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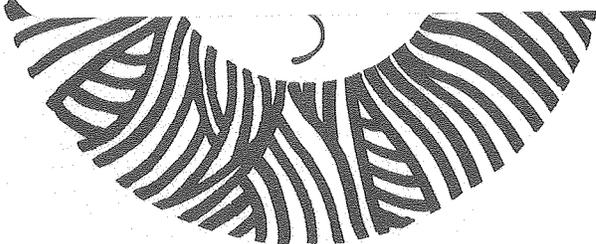
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KINETICS OF THE FORMATION OF HYDROXYLAMINE DISULFONATE
BY REACTION OF NITRITE WITH SULFITES

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ABSTRACT

The reaction between nitrite and bisulfite to form hydroxylamine disulfonate has been investigated and found to consist of three concurrent processes. The reaction rate law can be expressed as

$$\frac{d[\text{HADS}]}{dt} = k_0 [\text{H}^+]^2 [\text{NO}_2^-] + k_I [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] \\ + k_{II} [\text{NO}_2^-] [\text{HSO}_3^-]^2$$

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 , and 9.6×10^{-3} liter²/mole²-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.

INTRODUCTION

The formation of hydroxylamine disulfonate (HADS) has been studied by chemists for many decades.^{1,2} Most of the interest has been on the reaction of nitrite with sulfites to form HADS as a first step toward the production of hydroxylamine.³⁻⁶ More recently there has been interest in the reactions of nitrites and sulfites in terms of atmospheric aerosol formation and chemical treatment of flue gas.⁷

The kinetics of HADS formation was first studied between pH of 5 and 7 by Seel and Degener over two decades ago.⁴ They found two concurrent processes for HADS production as summarized by the following rate law:

$$\frac{d[\text{HADS}]}{dt} = k_a [\text{H}^+]^2 [\text{NO}_2^-] + k_b [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] .$$

Yamamoto and Kaneda identified the same two processes.⁵ However, they found that the first term was really a combination of both general acid and acetic acid specific catalyzed reactions. Seel and Knorre⁶ later investigated this reaction in less acidic solutions and interpreted their results as a single process having the following rate law:

$$\frac{d[\text{HADS}]}{dt} = \frac{k_c [\text{NO}_2^-] [\text{HSO}_3^-]^2}{1 + k'_c [\text{SO}_3^{2-}]}$$

Because of the discrepancies between these results, and the need for accurate rate laws, we have undertaken a systematic study of this reaction under a wide variety of conditions.

EXPERIMENTAL

Kinetic Studies

Reaction mixtures were prepared by dissolving reagent grade NaNO_2 , $\text{Na}_2\text{S}_2\text{O}_5$, and Na_2SO_3 in appropriate buffers. The kinetic data were obtained by monitoring

the nitrite concentration spectrophotometrically using a Beckman DU or Bausch and Lomb Spectronic 20 spectrophotometer. Measurements were taken at 356 nm in a 1-cm cell. Calibration was achieved using solutions containing known weights of dry NaNO_2 . Absorbance due to nitrous acid does not interfere under the conditions of this study. Typical initial nitrite concentrations were 2-30 millimolar. Concentrations of sulfur (IV) species were determined by using known weights of dry salts, the purities of which were checked by standard iodometric techniques.⁸ To maintain sulfur (IV) species at a nearly constant value throughout the run, the initial concentration was at least 10 times that of nitrite.

The pH of each solution was measured at the start of each run with a Beckman Model 4500 pH meter, equipped with a combination glass electrode. The electrode was calibrated prior to each measurement with Mallinckrodt BuffAR buffer solutions. The pH was maintained throughout the reaction with either a sulfite-bisulfite buffer (pH 6-7) or a phthalate-biphthalate buffer (pH 4.5-6). In several runs an acetate-acetic acid buffer was used to show that the phthalate buffer does not interfere with the reaction. Reagent grade chemicals were used as supplied. The phthalate-biphthalate buffer was sufficient to keep the ionic strength of the solution constant ($\mu = 0.2$) throughout the run. When sulfite-bisulfite buffers are used, NaNO_3 and Na_2SO_4 were added as nonreactive salts to keep the ionic strength constant ($\mu = 1.2$). In each set of conditions, the initial concentrations of mono and divalent ions were identical. For ionic strength studies in both buffer systems, varying amounts of nitrate and sulfate salts were added to change the initial ionic strength while maintaining a constant buffer capacity.

The temperature dependence was investigated by varying the solution temperature between 15 and 30°C. An insulated water bath was used to control the

temperature to at least $\pm 0.2^\circ\text{C}$. All other runs were carried out at $22 \pm 1^\circ\text{C}$.

Stoichiometric and Mass Balance Studies

The stoichiometry of the reaction was determined by measuring the concentrations of both the nitrite and sulfur (IV) species during the same run. Only a small excess of sulfur (IV) was used for these runs. Nitrite was measured spectrophotometrically as before. Sulfur (IV) was measured using standard iodometric techniques after quenching the reaction in an excess of iodine.⁸ The analysis was carried out in an acetate-acetic acid buffer ($\text{pH} = 5.6$) to minimize the interference that could arise from the reaction of nitrite with I_2 or I^- .⁴ Calibration against known standards showed there was no NO_2^- interference under the conditions of the investigation.

A mass balance between nitrite and hydroxylamine disulfonate was demonstrated by monitoring the concentrations of both species during identical runs. Sulfur (IV) was present in large excess to ensure pseudo-first order reaction conditions. Nitrite was measured as before. HADS was determined by oxidation to nitrosodisulfonate ion (NDS) followed by colorimetric analysis at 545 nm.⁴ Calibration was obtained using potassium nitrosodisulfonate, prepared by the method of Moser and Howie.⁹

Analysis for HADS consisted of quenching an aliquot of the reaction solution with H_2O_2 to remove the excess sulfur (IV) species, which could react with NDS. HADS is unaffected by the peroxide, except in strongly basic solutions. Oxidation was then brought about by addition of AgNO_3 followed by NaOH to form Ag_2O , which acts as an oxidizing agent and also removes the excess peroxide. The Ag_2O and Ag metal were removed by filtration and the absorbance of the solution measured. The technique was shown to be quantitative by analyzing samples of potassium hydroxylamine disulfonate prepared by the method of Rollefson and Oldershaw,³ and recrystallized in KOH .¹⁰ Care must be taken not

