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KINETICS OF THE INITIAL REACTION OF NITRITE ION IN BISULFITE SOLUTIONS

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The kinetics of the reaction of nitrite ion in bisulfite solutions to form hydroxylamine disulfonate have been investigated. Evidence has been presented that nitrososulfonic acid is an intermediate in this reaction, and it can undergo sulfonation or hydrolysis reactions. The hydrolysis reaction yields N₂O under the present conditions of study (acid solutions) which complicates the determination of the rate of formation of hydroxylamine disulfonate. The ratio of the rate constants for sulfonation and hydrolysis (k_A/k_B) is 1.7 ± 0.5 . The previously determined rate law for the formation of the disulfonate has been verified, although one term has been shown to be dependent on which buffer solution is chosen to maintain the desired acidity.

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Introduction

At the beginning of this century, Raschig proposed a reaction scheme describing the reduction of nitrous acid by aquated sulfur dioxide in an effort to understand the mechanism of sulfuric acid formation in the lead chamber process.¹ Since then a number of papers have discussed the reactions involved in this scheme. Of these, few have described systematic kinetic investigations, and only four have dealt with the initial reactions of nitrite ion.²⁻⁵ The portion of the overall scheme which is important to the current investigation is shown as follows:

The nitrous acid reacts with bisulfite ion to form nitrososulfonic acid, which further reacts with bisulfite ion to form hydroxylamine disulfonate (HADS), or undergoes hydrolysis to form nitroxyl radical. Under the conditions at which hydrolysis is expected to occur, the $\text{NOH}\cdot$ will dimerize and decompose to yield N_2O and water.

The earliest three investigations²⁻⁴ of these initial reactions yielded conflicting rate laws, but all three showed that HADS was the only product. No evidence was reported for nitrososulfonic acid as an intermediate. A recent investigation⁵ by our laboratory has resolved these differences and reports a rate law of the following form:

$$d[\text{HADS}]/dt = k_1 [\text{H}^+]^2 [\text{NO}_2^-] + k_2 [\text{H}^+] [\text{HSO}_3^-] [\text{NO}_2^-] + k_3 [\text{HSO}_3^-]^2 [\text{NO}_2^-] \quad (1)$$

The first term in this rate expression is the result of a process whose rate is independent of the bisulfite ion concentration. At lower bisulfite ion concentrations (or high acidity) this process should be the dominant one. This has created an interest in this reaction among atmospheric chemists studying sulfate aerosol formation and flue-gas scrubber technology. All three laboratories which have studied this reaction scheme have observed this process, but in each case conditions have been such that it is only a minor portion of the total observed rate. In order to more fully understand this bisulfite independent process, we have undertaken an investigation designed to verify the existence of this process and to search for evidence of the intermediate species. The results do show that the hydrolysis reaction can interfere with the determination of the kinetics of HADS formation.

Experimental Section

The reactions were carried out by the addition of sodium nitrite to solutions of sodium bisulfite at various pH's. Acidity was controlled by using phthalate-biphthalate, oxalate-bioxalate, tartrate-bitartrate, or bisulfite-sulfurous acid buffers, as noted below. Nitrite concentrations were monitored by spectrophotometry in the visible region (354 nm). Concentrations of sulfite species were determined by iodometric titrations; acetate buffers were used to eliminate interference from nitrite or nitrous acid.³ Typical initial concentrations were 0.5 to 50 mM for bisulfite ion and 0.1 to 1 mM for nitrite ion. All solutions were prepared in deionized water from analytic reagent grade chemicals. For bisulfite ion, $\text{Na}_2\text{S}_2\text{O}_5$ was used. Temperature was maintained at $295 \pm 1\text{K}$.

