosols. Although this goal has not yet been attained, considerable progress has been made in this direction. The more immediate objectives will be reviewed first.

The rates of reaction between nitrite and bisulfite ions have been evaluated for those conditions where HADS is the principal product. Under more acidic conditions the reaction rate is too fast to measure by the present techniques, and kinetic information is not available. The reaction was found to consist of two concurrent pathways--one dependent on the square of the bisulfite ion concentration and independent of pH, the other linearly dependent on both bisulfite and hydrogen ions. Both processes are linearly dependent on concentration of the nitrite ion, making each term in the rate law third order. The rate has been observed to vary with changes in ionic strength and temperature of the reaction solution but was insensitive to the presence or absence of the buffer species or the presence of oxygen.

Of the two processes, the one which shows a linear dependence on bisulfite ion is the more important, with the process second order in bisulfite ion only observed at high sulfur (IV) concentrations (greater than 0.1 M) or slightly basic solutions (pH greater than 6.5).

Evidence was obtained indicating the existence of an intermediate ($ONSO_3^-$) in the production of HADS. Although this intermediate species could not be directly observed, there was evidence for a competition for it to undergo sulfonation to form HADS or hydrolysis to form nitrous oxide (or hyponitrous acid). This competition was observed only in rather acidic solutions (pH less than 3) or at very low bisulfite concentrations ([S(IV)] less than $[H^+]$). The nature of the competition was such that in acidic solutions nitrous oxide should be the only product formed at sufficiently low bisulfite concentrations. The kinetics of these two competing processes could not be directly obtained; however, analysis of the competition suggests that the rate law resulting from the process producing HADS which was first order in bisulfite ion should apply here as well, except for the change in product. This is believed to be due to the rate of formation of the intermediate being the rate-determining step for both processes.

The possibility that nitrous oxide was formed after the hydrolysis of HADS to HAMS was ruled out because the hydrolysis rate was too slow to account for the observed formation of N_2O. As further substantiation, the kinetics of the production of nitrous oxide from hydroxylamine monosulfonate and nitrite ion was investigated. The rate was determined to be second order in hydrogen ion, first order in nitrite

ion, and either zero or first order in HAMS, depending on its concentration. Even if the hydrolysis of HADS to form HAMS had been rapid, the reaction with nitrite ion has a rate too slow to account for the N_2O produced in the competition described above. The reaction rate was again observed to vary with the solution temperature, but this time it was insensitive to the ionic strength. Buffer species acted as catalysts and nitrate salts inhibited the reaction through some form of specific ion effect.

Mechanisms have been proposed for the reactions which can account for all the observations. The nature of the rate laws, and particularly the hydrogen ion dependence, guarantees that the proposed mechanisms will be ambiguous. The differences between the kinetically indistinguishable choices are not drastic enough to alter any of the conclusions. One of these conclusions which was of interest from the outset of the investigation was the fate of the reactants at very low concentrations, as found in aerosol droplets. Eventually all the sulfur (IV) species which enter the reaction will be oxidized to sulfate species. Nitrite ions will initially be reduced to a number of intermediates, depending on conditions, and will finally result as nitrous oxide. If the reaction is carried out at elevated temperatures (above 50°C), hydroxylamine may be obtained; and at both elevated temperatures and high sulfur (IV) concentrations, any of the amine sulfonates or ammonia may be the product. These conditions are not expected in ambient atmospheric aerosols and were not investigated in this study. However, data regarding the kinetics forming these other

products are available[14,15] and their contributions to the overall rate may be estimated.