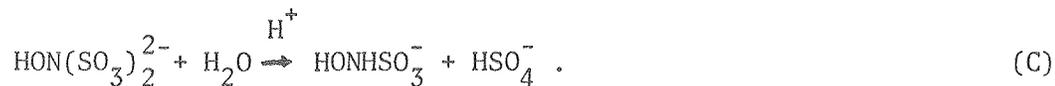
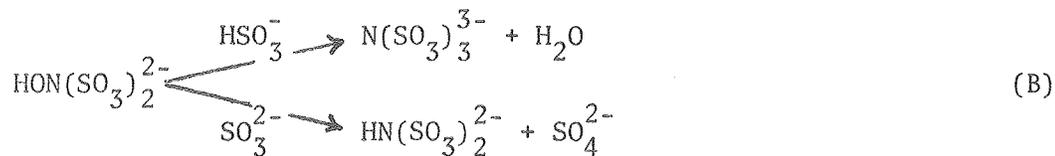
to add a large excess of H_2O_2 or make the solution too basic ($\text{pH} > 11$) or quantitative conversion does not occur.

RESULTS AND DISCUSSION

Hydroxylamine disulfonate is formed according to the following net reaction:



Kinetic study of its formation is complicated by both the further sulfonation of HADS to produce amine trisulfonate and amine disulfonate and the hydrolysis of HADS in acidic solutions:



The kinetic data for the formation of HADS were obtained by initial rate studies where the contribution from these secondary processes (sulfonation and hydrolysis) is small.

Determination of Reaction Order

The experiments were carried out at several pH's in light of the different orders with respect to bisulfite which had been noted in the literature. The first set of experiments determined that the reaction was first order with respect to nitrite over the entire pH range between 4.5 and 7. An excess of bisulfite was used in these runs. Figure 1 shows a semi-log plot of NO_2^- concentration vs. time for several initial concentrations. Parallel lines indicating a first order dependence on nitrite were also observed at pH of

4.5 and 5.5. The departure from linearity towards the end of the reaction is due to a breakdown of the pseudo-first order reaction conditions. For this reason all the rates were determined by the initial slope of the reaction curve.

The dependence of the reaction on bisulfite — or S (IV) — was determined by varying the excess bisulfite concentration for a fixed nitrite concentration. Because the nitrite is first order as determined above, one can write the rate law as

$$\text{Rate} = k[\text{NO}_2^-][\text{HSO}_3^-]^n = -\frac{d[\text{NO}_2^-]}{dt},$$

where one can define

$$Q = \frac{-d \ln[\text{NO}_2^-]}{dt} = k[\text{HSO}_3^-]^n.$$

A log-log plot of Q vs. $[\text{HSO}_3^-]$ should give a straight line with the slope equal to the order of the reaction with respect to bisulfite. At pH of 4.5 and 5.5, the slopes have values of 1.0 and 1.1, respectively, as shown in Figure 2. The values of Q for these two pH's are not equal, but are separated by almost exactly one order of magnitude. This difference can only be accounted for by the fact that k as defined in the above equation cannot be a constant, but contains a first order dependence on the hydrogen ion concentration.

Alternately one can plot Q vs. HSO_3^- on linear scales which will yield a straight line for a first order bisulfite dependence. This is shown in Fig. 3 at several pH's. The slope is related to the value of the rate constant, while the intercept (obtained by extrapolation) indicates that some reaction independent of bisulfite concentration is also taking place. This bisulfite independent contribution to the overall rate is generally small. The variation of the intercept with pH shows that this zero order bisulfite term is second order in H^+ , in agreement with Seel and Degener.⁴ Since there is no acetate present

(A phthalate buffer system was used.), this is also in agreement with Yamamoto and Kaneda.⁵ For simplicity these processes will be referred to only by their order with respect to bisulfite (i.e., zero or first order process). This convention will be used throughout the paper.

The value of Q calculated from the rate law of Seel and Knorre (second order in bisulfite) at pH of 5.5 is small (< 5%) compared to the measured first order value. On the other hand, the Q value calculated from the rate law of Seel and Degener (first order process) at pH of 7 accounts for up to 50% of the values obtained in the present study. Therefore the first order contribution must be subtracted from the measured rate prior to analyzing the data for a second order term. This corrected value of Q is plotted against $[\text{HSO}_3^-]$ on a log-log plot, and the slope (or order of reaction) is 1.9 (Fig. 4). The rate constant is then calculated by fitting the corrected rates to a second order bisulfite rate law (Table I). All these runs were carried out at constant initial ionic strength ($\mu = 1.2$) because, as will be shown later, the reaction rate is dependent on ionic strength. The results also indicate that this process (second order in bisulfite) is independent of the sulfite or hydrogen ion concentration used in this experiment. This result is contrary to that proposed by Seel and Knorre.⁴ They found that the rate decreased when the concentration of sulfite was increased at a fixed bisulfite concentration. However, these authors did not correct their data for the first order process. Our study explains this discrepancy as a decrease in the contribution from the first order process, rather than a complex dependence on sulfite.

We demonstrated that dissolved oxygen is not involved in this reaction by following the reactions both before and after purging the solution with nitrogen for 5 minutes. Runs were performed at pH of 6.3, where both the first and second order processes contribute substantially. No difference could be

detected between the rates obtained under these two opposite conditions.

Stoichiometry and Mass Balance

Experiments were carried out to verify that the same net reaction (A) is taking place under each set of experimental conditions. For all three pH regions investigated, the ratio of sulfur (IV) which reacts with nitrite (measured after at least one reaction half-life) was 2.2 to 2.4. These ratios increased when measured after longer reaction times. Both the further sulfonation reactions and the oxidation of sulfur (IV) species in solution could explain why this ratio is greater than the expected value of 2.0.

A mass balance between nitrite and HADS confirms the stoichiometry predicted from Eq. A. Figure 5 shows the results at pH of 6.3, where both the first and second order processes contribute to the rate. After about 10-15 minutes, there is an apparent loss of nitrogen species. This could be due to a loss of HADS by sulfonation or hydrolysis (Eqs. B and C), since the nitrite concentration continued to drop. Because hydrolysis and sulfonation reactions are both first order in HADS, the above effect becomes more pronounced as the HADS concentration builds up.^{11,12} Because this problem is only significant after long reaction times, it does not affect the results obtained from initial rates.

