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REACTION OF NITRITE ION WITH HYDROXYLAMINE-N-SULFONATE IN AQUEOUS SOLUTION†

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Abstract

The reaction between nitrite ion and hydroxylamine-N-sulfonate (HAMS) has been investigated in aqueous solutions; nitrous oxide and sulfate ions are the major products. The reaction kinetics exhibit a first-order dependence on nitrite ion, a second-order dependence on hydrogen ion, and between a zero- and first-order dependence on HAMS, depending on the concentration. An activation energy of 30 kJ/mole was determined for the reaction in the temperature range of 10 to 40°C. The ionic strength dependence was studied in the range of 0.2 to 1.5 M. Oxalate, tartrate, and phthalate buffer systems were found to enhance the rate of reaction to varying degrees. An empirical rate law and the determined rate constants are reported. The results are explained in terms of a mechanism which consists of the nitrosation of HAMS, followed by a decomposition into products.

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Introduction

The reaction of hydroxylamine-N-sulfonate (also referred to as hydroxylamine monosulfonate or HAMS) with nitrite ion has been known since Raschig studied the reduction of nitrous acid with sulfur dioxide.[1] Reaction between HAMS and nitrite ion was considered a side reaction in the synthesis of hydroxylamine, as it yields nitrous oxide. This particular reaction, however, has become useful for the laboratory preparation of hyponitrite salts in alkaline solutions.[2,3] In acidic solutions the reaction has been much less thoroughly studied, although nitrous oxide (rather than hyponitrites) is usually formed.[4]

Our primary interest in this reaction grew out of an investigation of the importance of nitrite and sulfite ion interactions in atmospheric aerosols and power-plant flue-gas scrubbers. Under sufficiently acidic conditions, nitrous oxide has been detected as a product.[6] The N_2O can result either from a direct interaction of nitrite and sulfite ions or from an indirect process involving HAMS. To determine the source of the gaseous product a complete kinetic investigation of the HAMS-NO_2^- reaction was undertaken. Previously there was only one kinetic investigation of the reaction of NO_2^- with HAMS,[4] although a number of other reactions involving HAMS and reactants in the Raschig synthesis for hydroxylamine have been investigated.[7-9]

The kinetics of the nitrite ion-HAMS reaction to produce nitrous oxide were investigated by Seel and Pauschmann at a HAMS concentration greater than 0.1 M.[4] The reaction rate was independent of the HAMS concentration in this range and followed a rate law of the form:

$$\text{Rate} = (k[H^+] + k'[HOAC])[H^+][NO_2^-] \ ,$$

when acetate buffers were used to control the pH. The questions of the nature of the buffer enhancement and the possible dependence of the reaction on HAMS at lower concentrations were not investigated.

The emphasis of this study is to evaluate the kinetics of the reaction under low concentration conditions. By determining a rate law which may be extrapolated to concentrations of ionic species in water droplets in a polluted atmosphere, chemists interested in atmospheric aerosol formation[5] and flue gas scrubber technologies[10,11] will be able to evaluate the importance of the HAMS-NO_2^- reaction. The role of the buffer species in the reaction was also investigated as this has particular significance in the design of an optimum wet scrubber process. Finally, a mechanism will be proposed to explain the results of this and the previous investigation.

Experimental Section

Reagents. Potassium hydroxylamine-N-sulfonate was prepared by acid hydrolysis of potassium hydroxylamine-N,N-disulfonate as described by Seel and Degener.[5] The method was modified to use the tri-basic salt of the disulfonate species rather than the di-basic salt. The disulfonate species was prepared by the method of Rollefson and Oldershaw[12] and recyrstallized in a KOH solution. Although the yields are lower with the tri-basic salt, the purity is quite high (elemental analysis for $HONHSO_3K$: calculated K:S:N:H = 25.9 : 21.2 : 9.3 : 1.3; found = 27.5 : 21.7 : 8.9 : 1.3). The main impurity is potassium sulfate. The salt showed no sign of decomposition when stored for several months at 0°C in a vacuum dessicator over P_2O_5.

All other reagents used in this study were of analytic reagent grade and were used as supplied. Solutions were prepared in de-ionized water. All solutions were prepared immediately before use with the exception of the buffer solutions, which were made up in large batches to minimize differences in solution composition. The pH values of the buffer solutions were measured with a combination glass electrode at the time of preparation and were unchanged upon addition of the reactant salts.

Kinetic measurements. The reaction kinetics were determined by monitoring the concentration of nitrite ion spectrophotometrically at 354 nm with a Cary 219 spectrophotometer, using either 1- or 10-cm cells. Interference by weakly absorbing buffers was eliminated by using a sample of the buffer as the reference solution. The solutions as well as the cell housing were temperature-controlled to within 0.2°C. Solutions were volumetrically prepared by dissolution of a known weight of pure K-HAMS in an appropriate buffer. The solution was then transferred to the spectrophotometer cell and approximately 1-5 mg of solid sodium nitrite was added. All reactions were carried out under pseudo-first-order reaction conditions, with a large excess of HAMS.

