KINETICS OF OXIDATION OF AQUEOUS SULFUR(IV) BY NITROGEN DIOXIDE

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INTRODUCTION

Although it is generally recognized that SO_2 and NO_x ($\equiv$ NO + NO_2) are the precursors of the strong acids (i.e., H_2SO_4 and HNO_3) found in precipitation,[1] the detailed mechanisms for the oxidation of these compounds and their incorporation into atmospheric liquid water are not fully understood. In principle, the incorporation of acids into cloud- or rainwater can take either or both of two pathways: (1) homogeneous gas-phase oxidation of SO_2 and NO_x to produce gaseous H_2SO_4 and HNO_3 (and possible subsequent formation of clear-air aerosol) followed by incorporation into liquid water, or (2) absorption of SO_2 and NO_x, as well as O_2 and possibly other oxidants (e.g., O_3 and H_2O_2), into cloud- or rainwater followed by chemical reactions in the liquid phase, either catalytic or noncatalytic. The former process has been the focus of much atmospheric research in the past decade, and a body of useful information has been attained, which appears adequately to describe and predict the chemistry and physics involved in clear air.[2-6] The latter pathway, on the other hand, is less adequately described. Nonetheless, some information obtained to date on the aqueous-phase oxidation of SO_2[7-13] and NO_x[14,15] has clarified the role of aqueous-phase production of strong acids in the atmosphere.

Oxidation of dissolved sulfur(IV) ($\equiv SO_2(aq) + HSO_3^- + SO_3^=$) has been shown to be effected by various oxidants such as O_2,[7,8] O_3,[9,10] H_2O_2,[10-12] and HNO_2,[13] in some instances involving catalysts such as transition metal ions.[16-18]. The potentially important oxidation of aqueous S(IV) by NO_2, however, has not been studied in a rigorous fashion. Besides being a major atmospheric pollutant present in significant concentration, NO_2 is a relatively strong oxidant, comparable to Br_2.[19a] Historically one would also note that NO_2 (along with other nitrogen oxides and oxyacids) has been employed as a catalyst for the manufacture of H_2SO_4 from SO_2 by the lead chamber process.[19b] In the context of possible atmospheric significance, reaction of aqueous S(IV) and NO_2 has been studied by a number of investigators. Nash[20,21] and Takeuchi et al.[22] studied the absorption of NO_2 by S(IV) solution; although fast reaction was indicated by strong absorption of NO_2, reagent gas solubilities, mass transfer, stoichiometry, and reaction rate were not systematically investigated.

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This reaction system has also been studied by Sato[23] but at reagent concentrations significantly greater (p_{NO_2} = (6 ~ 20) x 10^{-4} atm and [S(IV)] = 0.24 ~ 0.38 M) than are characteristic of the ambient atmosphere. Although various products were identified, the reaction kinetics was not addressed.

We report here a study of stoichiometry and kinetics of the oxidation of aqueous S(IV) and NO_2 under controlled conditions at low reagent concentrations pertinent to evaluation of the rate of this reaction in ambient atmosphere.

GENERAL CONSIDERATIONS

The approach employed in this study is that of contacting gaseous NO_2 in N_2 with aqueous solution of sulfur(IV) at known pH in a reactor of known convective mixing time constant, similar to that employed previously in the study of NO_2 disproportionation.[14] The rate of acid formation is directly and continuously measured either as increase in electrical conductivity (due largely to H^+ ions) or as the rate of base addition required to maintain constant pH. The intrinsic reaction rate (i.e., in the absence of mass-transfer limitation) is determined from the dependence of the measured rate upon the convective mixing time constant.

Phase-mixing. In the study of gas-liquid reactions it is imperative to quantify the effect of mass-transfer as a limiting factor in the overall kinetics. In our previous work[14,24] criteria have been given for various mass-transfer limitation "regimes" in terms of the relative magnitudes of characteristic times for the intrinsic chemical reaction (τ_r) and for the convective mixing process (τ_m) of the two phases. The criterion for a phase-mixed situation (i.e., the aqueous-phase saturated in the reagent gas) is $\tau_m \ll \tau_r$. Unless this condition is satisfied, the overall observed reaction rate is invariably subject to the convective mixing rate.