Evidence that the zero order process is producing HADS is less direct since contribution of this process is small under the conditions of this study. Previous studies observed this process by monitoring sulfur species.^{4,5} The present study detected the same process by measuring the nitrite concentrations. These two results indicate that both species are involved, in a two-to-one ratio, and therefore it is unlikely that another product besides HADS would be formed.

Temperature Dependence

The activation energies for the first and second order processes were also investigated. The log of the rate constant k_1 (first order process) as a function

of $1/T$ is shown in Fig. 6. The slope of this Arrhenius-type plot yields a value for the activation energy of 51 kjoule/mole. This agrees with the literature values.^{4,5} The activation energy for the second order process is determined after correcting the data for the contribution of the first order process. This calculation yields an activation energy of -3 kjoule/mole. Considering the experimental error, this value could be regarded as essentially zero. Seel and Knorre, considering the entire rate as a second order process, obtained an activation barrier of 35 kjoule/mole, which is not in agreement with this work. The conclusion from our study is that at least two paths are present for HADS formation, with substantially different transition states.

Ionic Strength Dependence

Information on the charges of reacting species in both the first and second order processes has been obtained by investigation of the dependence of the reaction rate on ionic strength. It is difficult to carry out the reaction at concentrations low enough for proper interpretation by Debye-Hückel limiting law. The experiments were therefore performed at intermediate concentrations. These results nevertheless yield useful information. The data obtained for the first order process are shown in Table II. The scatter is due to variations in temperature from run to run. The reaction is independent of ionic strength at these concentrations. The second order process, again after correction for the first order contribution, varies strongly with ionic strength (Fig. 7). This supports the evidence for at least two concurrent processes.

Neither process shows any deviation from typical results of the Debye-Hückel law. Interpretation using this theory indicates that the first order process is a reaction of an ion with a neutral molecule, whereas the second order process represents a reaction of two similarly charged ions. The slope of 2 (Fig. 7) indicates that one of these ions is doubly charged. It is also

possible that the ionic strength effect for the first order process has been suppressed at the ionic strength used, but we consider this unlikely.

Finally, to summarize all the experimental results, the rate of formation of HADS from nitrite and bisulfite can be expressed by the following equation:

$$\frac{d[\text{HADS}]}{dt} = k_0 [\text{H}^+]^2 [\text{NO}_2^-] + k_I [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] + k_{II} [\text{NO}_2^-] [\text{HSO}_3^-]^2 \quad (\text{D})$$

where $k_0 \approx 8 \times 10^5$ liters²/mole-sec,

$$k_I = 3.7 \times 10^{12} e^{-6100/T} \text{ liter}^2/\text{mole}^2\text{-sec}$$

$$k_{II} = 9.0 \times 10^{-4} e^{2.1(\mu)^{1/2}} \text{ liter}^2/\text{mole}^2\text{-sec}$$

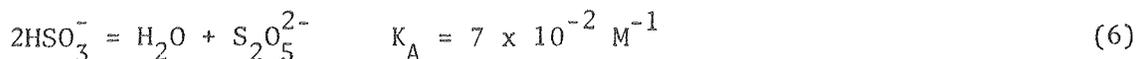
(T is temperature in Kelvin, and μ is ionic strength in moles/liter.).

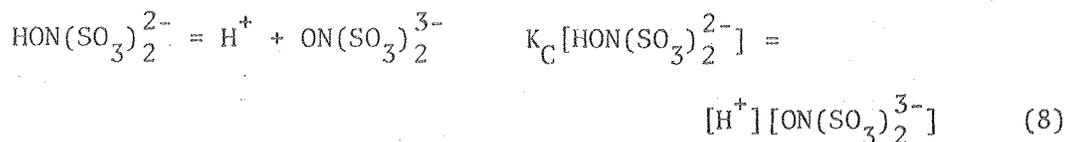
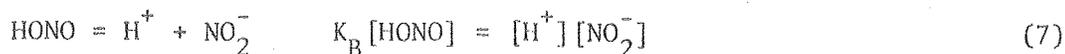
Derivation of the Rate Expression

Based on the experimental results, we propose the following reaction mechanism:



The following three equilibria are considered to be rapid:





For the purposes of this study, both the protonated and deprotonated forms of HADS are equivalent — $\text{HON}(\text{SO}_3)_2^{2-}$ and $\text{ON}(\text{SO}_3)_2^{3-}$. The rate of HADS production is equal to the sum of the rates of production of its two forms:

$$\text{Rate} = \frac{d[\text{HADS}]}{dt} = k_5 [\text{NO}_2^-] [\text{S}_2\text{O}_5^{2-}] + k_4 [\text{NOSO}_3^-] [\text{HSO}_3^-] - \frac{k_{-5} K_C [\text{HON}(\text{SO}_3)_2^{2-}]}{[\text{H}^+]} - k_{-4} [\text{HON}(\text{SO}_3)_2^{2-}] \quad (9)$$

Using the steady-state approximation and solving for both intermediates (NOSO_3^- and NO^+), one finds

$$[\text{NOSO}_3^-]_{\text{SS}} = \frac{k_3 [\text{HONO}] [\text{HSO}_3^-] + \frac{k_1 k_2 [\text{HSO}_3^-] [\text{H}^+] [\text{HONO}]}{k_{-1} + k_2 [\text{HSO}_3^-]} + k_{-4} [\text{HON}(\text{SO}_3)_2^{2-}]}{k_{-3} + k_{-2} [\text{H}^+] - \frac{k_{-2} [\text{H}^+] k_2 [\text{HSO}_3^-]}{k_{-1} + k_2 [\text{HSO}_3^-]} + k_4 [\text{HSO}_3^-]} \quad (10)$$

A complete rate law is obtained by substitution of Eq. 10 into Eq. 9. Because the concentration of HADS is near zero in an initial rate study, the last two terms in Eq. 9 and the last term in the numerator of Eq. 10 can be neglected. Making two additional assumptions,

$$k_2 [\text{HSO}_3^-] \gg k_{-1} ,$$

$$k_4 [\text{HSO}_3^-] \gg k_{-3} ,$$

and using the equilibrium expressions, the rate law becomes

$$\frac{d[\text{HADS}]}{dt} = \frac{k_1}{K_B} [\text{H}^+]^2 [\text{NO}_2^-] + \frac{k_3}{K_B} [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] + k_5 K_A [\text{NO}_2^-] [\text{HSO}_3^-]^2. \quad (11)$$

This rate expression agrees with the experimentally determined rate law. Eqs. 1, 3, and 5 correspond to the rate determining steps of the zero, first, and second order processes, respectively. The ionic strength data, as interpreted by Debye-Hückel limiting law, is consistent with the mechanism that we propose. The rate determining steps for the first and second order processes are ion-neutral molecule and anion-anion reactions, as the data suggested. Finally, the rate determining step for the second order process also supports the finding that the process is dependent on bisulfite, but independent of sulfite concentration or pH.