Initial reaction conditions were typically 0.01 to 0.40 M in HAMS and 1 to 10 mM in nitrite ion. These experiments were performed in phthalate buffers between pH of 3.8 and 5 at an ionic strength of 1.2 and temperature of 293 K. This ionic strength allowed comparison to the results of the previous study.[4] Order with respect to each reactant was determined by varying the concentration of that species while keeping all other parameters constant. Reaction conditions for a representative sample of experiments are given in Table I.

The temperature dependence was determined by performing the experiments at various temperatures between 283 and 313 K. These reactions were run in phthalate buffers because these buffers have a very small change in pH ($\sim$ 0.02 units) over this temperature range. Ionic strength effects were investigated by addition of sulfate, nitrate, or phosphate salts. Because the change in ionic strength (μ) does affect the pH of the buffer, the pH of each solution was measured immediately prior to its use.

The dependence of the reaction rate on the buffer species was also investigated. Experiments were performed using phthalate, tartrate, and oxalate buffers, as well as by varying the concentrations of each buffer. All these

experiments were performed at 293 K and $\mu = 1.2$, using sulfate to adjust the ionic strength.

Results

Seel and Pauschmann determined a first-order dependence of the reaction on nitrite ion by monitoring the rate of formation of N_2O.[4] They also determined the net reaction to be

$$NO_2^- + 2H^+ + HONHSO_3^- \rightarrow N_2O + HSO_4^- + H_3O^+ \quad . \tag{1}$$

In the present investigation the same reaction was observed, but the reaction rates were measured by the loss of nitrite ion over time. When the decay curve is plotted as the logarithm of the nitrite ion concentration vs. time, a straight line is obtained. The slope of this line is invariant to the initial nitrite concentration. These results indicate that the reaction is first order with respect to nitrite ion, confirming the previous observations. Whereas the solubility of nitrous oxide placed a lower limit on the nitrite ion concentration that the previous investigators could study, the use of spectrophotometry allows the nitrite ion concentration to be several orders of magnitude lower (as low as 5×10^{-5} M).

The dependence of the reaction rate on the HAMS concentration is shown in Fig. 1, with typical experimental results shown in Table I. The change in reaction order from first- to nearly zero-order in HAMS as the concentration is increased indicates that there is a change in rate-determining step for the reaction. The mathematical expression for a mechanism of this type, if a steady-state assumption is applied, would be of the form

$$Q = \frac{-1}{[NO_2^-]} \frac{d[NO_2^-]}{dt} = k[HAMS]/(1 + k'[HAMS]) \quad . \tag{2}$$

By a least squares fit of 1/Q vs. 1/[HAMS], both constants were determined;

the resulting fit is shown as a solid line in the figure. Unfortunately this procedure is least sensitive at the highest concentrations and causes the poorer fit in this region. A better fit at high concentration may be obtained by a weighted least-squares fit resulting in only small changes in the value of k'. These changes are small compared to the estimated error in the values. More accurate values of the rate constants are given later after a discussion of the temperature and ionic strength results. Because there are two different regimes for the reaction, HAMS-dependent and -independent, the other parameters must be determined in each of these regimes.

The dependence of the reaction rate on the hydrogen ion concentration is shown in Fig. 2. These particular experiments were performed under conditions where the reaction was first order in HAMS. The slope of the line is 1.9, which indicates a second-order dependence in H^+. Similar results are obtained under HAMS-independent conditions, in agreement with the previous study.[9] The slight discrepancy in the order (1.9 vs. 2.0) is explained by the dependence on the rate of the buffer concentration. In changing the pH at fixed ionic strength, it was necessary to change the buffer concentration in order to maintain the maximum buffering capacity. This will be explained in greater detail later.

One consequence of the fact that both regimes are second order in hydrogen ion is that the entire role of H^+ is probably involved before the step in which HAMS reacts. This indicates that an intermediate is formed from two hydrogen ions, one nitrite ion, and possibly one or more water or buffer molecules. This strongly suggests that NO^+ is being formed to react with HAMS, an idea which was proposed earlier.[4]

The results of the temperature dependence study of the first-order HAMS regime are shown in Fig. 3, plotted as an Arrhenius function. The activation

energy was determined to be 30 kJ/mole. The zero-order regime results are similar, with a value of 33 kJ/mole, which is surprising since a different reaction step is rate limiting. By applying activated complex theory,[13] one can obtain values for the entropy of activation ($\Delta S^{\ddagger}$) as well as the enthalpy of activation ($\Delta H^{\ddagger}$). The enthalpies are in agreement with the Arrhenius activation energies, and the values of $\Delta S^{\ddagger}$ are -2 and -12 entropy units for the HAMS-dependent and -independent regimes.

