2 (bp 72–73 °C (0.02 torr); yield 1.19 g, 21%) was identified as **9** (Tables I and II).

Reactions of Bis[bis(trimethylsilyl)amino]alkylphosphines 1–5 with CCl_4. In a typical reaction in the absence of solvent **1** (5.15 g, 14.0 mmol) was placed in a 50-mL round-bottom flask equipped with a nitrogen inlet, septum, and magnetic stir bar. After the flask was cooled to 0 °C, an excess of CCl_4 (ca. 6.5 mL) was added via syringe. After being stirred at room temperature for ca. 18 h, the mixture was distilled (Tables I and II). The major product was **10a** along with minor amounts of **11a**.

The reactions in the presence of CH_2Cl_2 were carried out in a similar fashion at 0 °C with the addition of ca. 40 mL of CH_2Cl_2 to the phosphine (ca. 14.0 mmol) before 1 molar equiv of CCl_4 was added. After the mixture was stirred at room temperature for ca. 18 h, the solvent was removed and the residue was distilled, giving **11** as the major product and smaller amounts of **10** (Tables I and II). More dilute solutions favored the formation of the Me_3SiCCl_3 elimination product **11**.

Compound **1** in pentane was also treated with CCl_4 at 0 °C. After ca. 18 h of stirring, workup and distillation afforded a 27% yield of **10a**.

Under the conditions described above, **5** reacted with either CCl_4 or CCl_4/CH_2Cl_2 to give **10d**.

Acknowledgment. The authors thank the U.S. Office of Naval Research, the U.S. Army Research Office, and the Robert A. Welch Foundation for generous financial support of this research.

Registry No. **1**, 82581-87-1; **2**, 84050-72-6; **3**, 84050-73-7; **4**, 84050-74-8; **5**, 84050-75-9; **6**, 84050-76-0; **7**, 84050-77-1; **8**, 21385-93-3; **9**, 84056-89-3; **10a**, 76946-98-0; **10b**, 84050-78-2; **10c**, 84050-79-3; **10d**, 84050-80-6; **11a**, 84050-81-7; **11b**, 84050-82-8; **11c**, 76946-98-0; **11d**, 84050-83-9; $LiN(SiMe_3)_2$, 4039-32-1; PCl_3, 7719-12-2; $[(Me_3Si)_2N]_2PCl$, 53327-45-0; $Me_3SiCH(Li)Ph$, 37820-39-6; Me_3SiN_3, 4648-54-8; MeI, 74-88-4; MeLi, 917-54-4; *n*-BuLi, 109-72-8; CCl_4, 56-23-5; $(Me_3Si)_2NH$, 999-97-3.

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Reaction of Nitrite Ion with Hydroxylamine-*N*-sulfonate in Aqueous Solution

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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 first-order dependence on nitrite ion, second-order dependence on hydrogen ion in the pH region of 4–5, and between zero- and first-order dependence on HAMS, depending on the concentration. An activation energy of 30 kJ/mol was determined for the reaction in the temperature range of 10–40 °C. The ionic strength dependence was studied in the range of 0.2–1.5 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 that consists of the nitrosation of HAMS, followed by a decomposition into products.

Introduction

The reaction of hydroxylamine-*N*-sulfonate (also referred to as hydroxylaminesulfonate 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, yielding 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[5] 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. For a determination of 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 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 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 at a value near 5.

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 that may be extrapolated to concentrations of ionic species in water droplets in a polluted atmosphere, chemists

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Table I. Initial Conditions and Experimental Rates (All Solutions at 293 K)

[HAMS], M	$[SO_4^{2-}]$, M	$[\Sigma P]$,[a] M	pH	μ, M	$-d \ln [NO_2^-]/dt$, s^{-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

[a] $[\Sigma P]$ = total concentration of phthalate species.

interested in atmospheric aerosol formation[5,10] and flue-gas-scrubber technologies[5,11-14] will be able to evaluate the importance of the HAMS–NO2$^-$ reaction. The role of buffer species 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.[15] The method was modified to use the tribasic salt of the disulfonate species rather than the dibasic salt. The disulfonate species was prepared by the method of Rollefson and Oldershaw[16] and recrystallized in a KOH solution. Although the yields are lower with the tribasic salt, the purity is quite high. Anal. Calcd K:S:N:H for $HONHSO_3K$: 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 desiccator over P_2O_5.