Comparing the experimentally determined rate law (Eq. A) with the mathematically derived expression (Eq. 11), we have derived the rate constants for the elementary rate determining steps. The values for k_1 , k_3 , and k_5 at 298K and $\mu = 1.2$ are 300, 1.6, and 0.14 liter²/mole²-sec, respectively.

In conclusion, the results of this study have clarified the disagreement of previous papers on the order with respect to bisulfite. The complete reaction rate law will be of value in modeling aerosol formation as well as in developing flue gas treatment processes.

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Table I. Effect of pH or sulfite concentration on the rate of reaction.

Run #	[NO ₂ ⁻] (M)	[HSO ₃ ⁻] (M)	[SO ₃ ²⁻] (M)	pH	Q (10 ⁻³ ·sec ⁻¹)	Calculated first order contribution (10 ⁻³ ·sec ⁻¹)	Second order component (10 ⁻³ ·sec ⁻¹)
1	0.010	0.10	0.10	6.53	0.226	0.123	0.103
2	0.010	0.10	0.20	6.85	0.170	0.058	0.112
3	0.015	0.10	0.15	6.73	0.190	0.078	0.112
4	0.015	0.10	0.15	6.71	0.187	0.082	0.105
5	0.015	0.20	0.10	6.30	0.822	0.418	0.404
6	0.015	0.20	0.20	6.58	0.607	0.220	0.387
7	0.015	0.20	0.15	6.46	0.658	0.288	0.370
8	0.015	0.25	0.10	6.25	1.13	0.585	0.548
9	0.015	0.25	0.20	6.52	0.948	0.315	0.633
10	0.015	0.25	0.15	6.38	1.00	0.435	0.567

Table II. Rate constant for first order process at various ionic strengths.

Run #	$[\text{NO}_2^-]$ (M)	$[\text{HSO}_3^-]$ (M)	pH	Q ($10^{-3} \cdot \text{sec}^{-1}$)	k_1 $(\frac{\text{liter}^2}{\text{mole}^2 \cdot \text{sec}})$	$\mu^{1/2}$ $(\frac{\text{mole}}{\text{liter}})^{1/2}$
A	0.003	0.021	4.63	2.20	4.3×10^3	0.48
B	0.003	0.021	4.62	2.18	4.3×10^3	0.42
C	0.003	0.021	4.45	2.53	3.5×10^3	0.75
D	0.003	0.020	4.36	3.18	3.5×10^3	0.94
E	0.003	0.021	4.31	4.08	4.0×10^3	1.14
F	0.003	0.023	4.50	3.50	4.8×10^3	0.47
G	0.003	0.022	4.50	3.17	4.7×10^3	1.10
H	0.003	0.042	4.50	5.17	3.8×10^3	1.10

FIGURE CAPTIONS

Figure 1. Loss of NO_2^- as a function of time. Straight lines indicate first order dependence. Slope of line is based on initial points.

Figure 2. Dependence of rate of bisulfate concentration at pH of 4.5 and 5.5.

Figure 3. Extrapolation of first order rates to zero bisulfite concentration.

The non-zero intercepts indicate a bisulfite independent process. Variation of intercept with pH shows a second order H^+ dependence.

Figure 4. Dependence of the rate on bisulfite concentration at pH of 7.

Rates have been corrected for the first order process. Ionic strength was 1.2 M.

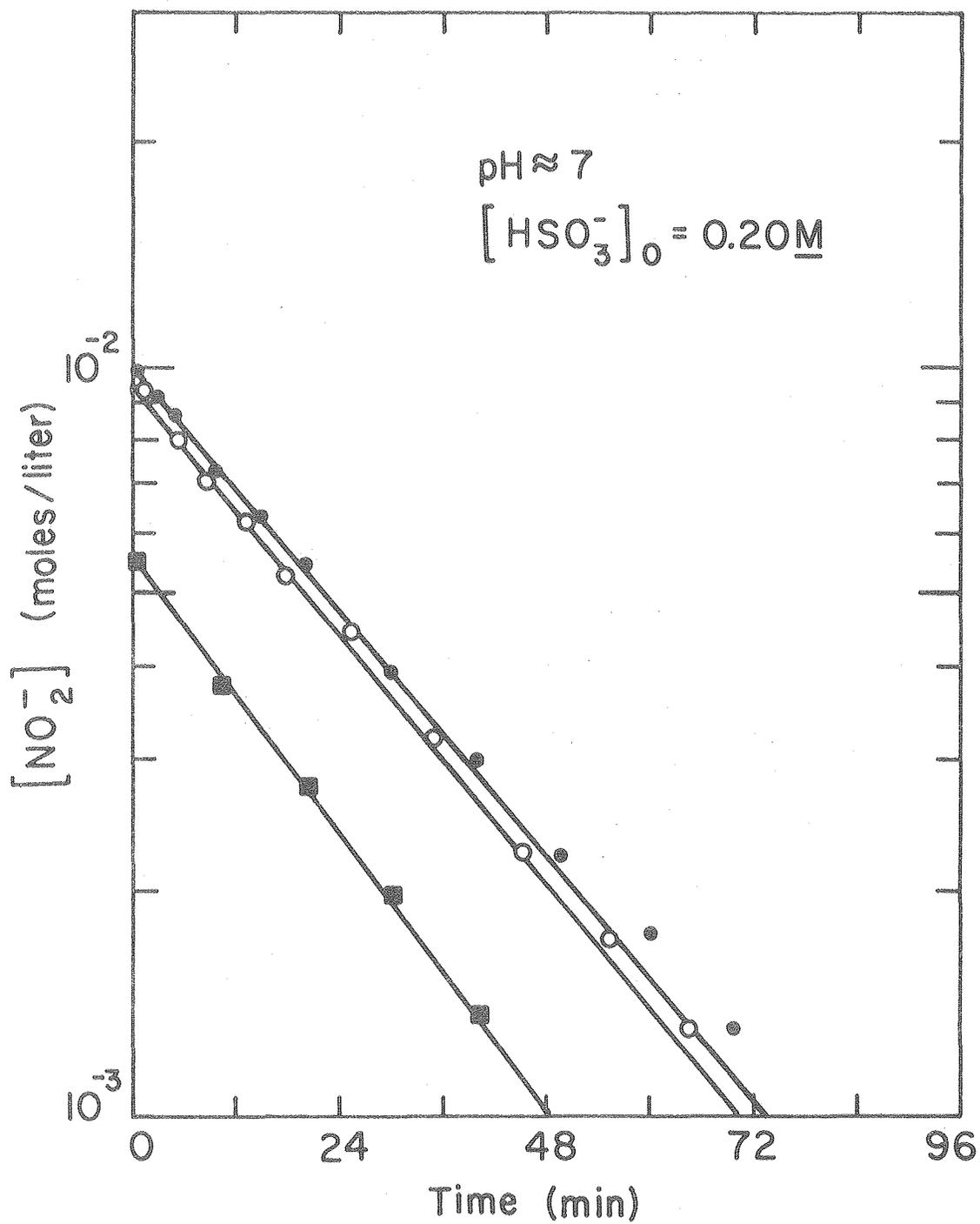
Figure 5. Mass balance of nitrogen species. ΣN is the sum of NO_2^- and HADS.