A further consideration in the present study is that since the concentration of S(IV) in solution is decreasing with time during a given kinetic run, the apparent characteristic reaction time, evaluated as

$$\tau_r = (k^{(2)}[S(IV)])^{-1} \qquad (1)$$

will be increasing during the course of the reaction; here $k^{(2)}$ is the effective second-order rate coefficient. In turn, in the event that the phase-mixed condition is not obtained, the extent of mass-transfer limitation will therefore change. To eliminate this complicating effect, reaction rate measurements were confined to initial rates, namely within the consumption of ~ 5% of the

[S(IV)]. Under this condition S(IV) concentration can be taken as the initial concentration.

pH Control and rate measurement. In the oxidation of dissolved S(IV) by NO_2, the sulfur species that contribute to the overall reactivity can be any or all of $SO_2(aq)$ (or H_2SO_3), HSO_3^-, and $SO_3^=$. The general rate expression, therefore, must include all of these species:

$$R = \frac{d[SO_4^=]}{dt} = (k_0\ [SO_2(aq)] + k_1\ [HSO_3^-] + k_2\ [SO_3^=])\ [NO_2(aq)]\ . \qquad (2)$$

It is clear that quantification of the individual rate constants is necessary to predict the pH dependence of this oxidation process. When expressed in the analytical concentration of S(IV) the rate can be written as

$$R = k^{(2)}[S(IV)][NO_2(aq)]\ , \qquad (3)$$

where the overall observed second-order rate coefficient $k^{(2)}$ is a function of pH and the acid dissociation constants of sulfurous acid (i.e., K_1 and K_2) as well as the individual rate constants,

$$k^{(2)} = \frac{k_0 + k_1\ K_1/[H^+] + k_2\ K_1\ K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2}\ . \qquad (4)$$

Since the pH will decrease as the reaction proceeds, it is thus seen to be necessary to maintain the solution acidity constant in order to maintain $k^{(2)}$ constant in a given kinetic run.

To maintain a constant pH, buffers might be employed; however, such an approach leads to complications: 1) the buffering species may exhibit general acid-base and/or nucleophilic catalysis that must be accounted for, and 2) conductivity measurement might no longer be used as a diagnostic tool for product formation because of increased background conductivity. To avoid these problems while retaining a continuous monitoring capability and maintaining constant pH, we have elected to use the pH-stat technique. In this approach the pH of the solution as measured by a pH electrode is compared to a pre-set value; whenever the pH falls below the pre-set value, standard base is added to the solution to keep the pH constant. The amount of titrant added as a function of time therefore gives the rate of the reaction. It should be noted that the pH-stat technique is of great advantage to the study reported here since it is sensitive and

Erratum

Equation 4 should read: $k^{(2)} = \dfrac{k_0 + k_1K_1/[H^+] + k_2K_1K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2}$

specific to the product of major interest, H^+, and maintains constant pH without the presence of buffers.

EXPERIMENTAL

Materials. An NO_2 permeation wafer (Metronics, Type 50T3) was used for NO_2 reagent gas source. An NO cylinder (47.6 ppm in N_2) obtained from NBS (SRM No. 1683A) was used as calibration standard. Reagent grade $NaHSO_3$, Na_2SO_3, $NaHSO_4$, Na_2SO_4, $Na_2S_2O_6$, KCl, $NaNO_2$, and $NaNO_3$ were used without further purification. Triple glass-distilled water and Millipore Milli-Q filtered water used had resistivity greater than 16 Mohm cm. Ultra high purity (UHP) N_2 (99.999%, Liquid Carbonic) was used as diluent gas. A copper catalyst (BASF catalyst R3-11, Chemical Dynamic Co.) was used to remove trace oxygen from the diluent gas. Sodium bisulfite stock solutions were prepared fresh daily in deoxygenated water and stored in a brown bottle.

Calibration of p_{NO_2}: NO_2 concentration in the reagent gas flow was determined by a NO_x chemiluminescence detector (TECO, Model 14B) whose sensitivity has been improved by a modified reaction chamber and the addition of a pre-reactor to give a detection limit of 0.2 ppb.[25] The NO_x detector was calibrated against the NBS 47.6 ppm NO standard. The NO_2 permeation rate of the Metronics permeation wafer maintained at 39.4 ± 0.1°C (Monitor Labs Permacal Model 8500) was determined as 515 ng/min.

Reaction cell. The gas-liquid reaction cell is depicted in Fig. 1. During the course of the reaction, reagent gas is brought into contact with the liquid as finely divided bubbles by passing through a disk-frit which comprises the bottom of a cylindrical reactor vessel. The bubbles increase the liquid-gas interfacial area and produce mixing by their upward motion, thereby enhancing the overall convective mixing rate. This enhancement is important to satisfy the condition, $\tau_r \gtrsim \tau_m$. The mass-transport characteristics of the reactor have been determined from the rate of dissolution of CO_2 into the liquid water under identical conditions.[14] The convective mixing time constant, which can be controlled by varying the gas flow rate and/or by varying the volume of solution employed, ranges from 1.7 to 5.3 sec.