All other reagents used in this study were analytical reagent grade and were used as supplied. Solutions were prepared in deionized water immediately before use with the exception of the buffer solutions, which were prepared 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 on addition of the reactant salts.

Kinetic Measurements. The reaction kinetics were determined by monitoring the concentration of nitrogen(III) species ($HONO + NO_2^-$) spectrophotometrically at 354 nm with a Cary 219 spectrophotometer, using either 1- or 10-cm cells. Molar absorptivity was determined at each pH and ranged between 23 and 44.4 L/(mol cm). Knowledge of the pH allowed the concentration of HONO or NO_2^- to be calculated. Interference by weakly absorbing buffers was eliminated by using a sample of the buffer as the reference solution.

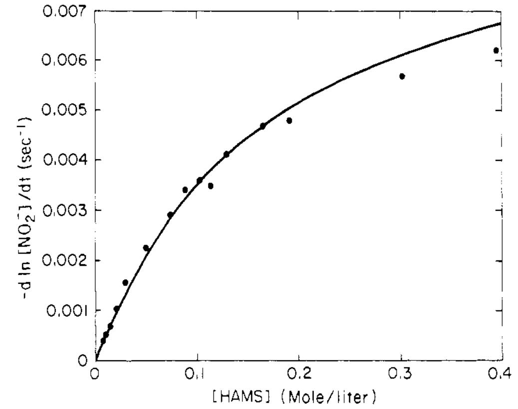

Figure 1. Reaction rate as a function of HAMS concentration for pH 4.35 (with 0.141 M phthalate buffer) at 20 °C and $\mu = 1.20$. The solid line is fit to the proposed rate expression (see text for explanation).

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 either 0.5 mL of sodium nitrite solution or 1–5 mg of solid sodium nitrite salt was added. The addition of the solid was preferred because it minimized the dilution of the HAMS or buffer species, particularly in the short-path-length cells. All reactions were carried out under pseudo-first-order reaction conditions, with a large excess of HAMS. Temperature was controlled to ±0.2 K.

Initial reaction conditions were typically 0.01–0.40 M in HAMS and 1–10 mM in nitrite ion. These experiments were performed in phthalate buffers between pH 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 all other parameters were kept 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 (~0.02 unit) over this temperature range. Ionic strength effects were investigated by addition of sulfate, nitrate, or phosphate salt. 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.

Experiments to determine buffer effects were performed by using phthalate, tartrate, and oxalate buffers at various concentrations. These experiments were performed at 293 K and $\mu = 1.2$ by 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

$$NO_2^- + 2H^+ + HONHSO_3^- \rightarrow N_2O + HSO_4^- + H_3O^+ \quad (1)$$

In the present investigation the same reaction was observed, but the reaction rates were measured by the loss of nitrite ion over time. A semilogarithmic plot of the nitrite ion concentration vs. time gives a straight line with a slope invariant with the initial nitrite ion concentration. These results indicate that the reaction is first order with respect to nitrite ion, confirming the previous observations. Whereas the ability to detect dissolved nitrous oxide placed a lower limit on the nitrite ion concentration in the previous 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 Figure 1, with typical experimental results listed in Table I. The change in reaction order from frist to nearly zero order in HAMS as the concentration is

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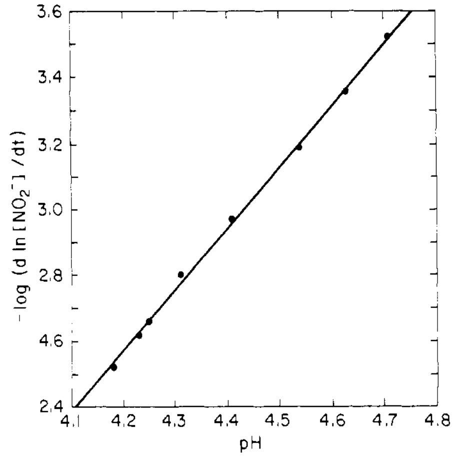