Loss of nitrogen species is due to hydrolysis and sulfonation of HADS.

Figure 6. Temperature dependence of rate constant for the first order process.

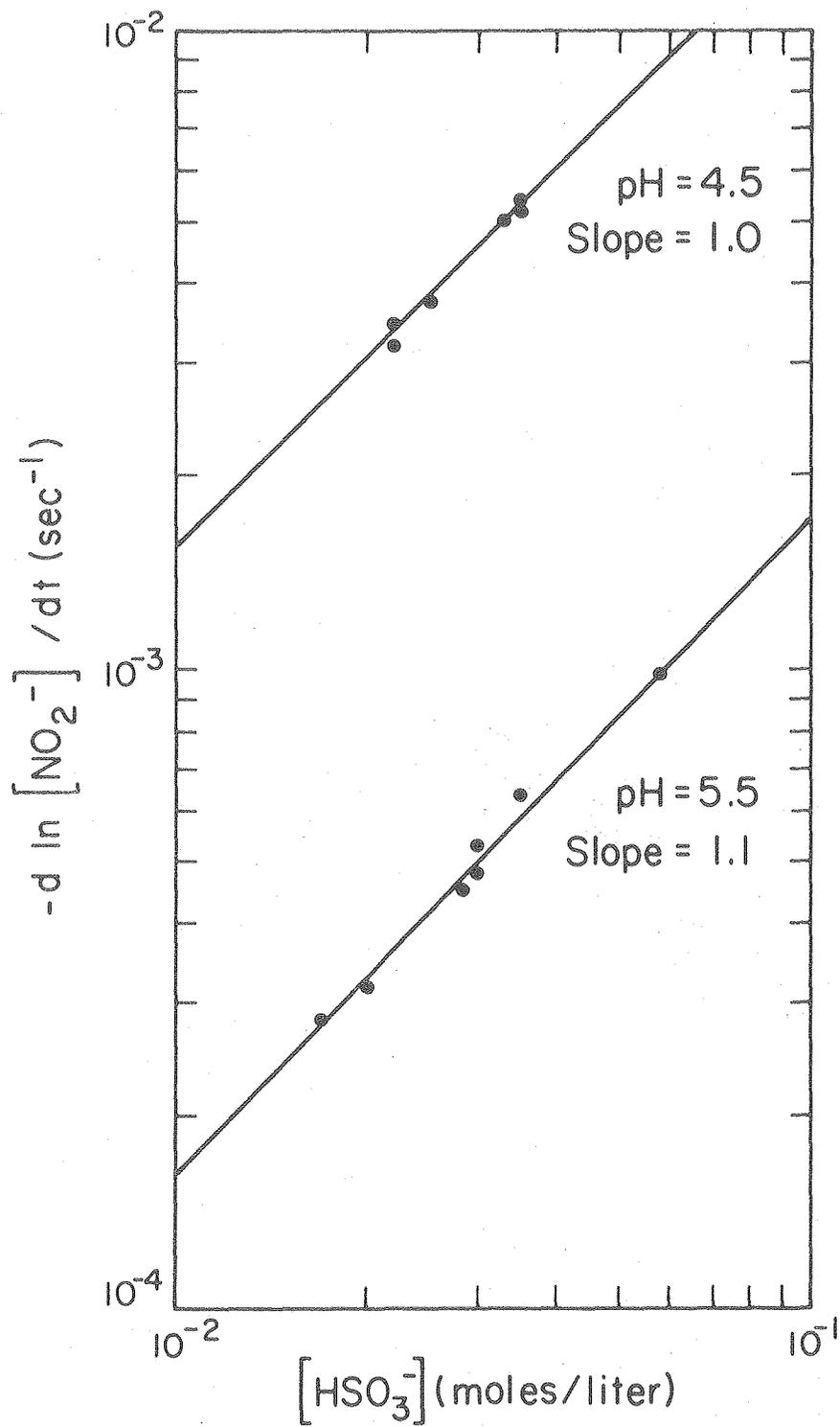
Arrhenius activation energy is 50 kJ/mole.

Figure 7. Dependence of rate constant for the second order process on ionic strength.