Although at this point these reactions involving nitrite ion are quite well understood, there are several questions which arose during the course of this investigation which remain unanswered. Several of these have been speculated upon during the discussion of the mechanisms, including the nature of the complex formed between phthalic acid and bisulfite ion, and whether or not N_2O is formed directly from the intermediate in the HAMS-nitrite ion reaction. While both these questions are intriguing, they have no bearing on the question of air pollution studies and are left for later investigations. Of more importance to the pollution studies and the extrapolation of the rate laws to lower concentrations is the question of what other reaction pathways are available to NOH and $ONSO_3^-$ (the reaction intermediates), and what effect will these other reactions have on the rate of loss of nitrite ion or the type of products formed. Because the two intermediates cannot be detected by the present techniques, the studies have not been undertaken. Until such time as a suitable analytic technique is found to observe these reactants directly, no studies can be carried out to conclusively determine which reactions are involved and at what rates.

At the beginning of this section, it was stated that the evaluation of reactions between nitrite and bisulfite ions as ambient-aerosol-formation mechanisms awaited further study. At this point the solution kinetics are essentially complete. The primary stumbling block is the

lack of knowledge about the rates of reactive dissolution of the gases (SO_2 and NO_x) to form ions. For the nitrogen oxides, it is not even clear what ratio of the ionic species are formed for a given concentration of the gases. Several conclusions can still be drawn based on the solution kinetics alone. In aerosol droplets the hydrogen ion concentration will be maintained in the acid range either by the buffering action of carbon dioxide or from sulfuric or nitric acids formed from other more rapid processes (carbon-catalyzed SO_2 oxidation, etc.). As the bisulfite concentration is lowered to approach a physically realistic situation, the process second order in bisulfite ion will become insignificant compared to the first-order process. At even lower concentration of bisulfite ion, nitrous oxide becomes the only product (in acidic solutions) and HADS is not even formed. The reaction of HAMS with nitrite ion is therefore not likely to take place in ambient aerosols, as HAMS only results from the hydrolysis of HADS. Regardless of the concentration level, the sulfite species are oxidized to sulfate, and the nitrite ions are reduced.

The question remains of the importance of the process forming N_2O compared to other atmospheric aerosol formation mechanisms. Because the processes described in this study are second order in dissolved gases (or ions formed from them) and the reaction produces acidic species, and because the solubilities of the gases decrease as the acidity is increased, the reaction is expected to be slow compared to other mechanisms. The carbon-catalyzed oxidation of SO_2 by oxygen

to sulfate species in wet aerosols is considerably faster,[3] making the present system a minor contributor to SO_2 oxidation. In terms of the production of nitrous oxide, so much of it is produced from nitrate fertilizers that the contribution from this reaction is not expected to be detectable. The real importance of these reactions to the ambient pollution levels probably lies in the removal of the oxides of nitrogen. Whereas most reactions involving NO_x merely convert it from one form to the other, this set of reactions takes it to a more reduced form and a less reactive tropospheric pollutant.

This reaction system will also be important to the maximization of efficiency and understanding of flue-gas scrubber systems which have already been briefly described. In most instances the simultaneous (SO_2 + NO_2) scrubbers have metal ions and/or other reagents added to increase the solubility of the NO_x. Because these are commercial ventures, much of the information is proprietary and not available; however, the observation of hydroxylamine and amine sulfonates is an indication that these processes are involved in some instances.[22] Much more study into the effects of the added reagents is needed; however, the "clean" system which has been investigated here should serve as a useful model for a baseline comparison for the actual scrubber conditions. Scrubbers naturally work at higher temperatures and concentrations than are available to aerosol droplets, and a few more reactions such as the sulfonation of HADS will need to be included. The kinetics reported herein, however, should be sufficient to describe the actual behavior of the scrubber without the addition of the metal ions.

Although this investigation has involved only three out of the more than twelve reactions involved in the Raschig scheme, the complete kinetic investigation has provided considerable insight into how the processes could be involved in the air pollution field. It is hoped that continued work to obtain a detailed understanding of all the involved reactions will allow rational control strategies to be applied to pollutants. Further, it is expected that as the atmospheric reactions of NO_x become more completely investigated, the present study will contribute to the understanding of the enhancement in sulfate production in the presence of NO_x, especially under nonphotochemical conditions.