Figure 2. pH dependence of reaction under HAMS-dependent conditions (with a 0.141 M phthalate buffer system). The slope indicates a second-order dependence on hydrogen ion.

increased indicates that there is a change in the rate-determining step for the reaction. The mathematical expression for a mechanism of this type would be of the form shown in eq 2. By a least-squares fit of $1/Q$ vs. $1/[\mathrm{HAMS}]$, both

$$Q = \frac{-1}{[\mathrm{NO_2^-}]}\frac{\mathrm{d}[\mathrm{NO_2^-}]}{\mathrm{d}t} = k[\mathrm{HAMS}]/(1 + k'[\mathrm{HAMS}]) \tag{2}$$

constants were determined; the resulting fit is shown as a solid line in the figure. Unfortunately this unweighted fit is least sensitive at the highest concentrations and causes the poorer fit in this region. A better fit at high concentration would be obtained by a suitable weighted least-squares fit. However, the difference between the two values of k' is small compared to the estimated error. 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 Figure 2, 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.

It is unfortunate that the pH could not be varied over a wider range to allow a more complete treatment of the kinetics. However, at higher pH the reaction slows to the point where other routes for loss of nitrite begin to interfere. Because these loss mechanisms appear to be somewhat variable (presumably the result of some contamination), they could not be easily corrected for. Under conditions more acidic than pH 3.8, the reaction proceeds too rapidly for measurement by the present technique; stop-flow measurements would be needed.

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 that has been proposed before.[4]

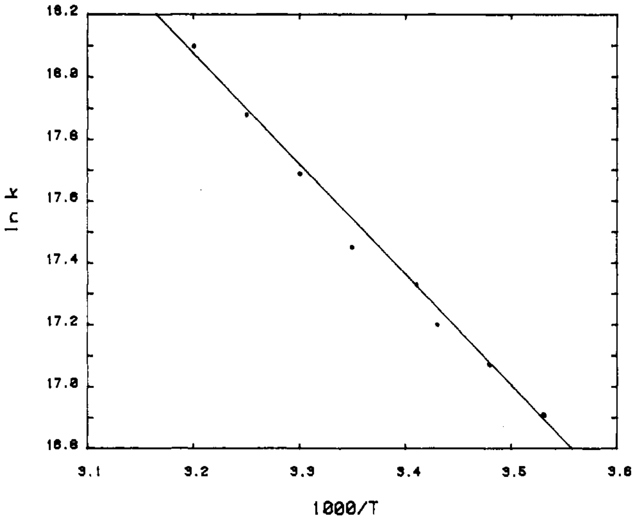

Figure 3. Arrhenius plot of the rate constant for HAMS-dependent reaction conditions ([HAMS] = 0.026 M; $[\sum P]$ = 0.141 M; pH 4.40).

The results of the temperature dependence study of the first-order HAMS regime are shown in Figure 3, plotted as an Arrhenius function. The activation energy was determined to be 30 kJ/mol. The zero-order regime results are similar, with a value of 33 kJ/mol. By applying the activated complex theory,[17] one can obtain values for the entropy of activation ($\Delta S^\ddagger$) as well as the enthalpy of activation ($\Delta H^\ddagger$). The values of $\Delta S^\ddagger$ are −2 and −12 eu for the HAMS-dependent and -independent regimes, respectively.

The data presented in Figure 3 suggest some curvature in the Arrhenius plot. This could be due to the limited number of points available or to a shift in the reaction mechanism with temperature. The most likely candidate for this shift is a change in the value of the ionization constant for nitrous acid as the temperature varies. Other possibilities include increased production of oxides of nitrogen with changes in temperature

$$2\mathrm{HONO} = \mathrm{NO} + \mathrm{NO_2} + \mathrm{H_2O}$$

$$3\mathrm{HONO} = \mathrm{HNO_3} + 2\mathrm{NO} + \mathrm{H_2O}$$

or a shift in the transition point from first- to zero-order HAMS dependence. A more detailed study over a wider temperature range is needed before this question can be completely resolved.