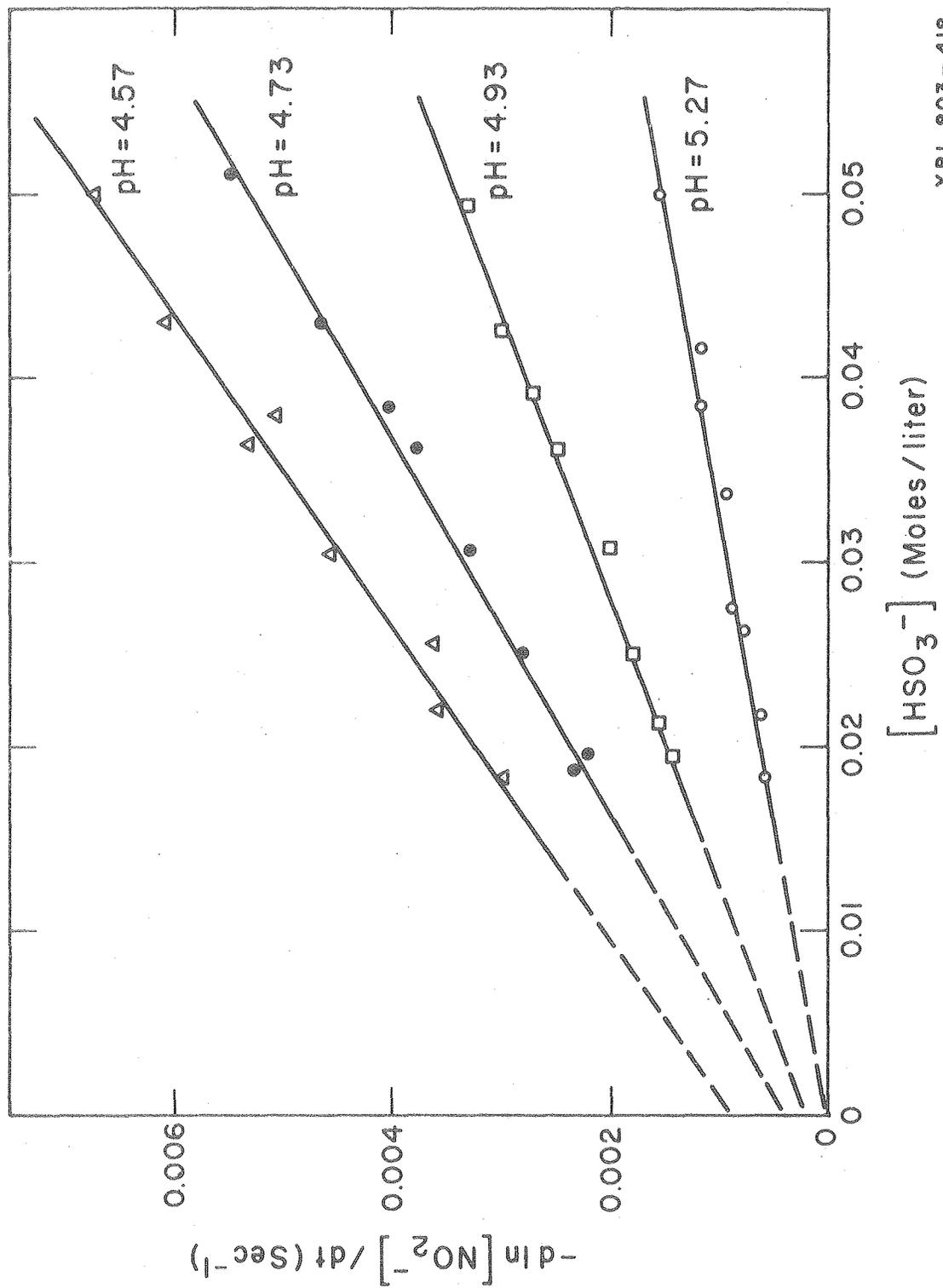
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Figure 1



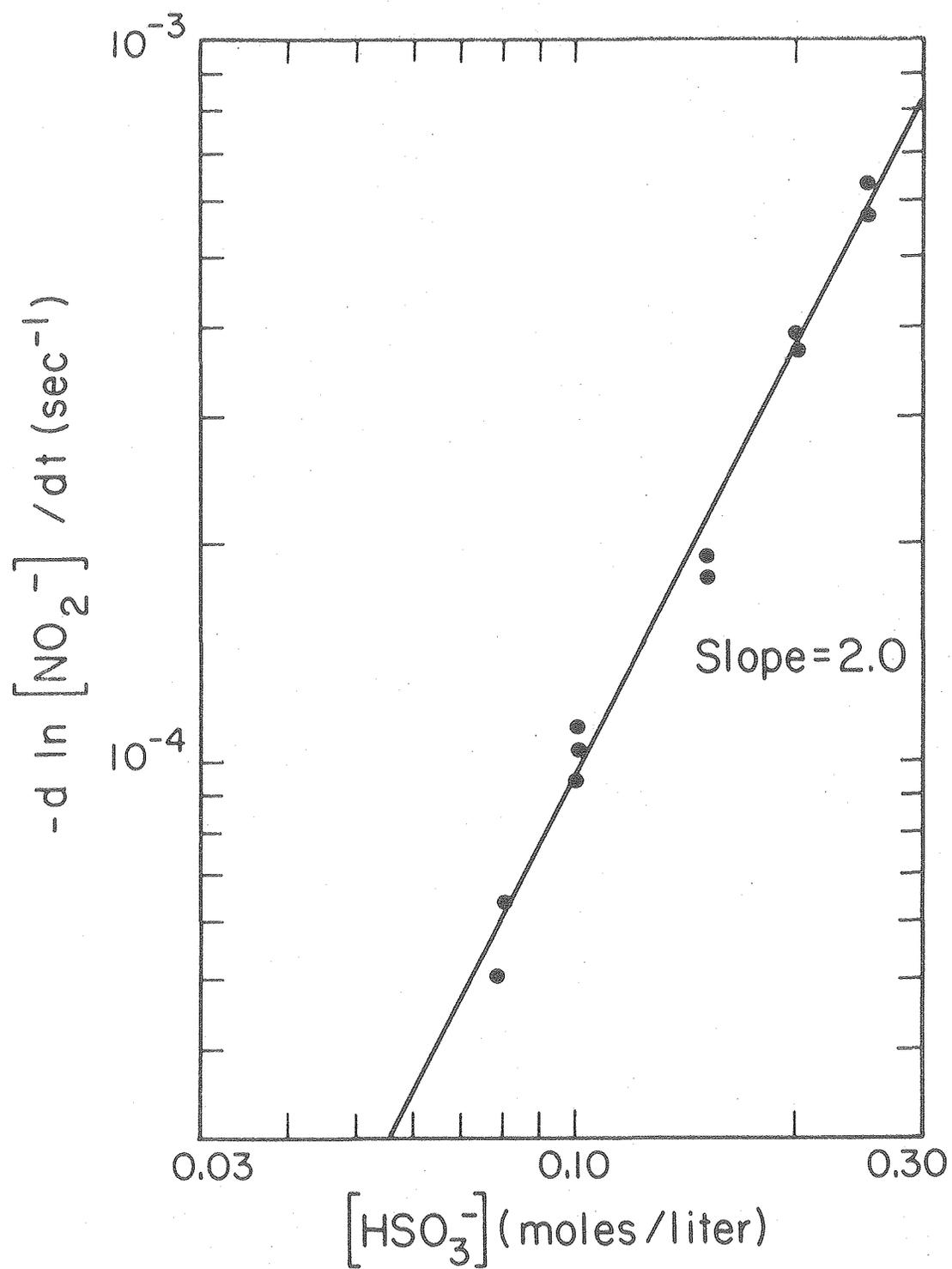
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Figure 2