Reaction rates for the production of HADS were determined by monitoring the loss of nitrite ion. The stoichiometry of the reaction was determined to examine whether HADS was the only product formed. Reactions were run with excess bisulfite ion to assure pseudo-first-order reaction conditions. Acidity

(pH range 3.2-5.3) was maintained with oxalate, tartrate, or phthalate buffers. Initial ionic strength was kept constant within each set of conditions by the addition of sodium sulfate. Previous studies showed that ionic strength had no effect on the measured rate.⁵

The stoichiometry of the reaction was determined by measuring the change in both nitrite and bisulfite ion concentrations as the reaction progressed. Initial concentrations were determined by dilution of stock solutions. The ratio of bisulfite ion reacted per nitrite ion consumed ($\Delta S/\Delta N$) was found to be constant over the course of reaction. In many cases it was sufficient to note the total change in bisulfite ion concentration and check that all the nitrite ion had reacted. Both methods yielded the same results. Reactions in these experiments were no longer run under pseudo-first-order conditions, but greater than stoichiometric amounts of bisulfite ion were used in each case. Reactions were complete within 20 minutes. pH was maintained in the ranges of 1 to 3 by sulfurous acid buffers. At greater pH phthalate buffers were used.

For a number of these experiments in which the $\Delta S/\Delta N$ ratio was less than 2:1, the reactions were carried out in flasks sealed with rubber septums to allow analysis of any gaseous products by gas chromatography. A Porapak Q column (7 ft, 100-120 mesh) was used at 45°C with a thermal conductivity detector and helium carrier gas. Qualitative N_2O standards were prepared by reaction of hydroxylamine with nitrous acid. Retention times for N_2 , O_2 , and CO_2 were determined by injection of air. Water vapor was removed periodically by heating the column.

Results and Discussion

For all experiments where the pH was greater than 3.2, the measured stoichiometry was 2:1, indicating that hydroxylamine disulfonate was the product being formed. In the range 10-50 mM bisulfite ion and at pH between 3 and 5,

the rate law (Eq. 1) predicts that the first two terms should predominate. The third term is negligible under all the conditions of the present study and will be ignored throughout this paper. If one plots the rate (normalized to the nitrite ion concentration) as a function of the bisulfite concentration, the slope will be related to the second term in Eq. 1, and the intercept related to the bisulfite independent term. Figure 1 shows the data obtained for a number of different pH's. Those pH's greater than 4.0 were examined in phthalate buffers, and those at a lower pH were in oxalate or tartrate. Only the phthalate buffer shows the positive intercepts which are expected for the bisulfite-independent process.

Seel and Knorr² and Yamamoto and Kaneda³ each observed this bisulfite-independent process in acetate buffers but were unable to carry out the experiments at pH less than 4, where it would become the dominant process. This process was attributed to formation of NO^+ followed by subsequent fast reactions with bisulfite ion. More recently, Seel and Pauschmann⁶ have shown that acetate ion can stabilize NO^+ and enhance its formation by shifting the equilibrium. Our work in phthalate buffers shows the same sort of behavior for the bisulfite independent pathway. Other preliminary work in our lab shows that phthalate ion may also be capable of stabilizing NO^+ . Tartrate and oxalate, on the other hand, show little, if any, capacity to stabilize NO^+ . These results indicate that the bisulfite-independent process is strongly dependent on the buffer system used, and in an unbuffered system would be negligible at a pH greater than 3.

The slopes in Fig. 1 yield values for k_2 which are in complete agreement with the values previously reported.⁵ However, a correction must be made for the amount of nitrite ion present compared to the total $\text{N(III)}(\text{NO}_2^- + \text{HONO})$. The spectrophotometric technique used only measures total N(III) , yet only one

of the two forms is reacting. (Present kinetic techniques cannot specify which species is reacting.) This correction becomes important at pH near the pK_a for nitrous acid ($pK_a = 3.5$). If the correction is not applied, there is an apparent slowing of the rate as the reaction medium becomes more acidic.

It is still conceivable that the bisulfite independent term will be significant at very low bisulfite concentrations or at lower pH. Attempts to investigate this were not successful because of an interfering reaction which lowers the measured stoichiometry of the reaction ($\Delta S/\Delta N$ becomes less than 2.). Results for the change in $\Delta S/\Delta N$ for various pH's at fixed bisulfite ion concentrations and at various bisulfite ion concentrations at fixed pH are shown in Figs. 2 and 3. In each figure, as one raises the amount of H^+ relative to the bisulfite concentration, the $\Delta S/\Delta N$ ratio drops towards 1:1. This is completely consistent and expected from the reaction scheme originally proposed by Raschig, where hydrolysis and formation of N_2O are expected.