The all-glass, thermostatted, gas-liquid reaction vessel is also equipped with a pair of platinum electrodes for electrical conductivity measurements. The detection limit for completely dissociated strong acids (e.g., HNO_3) is about 3×10^{-7} M, and reaction rates as low as 1×10^{-11} M s^{-1} have been measured. The rate of reaction is directly obtained from the rate of conductivity change, using the limiting equivalent conductivities of individual ions.

pH Control. The pH-stat unit (Metrohm) consists of a digital pH meter (model E632-3), an electronic control module (E614), which allows for the selection of the end point and the threshold, and a titration unit (E655), which accurately delivers the titrant in a predetermined aliquot upon each command signal from the control unit. The total amount of titrant added into the reaction cell as a function of time is recorded on a strip-chart recorder. The titrant concentration was chosen so that it is not too great so as to overshoot, causing large fluctuation in pH value, and not too low so as to increase the total reaction volume significantly, thereby causing changes in mass-transfer characteristics.

Experimental setup. The experimental setup is illustrated in Fig. 2. Diluted NO_2 was allowed to flow through the gas-liquid reactor containing a known amount of aqueous solution. The concentration of NO_2 was adjusted by the flow through MFC 2 while MFC 1 was accordingly adjusted so that total flow of UHP N_2 through the permeation chamber remained constant. Diluent N_2 was pre-humidified by bubbling through water that was maintained at 22°C. The flow of diluent gas was always greater than 95% of the total flow through the reaction cell.

Procedure. In a typical run a known amount of water (10-70 mL) was introduced into the reaction cell while N_2 was flowing through the system at ca. 2 L/min. After the conductivity of the solution reached a stable value (ca. 0.7 μmho cm^{-1}) when CO_2 (and O_2) were purged, a predetermined quantity ($\leq$ 100 μL) of $NaHSO_3$ stock solution (ca. 2 x 10^{-4} M) was added into the cell, resulting in an initial HSO_3^- concentration of typically 1 x 10^{-6} M. When the pH reading of the solution became stable, NaOH solution (or $NaHSO_4$ solution) was added to adjust

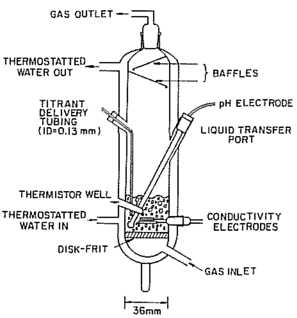

Fig. 1. Diagram of gas-liquid reactor.

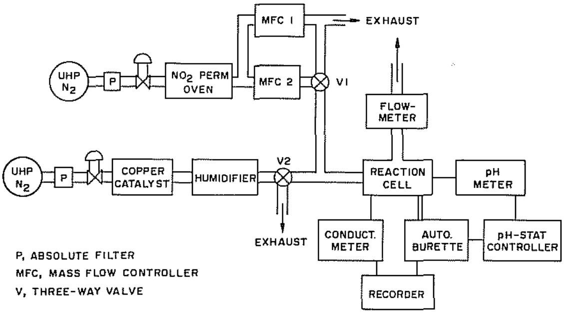

Fig. 2. Schematic diagram of gas-liquid reaction apparatus.

the pH to the desired value. The reaction was then initiated by introducing NO_2 gas into the N_2 flow through V1; the total flow of the reagent gas through the reaction cell was typically 2.0 L/min. With the pH-stat apparatus properly adjusted for the end point, threshold, sampling frequency, and titrant delivery rate, the pH of the solution was typically maintained to within 0.02 pH unit of the preset value during the course of the reaction.

Product analysis. In addition to the continuous measurement of H^+ production, specific chemical methods were employed for the determination of nitrogen and sulfur product concentrations at the conclusion of the runs. Sulfate was analyzed by ion chromatography; NO_2^- by azo-dye colorimetric method; NO_3^- by reduction to NO_2^- followed by NO_2^- analysis.

Rate measurement. In kinetic studies by electrical conductivity, the reaction rate (R) can be determined, for known stoichiometry, from the time dependence of the conductivity change, i.e.,

$$R = \frac{1}{\Delta\Sigma\Lambda}\,\frac{\Delta\kappa}{\Delta t} \tag{5}$$

where $\Delta\Sigma\Lambda \equiv \Sigma_p y\Lambda_Y - \Sigma_r x\Lambda_X$ and $\Delta\kappa$ is the change of conductivity in a time interval Δt, the Λ's are the limiting molar conductivity of the ionic reactants and products, x and y are the stoichiometric coefficients of species X and Y, and r and p represent reactants and products. For the reaction rate determined by the pH-stat technique, the rate of acid production ($M\ s^{-1}$) is given by the titration rate

$$R = \frac{d[H^+]}{dt} = \frac{1}{V_\ell}\,\frac{\Delta n_{NaOH}}{\Delta t}\ , \tag{6}$$

where n_{NaOH} is the amount of titrant added (moles) and V_ℓ is the volume of liquid in the reaction (liters).