The results of the ionic strength dependence study are not straightforward. The range which could be considered ($0.2 < \mu < 1.5$ M) is far too concentrated for explanation by Debye-Hückel theory and can only be considered empirical. The results from a set of experiments using sodium sulfate to adjust ionic strength show the variation in μ to have no effect on the rate. Because there is no effect, no problems were encountered when sulfate was used to maintain constant ionic strength in experiments where the concentrations of other reactants were varied. When phosphate was used (as NaH_2PO_4), the rate increased with increasing phosphate concentration. Phosphate, however, has been observed to form a partially covalent complex with NO^+, whereas sulfate does not[14]; and this complexation is likely to be the cause of the enhancement in rate. Nitrate salts cause a decrease in the rate when the concentration was increased, which is not yet entirely understood. Perchlorate salts were not used because of an observed reaction with nitrite ions (in the absence of HAMS) to form gaseous products. This reaction would interfere with the reaction of interest (by removing nitrite ions) and cause anomalously high rates.

The reaction rate was found to depend moderately on the concentration (sum of acid and conjugate base) of each of the buffer systems used; the results are shown in Fig. 4 (after correction of the rates for varying pH). An increase in the buffer concentration results in an increase in the rate. If

the rates are extrapolated to zero buffer concentration, the rate in all three buffers would be nearly the same. It is not clear why phthalate buffers give a higher rate when extrapolated to zero buffer concentration, although the values nearly agree within experimental error. A similar enhancement has been seen before for the phthalate species[13] and was explained with the carboxylic acid functionality's acting to complex the NO^+. If formation of a carboxylate complex is the reason, then all three buffers would be expected to act similarly. The enhancement, and differences between the buffers, are discussed more fully in the next section after a mechanism is proposed.

To summarize the results, the experimentally determined rate law can be expressed in the absence of buffer to

$$\text{Rate} = \frac{-d[NO_2^-]}{dt} = k[H^+]^2[NO_2^-]\ \frac{\text{HAMS}}{1 + k'[\text{HAMS}]}\ . \tag{3}$$

The best values for the rate constants at 20°C are

$$k = (1.5 \pm 0.3) \times 10^7 \text{ liter}^3 \text{ mole}^{-3} \text{ sec}^{-1}$$

and $k' = 5.5 \pm 0.6$ liter/mole .

The effect of the buffer activity may then be included mathematically by the equation:

$$\text{Total rate} = (\text{Unbuffered rate})(1 + k_{buffer}[\text{Buffer}])\ . \tag{4}$$

Values of the various k_{buffer} are shown in Table II.

Discussion Section

The results of this kinetic study may be explained by the following proposed reaction scheme:

$$H^+ + HONO \rightleftarrows NO^+ + H_2O \tag{5}$$

$$NO^+ + HONHSO_3^- \rightarrow N_2O + HSO_4^- + H^+\ , \tag{6}$$

which is in general agreement with the mechanism proposed by Seel and Pauschmann.[4] Reaction 6 is not likely to be a simple elementary reaction, but it is written as such because the present kinetic study cannot elucidate what the actual steps are. We agree with previous workers that nitrosation of $HAMS^-$ is the most probable first step in reaction 6. Any number of intermediates can be formed; and as long as no other reactants are involved, there will be no change in the calculated rate law. Although we have written NO^+ as the intermediate, $H_2NO_2^+$ or some other hydrated species could equally well be involved. We have chosen NO^+, based on agreement between previous measurements of the rate of NO^+ formation (by polarographic[15] and ion exchange[16] studies) and the current measured rates when reaction 5 is rate limiting (HAMS-independent region).

Despite the fact that reaction 5 looks as if it would only be first order in H^+, one must take into account the equilibrium between nitrite ion and nitrous acid. At pH greater than 4.0, where this study was carried out, greater than 85% of the N(III) is in the form of nitrite ion, which is the species whose decay is being measured. Thus a second-order hydrogen ion dependence is what one would expect. Also, because the HAMS is not involved in reaction 5, the mechanism predicts a change from first to zero order in HAMS as the concentration of HAMS is increased.

The temperature dependence for this reaction is somewhat unusual in that nearly the same activation energy is observed under two different rate-determining steps. If one assumes that the initial process in reaction 6 is the nitrosation of HAMS followed by rapid subsequent reactions leading to N_2O, then a steady state assumption results in a rate of loss of nitrite ion as given by the following equation:

$$\text{Rate} = \frac{k_6 k_5 [H^+]^2 [NO_2^-] [HAMS]}{K_A (k_{-5} + k_6 [HAMS])} , \qquad (7)$$

where K_A is the acid dissociation constant for nitrous acid. At low concentrations of HAMS, the observed rate constant should be given by $(k_6 k_5)/(k_{-5} K_A)$. At the HAMS-independent regime, the observed value is just k_5/K_A. The present results imply that the reactions represented by k_{-5} and k_6 have nearly equal activation barriers. The entropies of activation for the two limiting regimes are different. This is consistent with the idea of a different transition state in each of the rate determining steps, which would cause different solvation effects and therefore different values of $\Delta S^{\ddagger}$. Unfortunately, this information cannot give any new mechanistic insight in a complex reaction such as this.