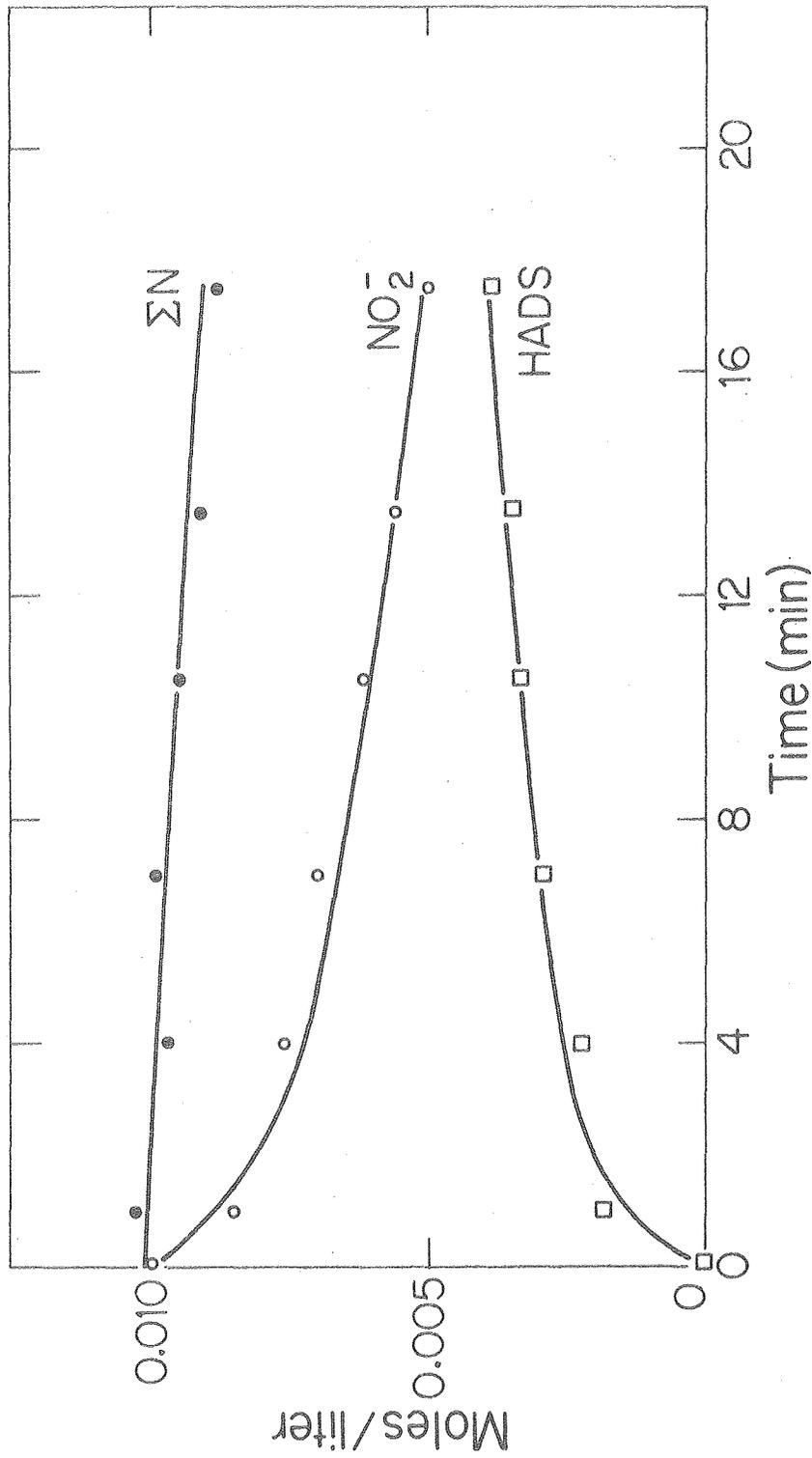
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Figure 3