In order to test this hypothesis, the gaseous products produced in those runs where $\Delta S/\Delta N$ is less than 2:1 were examined by gas chromatography. Analysis showed that N_2O was formed, and although only semiquantitative results were obtained, significantly more N_2O was formed at lower $\Delta S/\Delta N$ ratios. Typical results of these analyses are shown in Fig. 4.

The other possible explanation for these results is that HADS is formed and hydrolyzed to the mono-sulfonate species ($HONHSO_3^-$), followed by reaction with nitrous acid to form hyponitrous acid ($H_2N_2O_2$). This would rapidly decompose to N_2O and water. The rates for hydrolysis of HADS have been well studied⁷ and are too slow to account for the observed results in the time scale of the present experiments. Therefore, the present experiments offer the first evidence that there is an intermediate which can be hydrolyzed, $NOSO_3^-$ being the most likely candidate.

Although this reaction prohibits the possibility of obtaining rate information for the bisulfite independent process, the relative rates of hydrolysis and sulfonation may be determined. By considering the reactions at the beginning of this paper, one can express the fraction of the NOSO_3^- that reacts to form HADS as $(\frac{\Delta S}{\Delta N} - 1)$ and that which forms $\text{NOH}\cdot$ as $(2 - \frac{\Delta S}{\Delta N})$. Because these are simple competing reactions, they are related by the expression

$$\frac{k_A [\text{HSO}_3^-]}{k_B [\text{H}^+]} = \frac{(\frac{\Delta S}{\Delta N} - 1)}{(2 - \frac{\Delta S}{\Delta N})}$$

The results of our experiments give a value of $k_A/k_B = 1.7 \pm 0.5$. Because the H^+ ion concentration was held constant by the buffer system and the HSO_3^- ion concentration decreased during the course of the reaction, the calculations were made using the initial concentration of bisulfite ion.

Further, the observed rates of loss of nitrite ion at pH less than 3 seem to agree with the rates predicted by Eq. 1 if the first term is ignored. This is consistent with the proposed mechanism associated with Eq. 1 which had k_2 as the rate constant for formation of nitrososulfonic acid, followed by a fast reaction with bisulfite.⁵ Since k_A and k_B have been shown to be of the same order of magnitude and k_2 was shown to be much smaller than k_A in the previous study, k_2 should still be the rate-limiting factor in this regime. This same feature, however, precludes determination of the absolute value of k_A or k_B by the methods employed in this study.

Conclusions

The results of this study tend to verify the previously reported rate law for the formation of hydroxylamine disulfonate. The bisulfite independent term, of interest to atmospheric chemists, has been demonstrated to be dependent

on the buffer system which is used and was not apparent in either tartrate or oxalate buffers above $\text{pH} = 3$. Evidence has also been presented that an intermediate species is formed which can hydrolyze to form N_2O or go on to form HADS. Although this interfering reaction is only noted in very acidic solutions in this study, at lower bisulfite ion concentrations this reaction will become important in even weakly acidic solutions. The ratio of the rate constants for sulfonation and hydrolysis reactions (k_A/k_B) is 1.7 ± 0.5 ; this indicates that whenever H^+ and HSO_3^- are present in equal concentrations, substantial amounts of N_2O will be formed.

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Figure Captions

Figure 1. Rate of loss of NO_2^- as a function of bisulfite concentration.

Numbers at right of line indicate pH. Slopes in this figure have not been corrected for nitrous acid contribution (see text for explanation).

Figure 2. Stoichiometric ratio vs. pH at a fixed sulfur (IV) concentration of 4×10^{-3} M.

Figure 3. Stoichiometric ratio vs. $[\text{S}^{4+}]$ at a fixed pH of 2.9 using phthalic acid buffer.

Figure 4. Typical gas chromatograph. Trace a refers to experiment where $\Delta\text{S}/\Delta\text{N} = 1.5$ Trace b refers to $\Delta\text{S}/\Delta\text{N} = 2.0$.

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Figure 1

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Figure 2

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Figure 3

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Figure 4