RESULTS

Product analysis and stoichiometry. The principal sulfur-containing product was determined to be $SO_4^=$; the ratio of $SO_4^=$ formed to initial S(IV) was found to be $[SO_4^=]_f/[S(IV)]_0 = 1.00 \pm 0.05$. Examination was also made for formation of dithionate, $S_2O_6^=$, which has been reported previously by Sato et al.[23] in studies at higher concentrations. $S_2O_6^=$ ion, however, was found to exhibit a markedly different elution time from that of $SO_4^=$ in ion chromatographic analysis and cannot be mistaken for $SO_4^=$.

Nitrogen products sought for were NO, NO_2^-, and NO_3^-. NO might be expected for reaction proceeding according to the stoichiometry

$$NO_2 + HSO_3^- \longrightarrow NO + H^+ + SO_4^=, \qquad [1]$$

whereas NO_2^- would be expected for the stoichiometry

$$2NO_2 + HSO_3^- + H_2O \longrightarrow 2NO_2^- + 3H^+ + SO_4^= . \qquad [2]$$

The presence of NO_3^- would be indicative of hydrolysis of NO_2,

$$2NO_2 + H_2O \longrightarrow NO_2^- + NO_3^- + 2H^+. \qquad [3]$$

In reactions [1] and [2], S(IV) is written as HSO_3^-, the principal species for the pH range investigated. If the reaction were occurring according to stoichiometry [1], the rate of NO production would be equal to the rate of H^+ production, which is directly measured; the resulting NO partial pressure in the effluent gas stream would be ~ 1 ppb, for the conditions given in Table 1. NO was not detected under these conditions; the limit of detection is such that a NO yield equal to 5% of the S(IV) oxidation rate would have been detected. The yield of NO_2^- relative to S(IV) oxidized at the end of the reaction was determined to be $[NO_2^-]_f/[S(IV)]_0 = 1.5 \pm 0.4$. Finally we note that the yield of NO_3^- was less than 2% of the yield of NO_2^-, indicating that reaction [3] is not important.

The total yield of H^+ relative to initial S(IV) concentration was determined by pH-stat measurements at pH 6.4 to be $[H^+]_f/[S(IV)]_0 = 2.5 \pm 0.4$.

TABLE 1

PRODUCTS OF REACTION OF NO_2 and S(IV)[a]

		Theoretical	
	Observed	Reaction [1]	Reaction [2]
$[SO_4^=]/[S(IV)]_0$	1.0 ± 0.05	1	1
$[NO_2^-]/[S(IV)]_0$	1.5 ± 0.4	0	2
$[H^+]/[S(IV)]_0$	2.5 ± 0.4	1	3
$\Delta(NO)/\Delta(H^+)$	0 ± 0.05	1	0
$-\Delta(NO_2^-)/\Delta(NO_2)$[b]	1.0 ± 0.18	0	1

[a] $p_{NO_2} = 1.4 \times 10^{-7}$ atm; $[S(IV)]_0 = 1.3 \times 10^{-6}$ M; $\tau_m = 2.14$ s.

[b] $[S(IV)]_0 = 1.0 \times 10^{-4}$ M.

At the S(IV) concentrations generally employed in this study, ~ 1×10^{-6} M, NO_2 depletion is insufficient to permit measurement in the effluent gas stream. To measure this depletion, S(IV) concentration was increased to 1×10^{-4} M. In these runs the NO_2 depletion $(5.6 \pm 0.4)\%$ was found identical to the rate of NO_2^- formation, $-\Delta(NO_2)/\Delta(NO_2^-) = 1.0 \pm 0.18$.

The results of the stoichiometry studies are summarized in Table 1. Also shown for comparison are the values that would be expected for reaction according to [1] and [2]. The results are consistent with stoichiometry [2] but not with stoichiometry [1].

Reaction kinetics. A variety of exploratory and systematic measurements have been made of the rate of the NO_2-S(IV) reaction. Under the conditions of these studies it is readily established that phase-mixing is not obtained. This is demonstrated by a strong dependence of the reaction rate upon τ_m (Fig. 3). (Here we plot "rate" as the rate of conductivity change.) In support of this conclusion we note that τ_r, estimated as $H_{NO_2}p_{NO_2}/R^{(aq)}$, is the order of τ_m, not satisfying the condition $\tau_r \gg \tau_m$, that is necessary for the phase-mixed condition.