The ionic strength results are not unexpected. For sulfate there is no effect on the rate, which is probably due to little change in the activity coefficients for the reactant ions over the range of ionic strengths that could be investigated. Addition of phosphate salts increased the rate of reaction. Dihydrogen phosphate is the predominant form at pH between 4 and 5, and this has been shown to form a partially covalent complex with nitrosyl ion.[14] In this respect it acts similarly to the buffer species and is best considered in that light. Sulfate ion does not form a covalent complex with NO^+; its complex is strictly ionic (lead chamber crystals) and would be completely dissociated under the present conditions.[14]

Inhibition of the reaction rate by nitrate ion (by as much as 50%) can be explained by removal of a reactant by the nitrate ion. Nitrite ion cannot be reacting with nitrate ion, or the rate (measured by loss of nitrite ion) would increase. Hydrogen ion and HAMS are the only other reactants. It is unlikely that H^+ is involved, considering nitric acid is completely dissociated even at

concentrations as high as 1 mole/liter. A reaction between HAMS and nitrate ion is not an unreasonable explanation. Hydroxylamine is known to react with both nitrous and nitric acids,[17] and HAMS reacts with nitrite ion; so it is not unexpected that nitrate ion should react with HAMS. There is no reason to expect that the reaction with nitrate ion should give N_2O as a product. There was no obvious evidence for other products; but because nitrate was only used for this one set of experiments, no extensive search for other products was undertaken.

The effect of the buffer concentration has been described briefly. All the experiments with oxalate and tartrate were done in the HAMS-dependent regime. For phthalate the same results were found in both regimes, again indicating that the source of the effect is prior to the reaction involving HAMS and therefore would involve NO^+. The same buffer effects were noted with acetate in the HAMS-independent regime.[9] The idea of a covalent or partially covalent complex between NO^+ and phosphate species (which has already been discussed) can also be used to explain the effects of the other buffers. Acetate and phthalate buffers are also believed to form complexes.[14] The carboxylic acid functionality is believed to stabilize the nitrosyl ion, and thus tartrate and oxalate buffers would also be expected to exhibit this behavior. Other species such as Cl^-, Br^-, and I^- act in a similar manner,[9,14] although the halides do not have a carboxylate functionality. If all these species act by forming a weakly bound, partially covalent complex with NO^+, and if this complex can react with HAMS in a manner similar to NO^+, then there would be an enhancement of the rate due to the increasing concentration of reactive intermediates. Since NO^+ would be hydrated in solution, replacement of a water molecule by a weakly bound anion conceivably would not drastically affect its properties. Although it would be quite interesting to identify which of the two forms of each buffer is acting as the complexing agent, the present

study has been unable to determine the active form. The discrepancy in the slope of the log-log plot in Fig. 2 to determine the hydrogen ion dependence (1.9 vs. 2.0) correlates better with the total buffer concentration than with either the anion or dianion form. This makes sense if the $R\text{-}COO^-$ functionality is involved because both phthalate and biphthalate ions contain this functional group. The same is true for oxalate and tartrate. In theory, one could make the solution more acidic so that only one of the acid-conjugate base pair has a $R\text{-}COO^-$ group; but for the present reaction, the rates become so rapid under those conditions that the present techniques are unable to measure them.

One additional problem in determining the actual enhancing species is that the R-COOH functionality could also be acting as a proton donor, and there could be a general acid catalysis contribution as well. Because we have been unable to find a suitable buffer system which can donate protons and not form a partially covalent complex with NO^+, we have been unable to investigate this idea further. Sulfate, the one species which did not affect the rate, does not exist in the form of bisulfate ion in sufficient concentration to act as a suitable proton donor; again we are limited by the range of pH in which the rate can be measured. The additional possibility, that general acid catalysis and $R\text{-}COO^-$ stabilization occur simultaneously, cannot be ruled out, in which case what has been observed is simply some weighted average of the two effects.

A comparison of the curves in Fig. 4 reveals different slopes for each of the buffer systems. The varying inductive effects of the R groups in the $R\text{-}COO^-$ functionality could cause different degrees of complexation with NO^+. This in turn would affect the amount of NO^+ complex formed and thus explain the varying effectiveness of the different buffers at enhancing the reaction rate. The intercepts, which represent the rate in the absence of the buffer species,

should be the same for each system. The evidence in Fig. 4 supports the idea that an intermediate complex is formed which enhances the rate in the presence of buffer ions. It is believed that the phthalate buffer has shown a larger intercept because of discrepancies in the measurement of the pH of the solution, although the cause of this discrepancy could not be determined.