The range of the ionic strength dependence study ($0.2 < \mu < 1.5$ M) is far too concentrated for explanation by the Debye–Hückel theory and can be considered only 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;[18] 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.

The reaction rate was found to depend moderately on the concentration (sum of acid and conjugate base) of each of the

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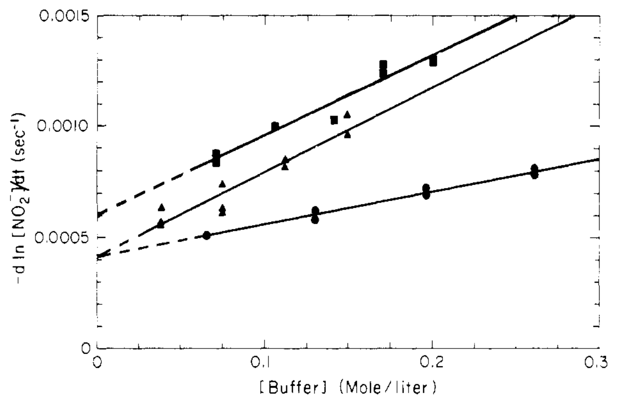

Figure 4. Effect of buffer concentration on reaction rate for phthalate (■), tartrate (▲), and oxalate (●) buffers. All data are obtained at 20 °C and normalized to pH 4.4, and [HAMS] = 0.020 M. Buffer concentration refers to the sum of acid and conjugate base. Intercepts—obtained by extrapolation—agree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

Table II. Rate Constants for Buffered Solutions

buffer	k_{buffer}, L/mol
phthalate	7.5 ± 0.7
tartrate	3.1 ± 0.2
oxalate	8.0 ± 0.8

buffer systems used; the results are shown in Figure 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 rates 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 estimated experimental error. A similar enhancement has been seen before for the phthalate species[17] and was explained as the carboxylate functionality acting to complex the NO^+. If formation of a carboxylate complex is the reason, then all three buffers would be expected to act similarly. Curvature is expected in the phthalate system at low concentration. The enhancement and differences between the buffers are discussed more fully in the next section after a mechanism is proposed.

In summary, the experimentally determined rate law can be expressed in the absence of buffer as

$$\text{rate} = \frac{-\mathrm{d}[NO_2^-]}{\mathrm{d}t} = k[H^+]^2[NO_2^-]\frac{[\text{HAMS}]}{1 + k'[\text{HAMS}]} \quad (3)$$

The best values for the rate constants at 20 °C are $k = (1.5 \pm 0.3) \times 10^7$ L^3 mol^{-3} s^{-1} and $k' = 5.5 \pm 0.6$ L mol^{-1}. The effect of the buffer activity may then be included mathematically:

$$\text{total rate} = (\text{unbuffered rate})(1 + k_{\text{buffer}}[\text{buffer}]) \quad (4)$$

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

Discussion

The results of this kinetic study may be explained by the proposed reaction scheme shown in eq 5 and 6. Reaction 6

$$H^+ + HONO \rightleftarrows NO^+ + H_2O \quad (5)$$

$$NO^+ + HONHSO_3^- \rightarrow N_2O + HSO_4^- + H^+ \quad (6)$$

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^+, on the basis of agreement between previous measurements of the rate of NO^+ formation (by polarographic[19] and ion exchange[20] studies) and the current measured rates when reaction 5 is rate limiting (HAMS-independent region).