The effect of mass-transport limitation may also be manifested in an apparent departure of the reaction order (slope of a log-log plot reaction rate vs. reagent concentration or partial pressure) from the true reaction order; however, it should be noted that inference of the true reaction order from such apparent orders is rarely unambiguous.[14,24] Figure 4 shows the dependence of the reaction rate on $[NaHSO_3]$ at a fixed phase-mixing condition (i.e., $\tau_m = 2.14$ s). The three NO_2 concentrations used are represented by the three straight

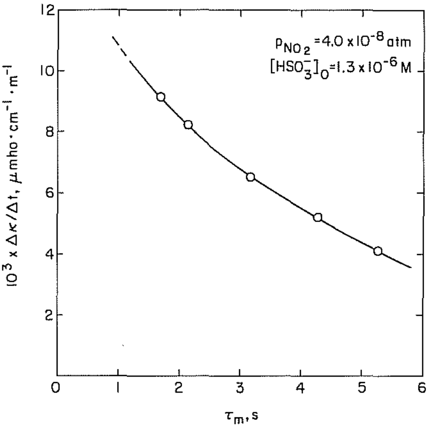

Fig. 3. Dependence of rate of NO_2-S(IV) reaction on characteristic convective mixing time of reactor, τ_m. Reaction rate is measured as increase of solution conductivity with time.

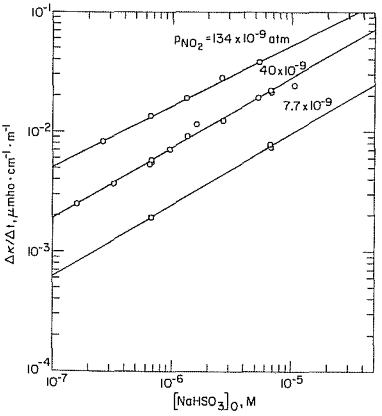

Fig. 4. Dependence of rate of NO_2-S(IV) reaction on HSO_3- concentration for indicated values of NO_2 partial pressure. τ_m = 2.14 s.

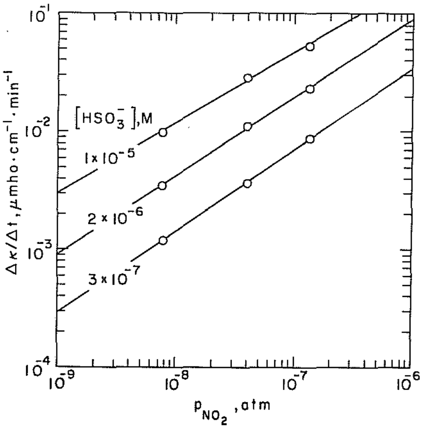

Fig. 5. Dependence of rate of NO_2-S(IV) reaction on NO_2 partial pressure for indicated values of HSO_3- concentration. τ_m = 2.14 s.

lines. The slopes (apparent reaction orders with respect to HSO_3^-) are 0.5 to 0.6. Figure 5 is a plot (also at fixed τ_m) of the dependence of rate on p_{NO_2}; the apparent reaction orders are 0.65 to 0.75. Values of reaction order less than unity are suggestive (but not conclusively) of a first-order reaction in the slow reaction regime,[26] i.e., intermediate between phase-mixed and convective controlled.

In order to examine the reaction rate and mechanism more fully a systematic series of initial rate measurements was conducted at fixed pH (6.40 and 5.80) using the pH-stat technique. Reactions were carried out with $[S(IV)]_0$ = 1.3 x 10^{-6} M and p_{NO_2} = 1.4 x 10^{-7} and 4.0 x 10^{-8} atm; τ_m was varied from 1.7 to 5.3 s. The experimental results are presented in Table 2 and are discussed below in terms of reaction mechanisms.

Effect of light. To examine whether the reaction rate was affected by room lights, (standard fluorescent lamps), comparative rate measurements were made both in the presence and absence of light. The reactions conducted at τ_m = 2.14 s, p_{NO_2} = 140 ppb and [S(IV)] = 1.3 x 10^{-6} M gave rates for "light" and "dark" reactions within 1% of the averaged value. It is concluded that the reaction rate is not affected by room lights.

TABLE 2

REACTION RATE (≡ $d[H^+]/dt$) OF NO_2 + S(IV)[a]

τ_m, s	$d[H^+]/dt$, 10^{-10} M s^{-1}		
	pH = 6.40		pH = 5.80
	p_{NO_2} = 4.0×10^{-8} atm	1.4×10^{-7} atm	~~1.4×10^{-7}~~ atm 4×10^{-8}
1.69	7.60	17.0	3.27
2.14	5.28	12.4	2.48
3.17	3.35	7.69	1.79
4.27	2.52	6.25	1.23
5.26	-	-	0.91

[a] Repeatability is typically 6%; $[HSO_3^-]_0$ = 1.3×10^{-6} M; t = 22.0 ± 0.1°C.

DISCUSSION

Interpretation of kinetic studies. Several attempts have been made, none entirely successfully, to identify a reaction rate law that is consistent with the measured dependence of the reaction rate upon reagent concentrations and convective mixing time constant.