APPENDIX A-1

Sample Mass Balance Data

reaction mixture:

0.951 gms $Na_2S_2O_5$

0.552 gms Na_2SO_3

0.0350 gms $NaNO_2$ all in 50.0 mls of solution

measured on Spectronic 20

5.0 ml aliquot — 1.6 ml of reagents added*

time (min)	354 nm Abs	545 nm Abs	$[NO_2^- M]$	[HADS]	$[\Sigma N]$ M
0	—	0.000	0.0100	0.0000	0.0100
1	0.193	0.036	0.0085	0.0018	0.0103
4	0.172	0.040	0.0076	0.0021	0.0097
7	0.160	0.053	0.0070	0.0029	0.0099
10.5	0.141	0.060	0.0062	0.0033	0.0095
13.5	0.130	0.063	0.0056	0.0035	0.0091
17.5	0.117	0.070	0.0050	0.0038	0.0088

* 0.4 ml H_2O_2
1.0 ml $AgNO_3$
0.2 ml NaOH

APPENDIX A-2

Sample Rate Determination Data

$[HSO_3^-]_0$ = 0.028 M Temp = 25°C

$[NO_2^-]_0$ = 0.00036 M μ = 0.2 M

pH = 3.90 buffer = phthalate (0.11 M)*

measured on CARY 219 - 10 cm cells

time (sec)	Absorbance (354 nm)
0	0.73
12	0.060
24	0.051
36	0.041
48	0.034
60	0.029
72	0.024
84	0.020
96	0.016
108	0.014

$$\text{Rate} = \frac{-d \ln A}{dt} = \frac{-d \ln [NO_2^-]}{dt} = 0.016 \text{ sec}^{-1}$$

* buffer refers to sum of acid and conjugate base.

APPENDIX A-3

Sample Stoichiometric Determination Data

pH = 5.4 buffer = phthalate system

$[S_2O_3^{2-}] = 2.00 \times 10^{-3}$

$[I_3^-] = 2.30 \times 10^{-3}$

measured on Beckman DU - 1 cm cells

Abs (354 nm)	mls sol'n	mls I_3^-	mls $S_2O_3^{2-}$	$[S^{4+}]$ M	$[NO_2^-]$ M
0.124	1.00	10.0	3.20	0.0198	0.0055
0.110	1.00	10.0	4.30	0.0186	0.0049
0.101	1.00	10.0	5.80	0.0173	0.0043
0.089	1.00	10.0	6.70	0.0165	0.0039
0.075	1.00	10.0	7.60	0.0154	0.0034
0.063	1.00	10.0	9.50	0.0[illegible]6	0.0026
0.048	1.00	10.0	11.00	0.0120	0.0019

both measurements taken within 30 seconds

time interval between consecutive measurements : 10-20 min

$$\Delta S/\Delta N = \frac{0.0078}{0.0036} = 2.2$$

APPENDIX B: Error Analysis and Calculational Methods

There are many possible sources of error throughout this investigation which must be considered when uncertainties for the values of the rate constants are reported. The errors are of two types: experimental uncertainties caused by instrumental or experimental techniques, and statistical uncertainties caused by propagation of the errors through the calculations. The majority of the errors in this investigation are due to experimental uncertainties because the calculations are all rather straightforward. One exception to this is the measurement of the pH, which is largely statistical as a result of the calculations; this will be dealt with later.

Values for the tolerances of the experimentally measured parameters are given in Table B-1. Of these values, those for the concentrations of reactants are most important as these quantities enter directly into the calculations of the rate constants. Hydroxylamine disulfonate has the largest tolerance because of the many additions of reagents required before a measurement may be made. The 2 percent tolerance is the combined results of all the random errors associated with the measurement. The concentration of HADS is only used in the mass balance studies and does not affect the rate constants. All the other quantities have tolerances no greater than 1 percent, with the errors being random in nature. Sulfur (IV) species are listed twice as the concentrations were measured in two different ways depending on the type of experiment performed.