Despite the fact that reaction 5 appears 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. Thus a second-order hydrogen ion dependence is what one would expect, unless one goes to higher acidities where nearly all the N(III) is in the form of nitrous acid. For the reasons already presented, the pH dependence cannot be studied over a wider range by the present technique. This leaves two questions unanswered: (1) whether a transition to first-order H^+ dependence is observed in sufficiently acidic solutions, where HONO is the predominate species; (2) what effect the ionization or protonation of HAMS might have on the reaction. Hydroxylaminesulfonic acid ($HONHSO_3H$) has been reported as a strong acid;[21] therefore, except in strongly acidic solutions, no protonation effect should be observed.

If it is assumed 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 approximation results in the rate of loss of nitrite ion:

$$\text{rate} = \frac{k_6k_5[H^+]^2[NO_2^-][\text{HAMS}]}{K_A(k_{-5} + k_6[\text{HAMS}])} \quad (7)$$

where $K_A = [H^+][NO_2^-]/[HONO]$. This expression indicates that, at high concentrations of HAMS, the rate should be independent of HAMS, whereas at lower concentrations a first-order dependence should be observed. A rigorous mathematical treatment can be carried out;[22] however, the results are essentially the same.

Even though the mechanism proposes a different rate-determining step for each HAMS regime, nearly the same activation energy is found under both conditions. This can be shown to be consistent with the proposed mechanism by again examining eq 7. At low concentrations of HAMS, the observed rate constant should be given by $(k_6k_5)/(k_{-5}K_A)$. In 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 different entropies of activation for the two limiting regimes are consistent with the idea of different transition states, which would exhibit different solvation effects and therefore different values of $\Delta S^{\ddagger}$. Unfortunately, this information cannot give any new mechanistic insight into a complex reaction such as this.

The ionic strength results are not unexpected. When sulfate was used, there was 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. The singly charged dihydrogen species is the major form of phosphate ion at a pH between 4 and 5, and this species has

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been shown to form a partially covalent complex with nitrosyl ion.[14] In this respect it behaves similarly to the carboxylate-containing buffer species and is probably acting to enhance the rate by opening a new reaction channel. This will be discussed in more detail later. Sulfate ions do not form a covalent complex with NO^+ (only completely ionic salts are formed), which would not give rise to any new reaction pathways; and, therefore, there is no enhancement of the rate.

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.

A reaction between HAMS and nitrate ion is suspected. Hydroxylamine is known to react with both nitrous and nitric acids,[19] and HAMS reacts with nitrite ion; so it is not unexpected that nitrate ion should react with HAMS. There was no obvious evidence for this reaction (other than inhibition of the rate), but because nitrate was used only for this one set of experiments, no extensive search was undertaken.

The effect of the buffer concentration in oxalate and tartrate systems in the HAMS-dependent regime has been described. For phthalate the same results were found in both regimes. 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 can be used to explain the effects of the buffers. Acetate and phthalate species are also believed to form complexes,[14] with the carboxylic acid functionality stabilizing the nitrosyl ion. Tartrate and oxalate buffers should also exhibit this behavior. Other species such as Cl^-, Br^-, and I^- act in a similar manner.[9,14] If all these species (including $H_2PO_4^-$) 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 at which HAMS reacts due to the increasing concentration of reactive intermediates. Since NO^+ is probably hydrated in solution, replacement of a water molecule by a weakly bound anion conceivably would not drastically affect its properties. It is also possible that the buffers can assist in the cleavage of HONO to form a complexed NO^+, creating a new pathway for NO_2^- loss and enhancing the rate in the HAMS-independent regime.

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. One problem in determining the actual enhancing species is that, besides the R–COO$^-$ complex formation, the R–COOH functionality could 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 that can donate protons and not form a partially covalent complex with NO^+, we have been unable to investigate this idea further. The additional possibility that general-acid catalysis and R–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 Figure 4 reveals different slopes for each of the buffer systems. The varying inductive effects of the R groups in the R–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. This would imply that there should be curvature in the low-concentration phthalate curve. Changes in the rates caused by different buffers could also be due to different activities for the ions in the different mediums.

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 that uses these schemes. In the consideration of nitrite–bisulfite reactions in flue-gas scrubbers, chelating agents added to enhance NO_x solubilities[24] 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 chnage the observed kinetics.

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