As an initial model of the mechanism, we assumed the reaction to be first order in both S(IV) and NO_2. The sequence of reactions corresponding to this mechanism, including establishment of Henry's law for NO_2 at the interface and convective mass transport of dissolved NO_2, is

$$NO_2(g) \overset{H_{NO_2}}{=} NO_2(s)$$

$$NO_2(s) \underset{k_m}{\overset{k_m}{\rightleftarrows}} NO_2(aq) \qquad [4]$$

$$NO_2(aq) + S(IV) \xrightarrow{k^{(2)}} \text{Products} \qquad [5]$$

Here $NO_2(s)$ represents the surface aqueous phase concentration of NO_2. Under assumption of Henry's law equilibrium at the gas-aqueous interface and steady-state for $[NO_2(aq)]$ as determined by [4] and [5], this mechanism gives rise, for constant [S(IV)], to a linear dependence of the quantity $(R/p_{NO_2})^{-1}$ upon τ_m,

$$\left(\frac{R}{p_{NO_2}}\right)^{-1} = \frac{1}{k^{(2)}[S(IV)]H_{NO_2}} + \frac{1}{H_{NO_2}}\tau_m \qquad (7)$$

Erratum

Table 2, col. 4, column head should read 4×10^{-8} atm

Equation (7) predicts a linear relation, which should permit evaluation of the two parameters $k^{(2)}$ and H_{NO_2} from the intercept and slope. Plotting the data according to (7), Fig. 6, revealed that although straight lines can be drawn through each individual set of data points, the slopes are somewhat different for different p_{NO_2} and pH. The values of the Henry's law coefficient of NO_2, derived from the slopes of the three data sets in Fig. 6, under the assumption of stoichiometry [2] are (4.3 to 9) x 10^{-3} M atm^{-1}. (It should be noted that under this assumption $R = 1/3\ d[H^+]/dt$). These values bracket that given in our study of the NO_2 disproportionation reaction,[14] (7.0 ± 0.5) x 10^{-3} M atm^{-1}, and are close to the value recommended by Schwartz and White,[24] (1.0 ± 0.3) x 10^{-2} M atm^{-1}, based upon an extensive review of NO_2 aqueous kinetics. However, the fact that these values seem to be dependent upon the reaction conditions (i.e., p_{NO_2}, pH) suggests that the treatment of first-order reaction in NO_2 is not totally satisfactory.

A second feature of Fig. 6 is the long extrapolation to obtain the intercept; i.e., the intercept is not well defined. In turn, as is seen in (7), information pertinent to the intrinsic reaction kinetics is not highly precise. From Fig. 6 it is possible to estimate an upper-limit intercept (~ 0.2 x 10^2 atm s M^{-1}) that can be differentiated from zero, as limited by the scatter of the experimental data. In turn a lower-limit effective second-order rate constant for the NO_2 - S(IV) reaction (according to stoichiometry [2]) is estimated as 2 x 10^6 M^{-1} s^{-1}.

Since stoichiometry [2] consumes 2 moles of NO_2 for every mole of S(IV) oxidized, it may be reasonable to test the data against a rate law that is second-order in NO_2 concentration, e.g., $R = k^{(3)} [NO_2]^2[S(IV)]$, where $k^{(3)}$ is a third order rate constant. Because [S(IV)] is constant, the rate law can be reduced to $R = k^{(2)'}[NO_2]^2$ where $k^{(2)'}$ is a pseudo-second-order rate coefficient. In an analysis[14] of a reaction of this type coupled to mass transfer it was shown that the apparent reaction order is always greater than 1, for mass-transfer regime ranging from phase-mixed to molecular diffusive controlled. The apparent reaction order with respect to p_{NO_2} of the NO_2-S(IV) system, shown in Fig. 7, ranges from 0.6 to 0.7. This rules out a second-order dependence of reaction rate on NO_2.

Additional Observations. In addition to the foregoing measurements, we also report here some observations that suggest a complexity to the NO_2 - S(IV) reaction beyond that of an overall-second-order rate-controlling reaction. In studies in which the NO_2 flow was turned off (N_2 still flowing) prior to

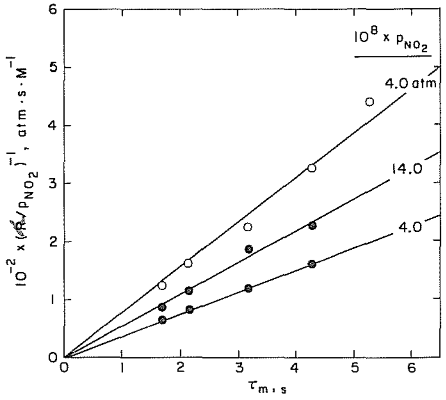

Fig. 6. Plot of rate of NO_2-S(IV) reaction according to model for a pseudo first-order reaction. Open circles, pH = 5.80; closed circles, pH = 6.40.