Conclusions

The reaction between nitrite ion and hydroxylamine-N-sulfonate to form nitrous oxide has been shown to occur under acidic conditions. The rate of reaction and the probable mechanism are straightforward as long as only these species are present, with the rate expressed by Eq. 3. Only on addition of supposedly nonreactive salts or buffers do complications ensue. An enhancement of the rate results from the addition of the buffer; the degree of the enhancement depends on which buffer system has been chosen.

When the reaction is placed in context with the other reactions in the Raschig scheme and is looked at from the point of view of atmospheric chemists and flue-gas scrubber technicians, these complications become important. For aerosol chemists, nitrate ion could possibly cause a slowing of the rate, which must be accounted for in any reaction model which uses these schemes. In considering nitrite-bisulfite reactions in flue-gas scrubbers, chelating agents added to enhance NO_x solubilities must be carefully evaluated to determine whether or not they will enhance the rates of reaction. More study will be needed before these questions can be answered. Because of the unknown nature of reaction 6 (presumably a nitrosation step), one must be careful in extrapolating this work to very low concentrations, as some interfering reaction may become rate limiting and change the observed kinetics.

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Table I. Initial conditions and experimental rates (all solutions at 293 K).

[HAMS] M	$[SO_4^{2-}]$ M	$[\Sigma P]^*$ M	pH	μ M	$-d \ln[NO_2^-]/dt$ sec^{-1}
0.0078	0.29	0.14	4.35	1.2	0.00045
0.015	0.29	0.14	4.35	1.2	0.00077
0.021	0.29	0.14	4.35	1.2	0.0011
0.050	0.29	0.14	4.35	1.2	0.0025
0.090	0.29	0.14	4.35	1.2	0.0034
0.191	0.29	0.14	4.35	1.2	0.0048
0.033	0.34	0.12	4.15	1.2	0.0048
0.033	0.33	0.13	4.25	1.2	0.0026
0.033	0.31	0.14	4.34	1.2	0.0020
0.033	0.31	0.15	4.57	1.2	0.00075
0.020	0.32	0.17	4.40	1.2	0.0012
0.020	0.35	0.11	4.40	1.2	0.0010
0.020	0.37	0.071	4.40	1.2	0.00087
0.020	0.31	0.20	4.40	1.2	0.0013
0.020	0.00	0.14	4.55	0.22	0.00057
0.020	0.13	0.14	4.48	0.62	0.00081
0.020	0.20	0.14	4.45	0.82	0.00097
0.020	0.27	0.14	4.42	1.0	0.0011
0.020	0.33	0.14	4.40	1.2	0.0012

Table II. Rate constants for buffered solutions.

Buffer	k_{buffer} (liter/mole)
Phthalate	7.5 ± 0.7
Tartrate	3.1 ± 0.2
Oxalate	8.0 ± 0.8