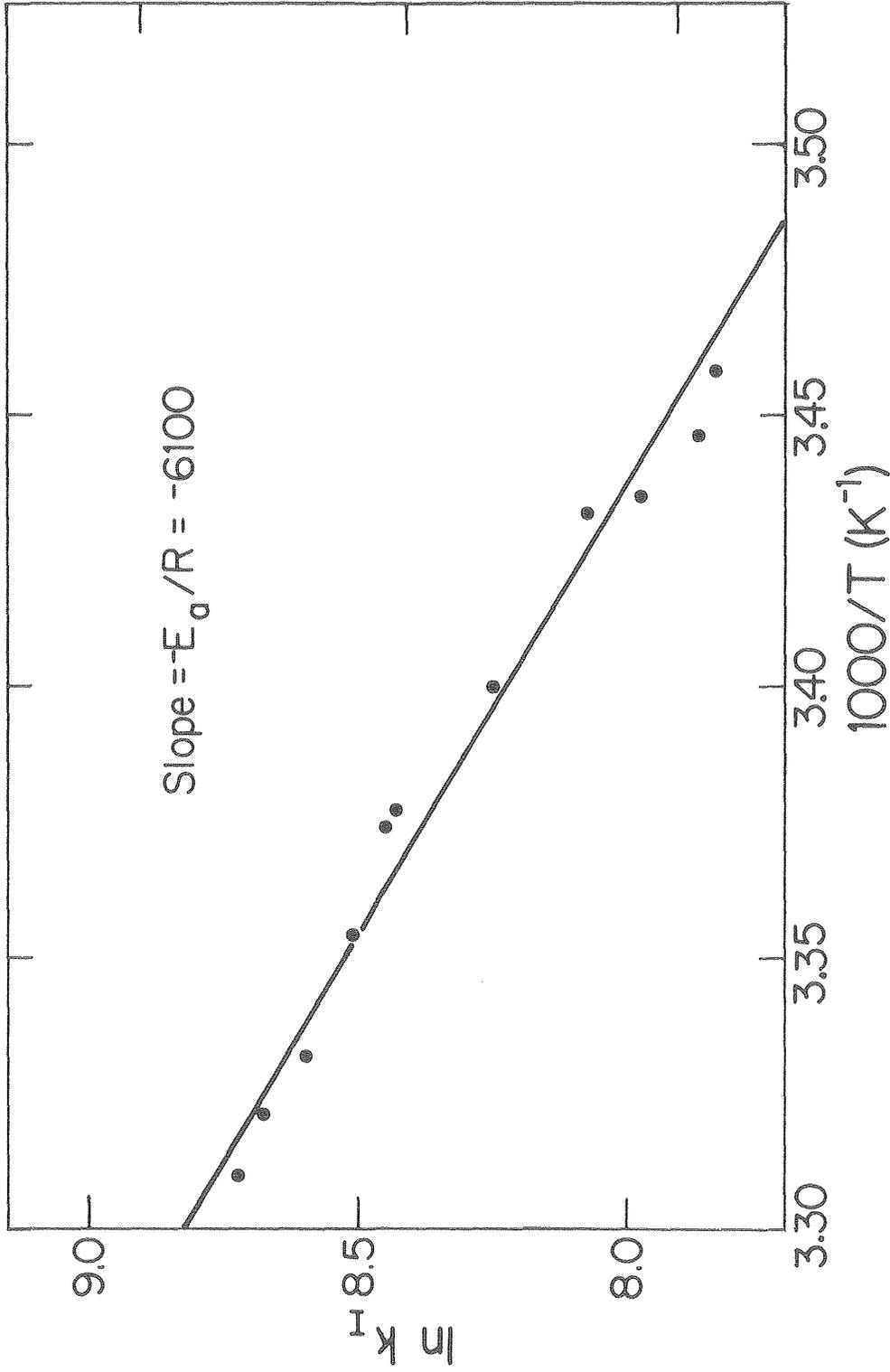
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Figure 4



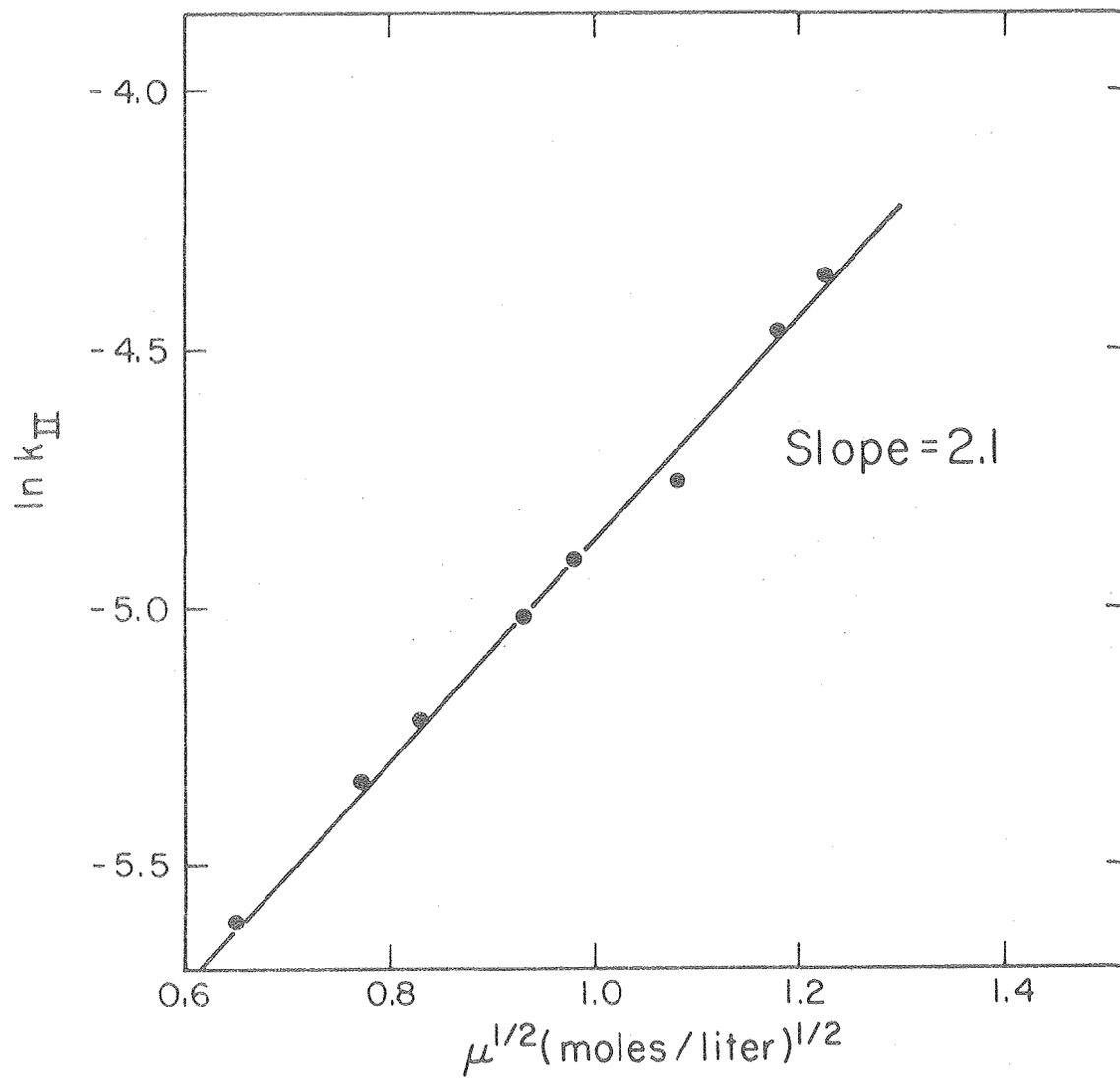
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Figure 5



XBL 7911 - 13319

Figure 6



XBL 7911-13320

Figure 7