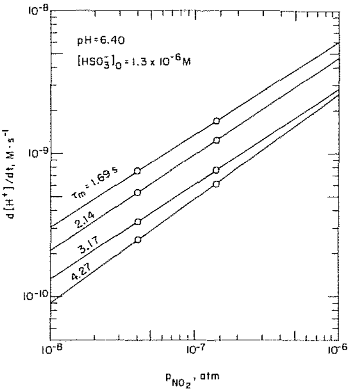

Fig. 7. Apparent order of NO_2-S(IV) reaction in NO_2.

complete reaction of S(IV) it was observed that the reaction (i.e., generation of H^+) proceeded for some time (~ 10 minutes) despite the fact that physically absorbed NO_2 would be purged in several seconds. Moreover, the extent of subsequent reaction greatly exceeded the amount of dissolved NO_2. This behavior is indicative of the participation of an intermediate, which may be simple or may be a free-radical chain carrier, consistent with the small but discernable induction period observed. Additionally, it was observed that the residual increase of conductivity (after the NO_2 is shut off) is much smaller if NO (140 ppb) is present throughout the course of the run. However, if NO is introduced only at the time the NO_2 is shut off, the residual conductivity increase is significantly accelerated, although the total increase remains unchanged.

Atmospheric Implications. Although it may not be justified, in the absence of an established mechanism, to extrapolate reaction rates beyond the conditions of measurement, we nonetheless proceed to do so here in order to examine the magnitude of possible SO_2 oxidation rate by the NO_2 - S(IV) aqueous-phase reaction under atmospheric conditions. A significant oxidation rate evaluated in this way gives justification for the potential importance of the reaction and for the continued investigation of the mechanism and kinetics.

The rate of reaction may be evaluated in terms of partial pressures of gas-phase reagents as

Erratum

Fig. 6, left axis label should read: $10^{-2} \times \left((d[H^+]/dt)/p_{NO_2}\right)^{-1}$, atm s M^{-1}

$$R = 3k^{(2)}\, H^*_{S(IV)}\, H_{NO_2}\, p_{NO_2}\, p_{SO_2}\ ,$$

where $H^*_{S(IV)}$ is the pH-dependent effective Henry's law coefficient of SO_2.[27] Here it has been assumed that there is no mass-transfer limitation to the rate of reaction because of the small size of drops contained within clouds.[28] Evaluation of the aqueous-phase rate at pH 6, employing the lower-limit values of $k^{(2)}$ given above ($2 \times 10^6\ M^{-1}\ s^{-1}$), yields $R = 9 \times 10^8\ p_{NO_2}\ p_{SO_2}$. For $p_{NO_2} = p_{SO_2} = 3$ ppb, $R^{(aq)} = 3 \times 10^{-5}\ M\ hr^{-1}$. As noted this figure represents a lower-limit rate, although it must be emphasized that the evaluation remains open to question because of the unresolved mechanism.

SUMMARY

The gas-liquid oxidation reaction of sulfur(IV) by NO_2 has been studied at neutral pH's, i.e., 6.40 and 5.80, and low reagent concentrations, i.e., $[S(IV)] \cong 1 \times 10^{-6}$ M and $p_{NO_2} \cong 1 \times 10^{-7}$ atm. Major products found under these reaction conditions are H^+, NO_2^-, and $SO_4^=$, and the stoichiometry is consistent with $2NO_2 + HSO_3^- + H_2O \rightarrow 3H^+ + 2NO_2^- + SO_4^=$. The reaction rate was determined by following acid production via a pH-stat apparatus as a function of mixing time constant of the gas and liquid phases ($\tau_m = 1.6 - 5.3$ s). The reaction rate was found to be significantly controlled by mass-transfer, even at the low reagent concentrations employed, and the extrapolation to the phase-mixed condition ($\tau_m = 0$) was able to yield only a lower-limit reaction rate constant. This rate constant, for reaction rate interpreted according to an overall second-order rate expression ($R = k^{(2)}[S(IV)][NO_2]$), was 2×10^6 $M^{-1}\ s^{-1}$ at both pH 6.40 and 5.80. However, evidence is represented of a comple reaction mechanism apparently involving intermediates.

An estimate of the contribution of NO_2-S(IV) reaction to acid production in cloud water made using the lower-limit second-order rate constant is 3×10^{-5} M hr^{-1} at pH 6 and $p_{SO_2} = p_{NO_2} = 3 \times 10^{-9}$ atm. Although the analysis is preliminary because of the use of a lower-limit value for $k^{(2)}$ and the uncertainties in reaction mechanism, such a rate would constitute a significant contribution to cloud acidification.