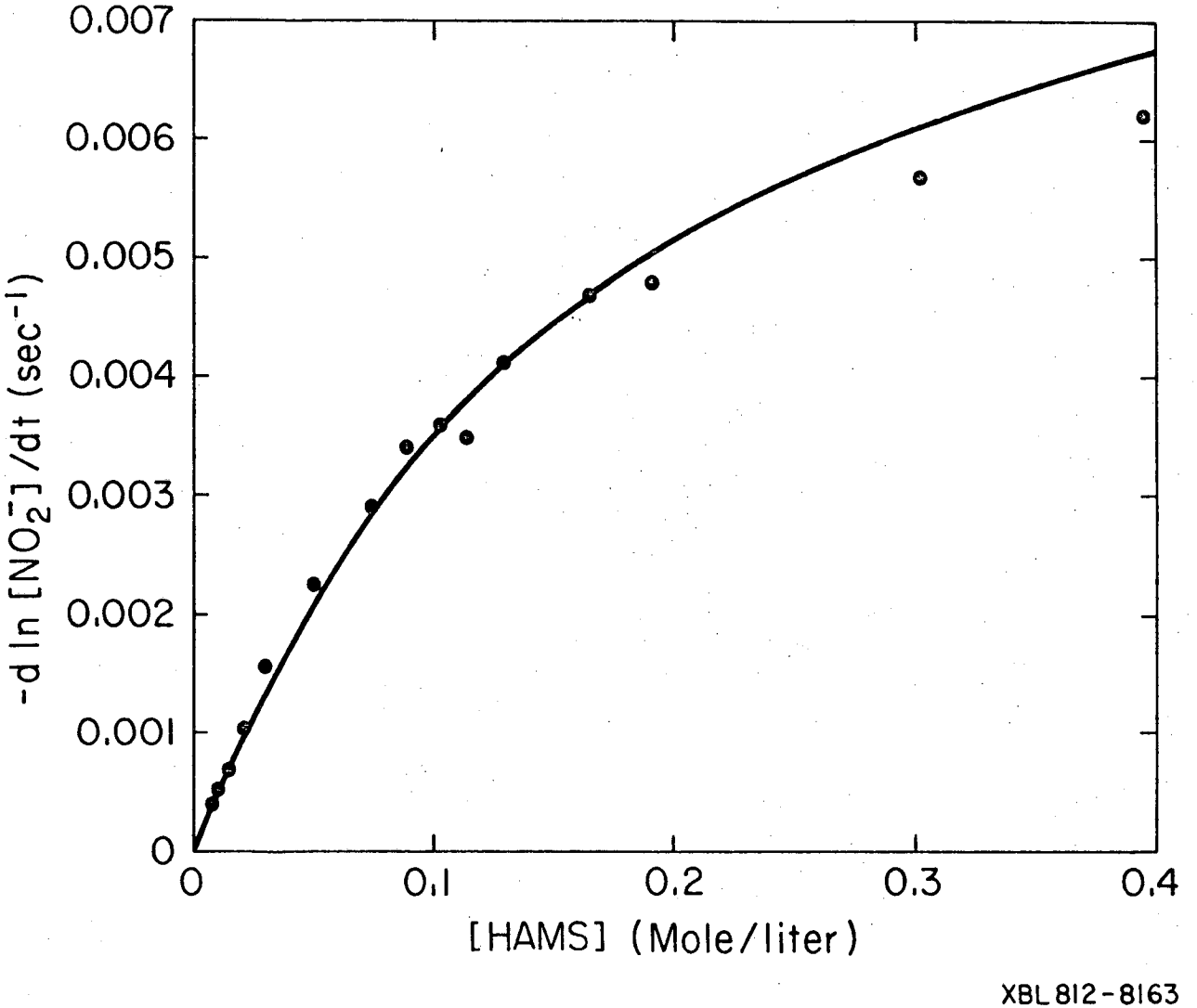
Figure Captions

Figure 1. Reaction rate as a function of HAMS concentration for pH = 4.35 (using 0.141 M phthalate buffer) at 20°C and μ = 1.20. Solid line is fit to the proposed rate expression (see text for explanation).

Figure 2. pH dependence of reaction under HAMS-dependent conditions (using a 0.141 M phthalate buffer system). Slope indicates a second-order dependence on hydrogen ion.

Figure 3. Arrhenius plot of rate constant for HAMS-dependent reaction conditions ([HAMS] = 0.026 M, [ΣP] = 0.141 M, pH = 4.40).

Figure 4. Effect of buffer concentration on reaction rate. Phthalate = ■ , tartrate = ▲ , and oxalate = ● buffers. All data are obtained at 20°C and normalized to pH = 4.4, and [HAMS] = 0.020 M. Buffer concentration refers to sum of acid and conjugate base. Intercepts — obtained by extrapolation — agree within the estimated experimental error.