Table B-1 Experimental Tolerances

	Estimated Standard Deviations
Absorbance	1.0 percent
volume of solution	0.2 percent
pH	0.02 units
time	2 seconds
[S(IV)] by weight	0.5 percent
[S(IV)] by iodometry	1 percent
[HAMS] by weight	0.2 percent
[HADS]	2 percent
$[S_2O_3^{2-}]$	0.1 percent
$[I_3^-]$	0.5 percent
Temperature	0.2°C

Systematic errors could be present, particularly in the time or pH measurements. Several clocks were used for various experiments, and the results show no deviation based on which clock was used. The same was true when different spectrophotometers and balances were used. Therefore, no systematic errors are expected to be involved from these sources. Several different pH electrodes were used, each one calibrated against the same standard buffer solutions. At low ionic strengths, all the electrodes give the same value of pH for a reaction mixture, within experimental error (based on repeatability). At higher ionic strengths, there is a deviation among results from the various electrodes, with certain ones consistently giving higher readings. This was believed to be due to either imperfections in the glass bulbs or junction potentials which do not cancel at the high ionic strengths. All the data used in the calculations were obtained from readings taken with a single electrode. This eliminated the scatter in the values but not necessarily the systematic error. The deviation was never greater than ± 0.1 pH units.

The hydrogen ion concentration has another uncertainty associated with it, even assuming that there were no systematic errors. The concentration of H^+ is related to the pH by the equation (ignoring activity coefficients)

$$[H^+] = 10^{-pH}$$

The random error of ± 0.02 units in pH propagates (using standard procedures)[44] to approximately 5 percent error in the concentration, depending on the value of the pH. Because all the rate constants require the use of the hydrogen ion in their calculations, and for the HAMS constants the square of the H^+ concentration is used, this becomes a significant source of error. In experiments where the buffer could not be made in batches, this error accounts for the scatter which is seen when the data are plotted.

The actual standard deviations or estimated uncertainties which are reported along with the values of the rate constants or other parameters were arrived at in one of two ways. The first method used a linear least-squares fit to the data, with either the slope or the intercept containing the desired information. The fit was obtained by solving the simultaneous equations:

$$\Sigma y_i = \Sigma a + \Sigma b x_i$$
$$\Sigma x_i y_i = \Sigma a x_i + \Sigma b x_i^2$$

with the solutions given as

$$a = \frac{1}{\Delta} (\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma x_i y_i)$$

$$b = \frac{1}{\Delta} (N \Sigma x_i y_i - \Sigma x_i \Sigma y_i)$$

$$\Delta = N \Sigma x_i^2 - (\Sigma x_i)^2$$

In addition, the standard deviations in a and b (the intercept and slope) can be estimated as:

$$\sigma_a^2 = \sigma^2/\Delta(\Sigma x_i^2)$$

$$\sigma_b^2 = N\sigma^2/\Delta$$

where

$$\sigma^2 = \frac{1}{N-2}\sum(y_i-a-bx_i)^2$$

A listing of Fortran programs which will perform these calculations has been reported by Bevington.[45] The programs were adapted to Basic and used on a Commodore P.E.T. computer. A similar adaptation was used on an Apple II computer to determine the initial slopes of the nitrite ion decay curves.

When the rate constant must be reported as a preexponential factor times some factor raised to an exponent, both of which have uncertainties (as in an Arrhenius function), a different approach was used. A least-squares fit was used to arrive at the value of the exponent as before. The data were then normalized to one value of the variable which removes the exponential term (i.e., temperature). The resulting preexponential factors all come from experiments which are identical except for the one parameter which has been eliminated (by normalization), so they can be averaged and a standard deviation determined. This standard deviation contains the errors which are normally associated with all the factors, including the one in the exponential term. These have been reported as estimated standard

deviations. All the temperature and ionic strength data have been treated in this manner.