XBL 812-8163

Figure 1

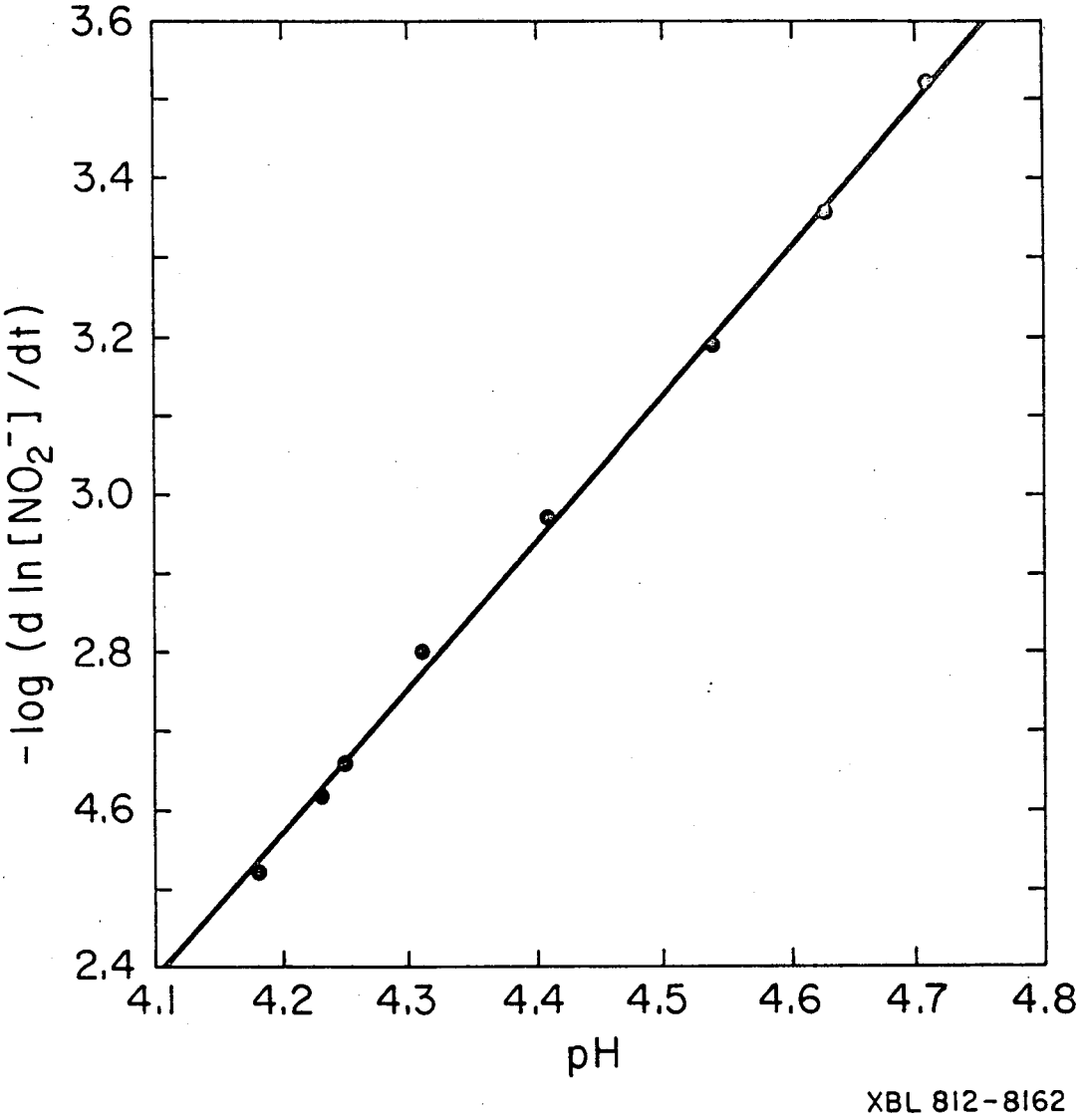

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Figure 2

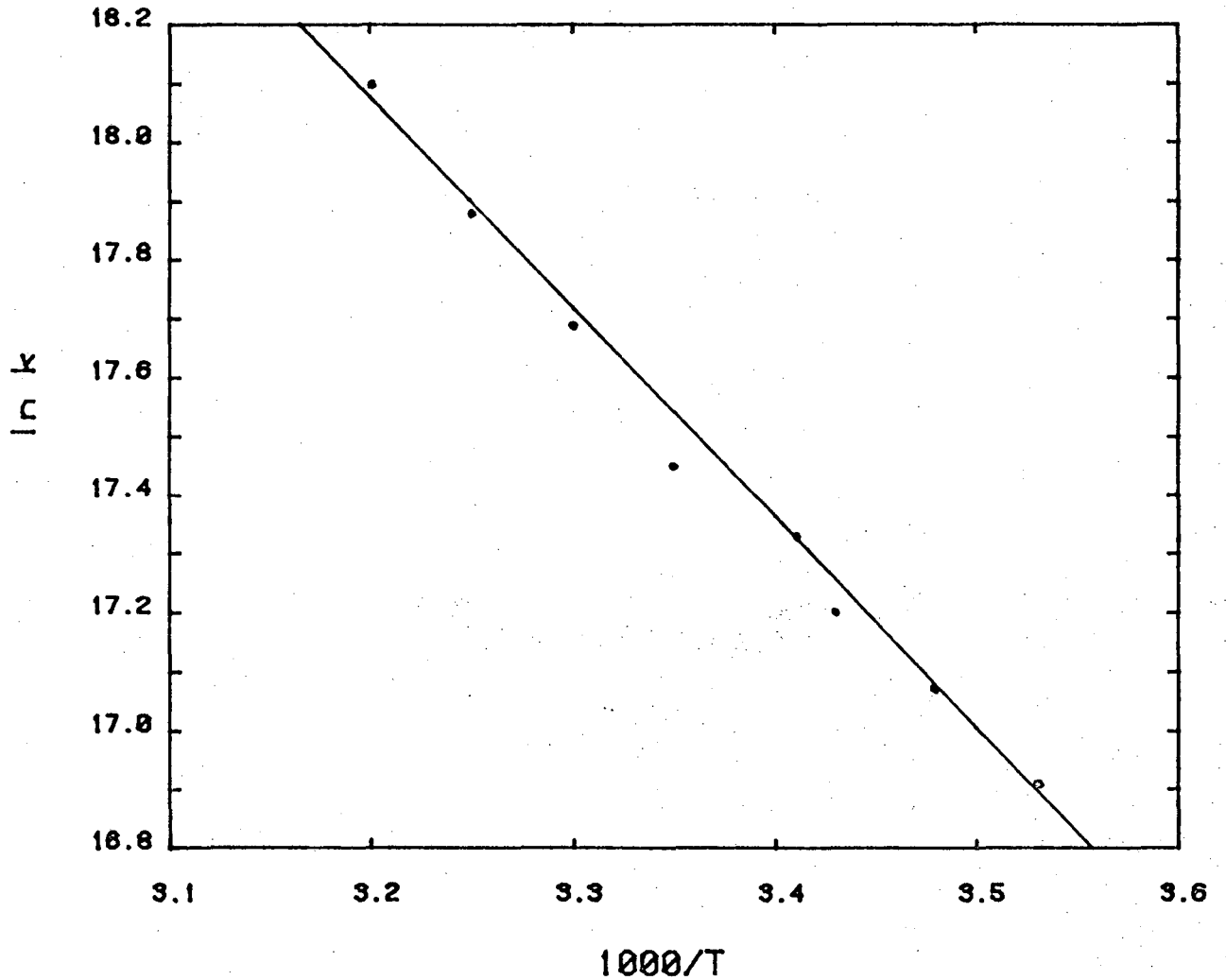

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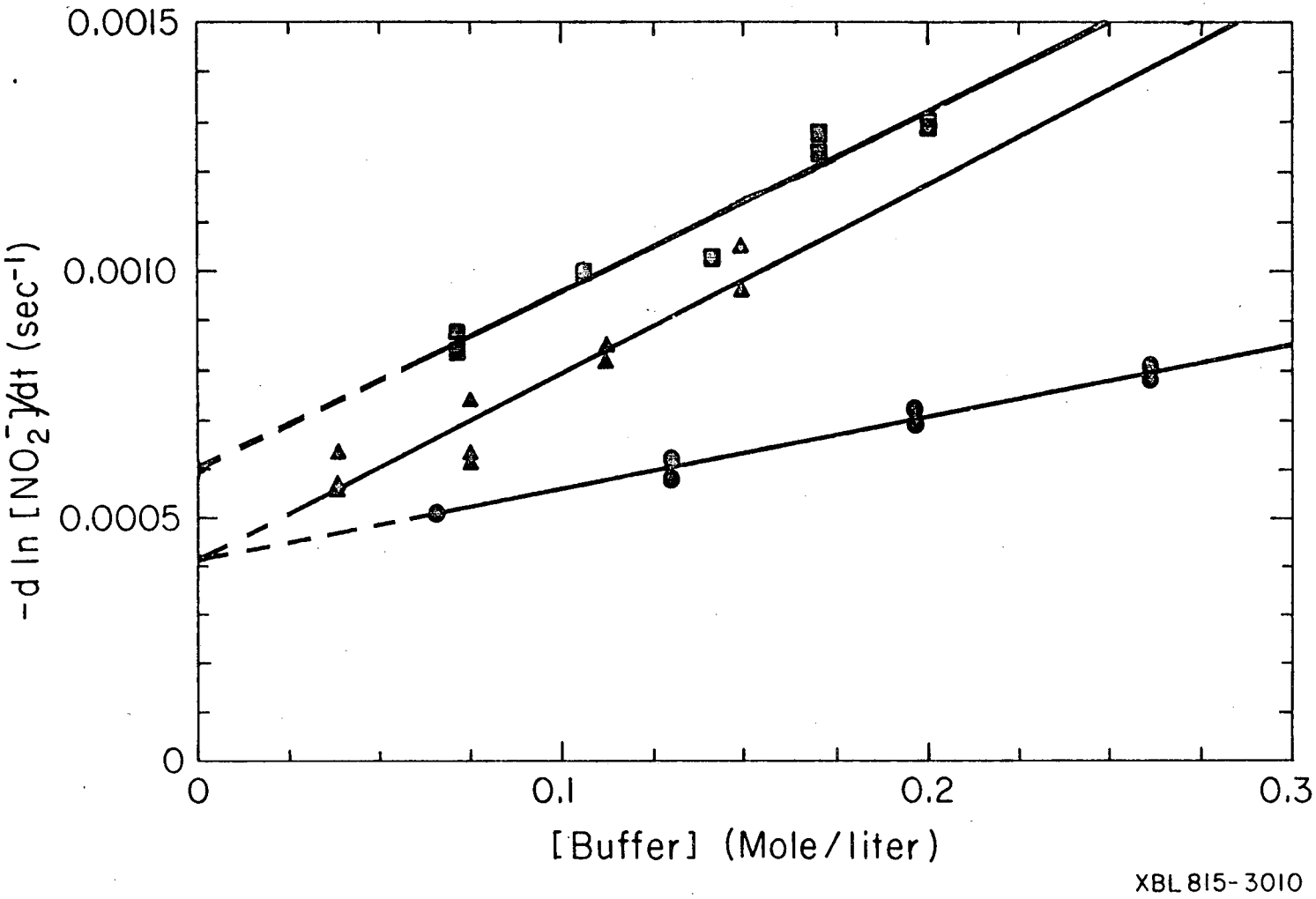
Figure 3


0.0015
0.0010
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0
0
0.1
0.2
0.3
-d ln [NO2-]/dt (sec-1)
[Buffer] (Mole/liter)
XBL 815-3010

Figure 4

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