The least-squares procedure described above was used to determine one of the rate constants for the HAMS-nitrite ion reaction. In this case the equation was inverted prior to fitting and the resulting equation was of the form:

$$1/\text{rate} = 1/(k[\text{HAMS}]) + k'/k \quad ,$$

which allows both k and k' to be determined. While k' is equal to k_4 as used in the Results section, k must be related to k_3 after removing the concentration dependences of the ions. This was accomplished by reducing the data to a set of standard conditions and averaging the resulting constant, as described above.

The concentrations of nitrite ion and HADS species were calculated by use of a Beer's law calibration curve. The standard curve was obtained from a least-squares fit to the absorbance readings from solutions of known concentrations, and the actual samples then determined by comparison to this curve. HADS concentrations were measured as nitrosodisulfonate ion and then corrected for dilution from addition of reagents needed to bring about oxidation. Different calibration curves were obtained for each size cell and each spectrophotometer used. The molar absorptivity was found to be the same for each calibration, within the standard deviation calculated from the fit.

A different type of calculation was used to determine the sulfur (IV) concentration from the iodometric titrations. This was done by use of the equation

$$[S(IV)] = \frac{V_I M_I - V_T M_T/2}{V_S} \quad ,$$

where V and M refer to the volumes and molarities, and the subscripts I, T, and S refer to triiodide ion, thiosulfate ion, and sample, respectively. The errors here are mostly random errors due to volumetric techniques. The estimated uncertainty listed in Table B-1 was obtained from replicate samples of the same solution, using the same and different batches of analytic reagents. This included testing these samples with triiodide solutions which had been diluted and restandardized. Errors in the determination of sulfur (IV) concentrations determined from the weights include uncertainty due to the purity of the salt. The purity was tested by using iodometric titrations in carefully prepared solutions. The error was found to be of the same order of magnitude as the random error due to weighing.

The one remaining and probably the largest source of error in the experiments comes from impurities in or contamination of the buffer solutions and is difficult to treat adequately. Trace metals in the solutions are suspected, coming either from the buffer salts which were used or from insufficiently cleaned glassware. This situation occasionally resulted in degradation of the bisulfite solutions or other spurious results. Whenever there were any signs of these

problems (usually irreproducibility), the data were discarded. In any one set of experiments which were all performed in solutions made from one batch of buffer solution, there was very little scatter. When several sets of experiments from different batches of the same buffer were compared, the differences between sets indicated there was a problem. The source of this difficulty could not be determined; however, it was due to something more than the slight differences in pH caused by different batches of buffer.

The statistical treatment by the least-squares method used data from only one set of experiments, as there is always a slight change in pH when using a different batch of buffer. The standard deviations which were obtained by reducing the data to a set of standard conditions give larger error bars, but include the undetermined effect caused by the irregularities in the different buffer solutions. These estimated deviations are felt to be more accurate, and were the ones reported.

APPENDIX C.

Abstract from:

Kinetics of the Formation of Hydroxylamine Disulfonate by Reaction of Nitrite with Sulfites*

S. B. Oblath, S. S. Markowitz, T. Novakov, and S. G. Chang

The reaction between nitrite and bisulfite to form hydroxylamine disulfonate has been investigated in weakly acidic solutions (pH 4.5 to 7) and found to consist of three concurrent processes. The reaction rate law can be expressed as

$$\frac{d[HADS]}{dt} = k_0[H^+]^2[NO_2^-] + k_I[H^+][NO_2^-][HSO_3^-] + k_{II}[NO_2^-][HSO_3^-]^2 .$$

The values for the specific rate constants k_0, k_I, and k_{II} (at 295 K and $\mu = 1.20$) are 8×10^5, 3.8×10^3, 9.6×10^{-3} liter^2/mole^2-sec., respectively. The dependence of the rate constants k_I and k_{II} on temperature and ionic strength were investigated. A reaction mechanism has been proposed which is consistent with these results. The rate constants for the three rate determining steps in this mechanism have been calculated.

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