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DISCUSSION

D.A. HEGG: The order of the proposed reaction appears to be less than second, i.e., less than first order in both NO_2 and S(IV). If one uses the data in Figure 7, one can extrapolate to $\tau_m = 0$ and obtain the order of the reaction with respect to NO_2 under, supposedly, phase-mixed conditions. It is still less than unity and suggests that extrapolation to low NO_2 pressures assuming a first order dependence is not correct. Would you comment.

Y.-N. LEE: The magnitudes of the slopes of log(rate) vs. log(p_{NO_2}) of 0.6 to 0.7 shown in Figure 7 certainly would appear to rule out a reaction order in NO_2 as great as 2. Without having established a mechanism that would give a theoretical basis for extrapolating these slopes to $\tau_m = 0$ [cf. eq. (7) for reaction first order each in NO_2 and S(IV)], we are hesitant to make such an extrapolation, and consequently do not think that these data argue strongly against a first-order dependence on NO_2. In the absence of an established mechanism extrapolation of the rate law to low partial pressure of NO_2 is something of an act of faith. We chose to do so in order to examine the possible importance of this reaction at representative atmospheric concentrations, but we agree that it is important to determine the details of the mechanism.

D.A. HEGG: What is the basis for the assertion in the discussion of Figure 6 that $\sim 0.2 \times 10^2$ atm s M^{-1} is the upper limit of $(R/p_{NO_2})^{-1}$? This value cannot be derived from the data presented.

Y.-N. LEE: The value of 0.2×10^2 atm s M^{-1} is a fairly generous estimate of the upper limit of the intercept, based on the scatter of the data. I would emphasize that plotting the data and extrapolating to $\tau_m = 0$ in this way is theoretically justified only for a first-order reaction in NO_2. I would also note that an upper limit in this intercept translates into a lower-limit estimate for the second-order rate constant $k^{(2)}$.

D.A. HEGG: The data shown in Table 2 suggest a pH dependence for the reaction. Because an appreciable fraction of the S(IV) will be present as $SO_3^=$ under the experimental conditions (~16% at pH 6.4 and ~4% at pH 5.8), the $SO_3^=$ may be considerably more reactive with respect to NO_2 than HSO_3^-. Indeed the factor of ~2.5 decrease in the rate from pH 6.4 to 5.8 is plausibly no different from the factor of ~4 decrease in $SO_3^=$ between the sample pH's (you do not give the uncertainty associated with the rate measurements). If so, this would suggest that $SO_3^=$ is the oxidized species in the reaction and that the rate coefficient for the reaction must be far larger than the quoted lower limit if the reaction is to be of significance under typical atmospheric conditions (pH ~5.0). Would you comment.

Y.-N. LEE: As noted by equations (2)-(4) we choose to present the reaction rate expressions in terms of total dissolved S(IV) rather than the individual species. This results in a pH-dependence in the effective rate coefficient $k^{(2)}$. The decrease in $k^{(2)}$ between pH 6.4 and 5.8 is suggestive that $SO_3^=$ may be the predominant reactive S(IV) species in this reaction. We felt, however, that it was somewhat premature to speculate because of the unsettled rate law as well as the fact that only two pH values have been examined. In order to address the importance of this reaction at lower pH we feel it is necessary to extend kinetic studies to such pH values.

As indicated in Table 2, the reproducibility of individual rate determination was typically 6%.

A.W. GERTLER: You do not adequately address the atmospheric implications of this reaction and how it ties in with scavenging.

Y.-N. LEE: The example treated in the Discussion ($p_{NO_2} = p_{SO_2} = 3$ ppb) gave rise to an aqueous-phase reaction rate of $\geq 3\text{x}10^{-5}$ M hr^{-1} at pH 6. For a liquid water content of 1 cm^3 m^{-3}, this rate would correspond to a SO_2 oxidation rate of $\geq$ 25% hr^{-1}. The lower bound results from the use of a lower-limit value for $k^{(2)}$.

A.W. GERTLER: The reaction was carried out in an N_2 atmosphere. This is good from a mechanistic standpoint; however, it makes it difficult to evalute its overall atmospheric importance.

Y.-N. LEE: In view of possible free-radical paths for S(IV) autoxidation and the possible role of NO_2 as an initiator we explored the effect of O_2 by carrying out the oxidation in air (ultra high purity) vs. N_2. Shifting from N_2 to air carrier resulted in an increase in the oxidation rate of no more than 10%.

A.W. GERTLER: You assume there is no mass-transport limitation to the rate of reaction because of small droplet sizes in clouds. Since you have measured only a lower bound for the rate, it could very well be false.

Y.-N. LEE: You are quite right. In fact for the conditions of the example given in the Discussion, there would be a roughly 20% decrease in the rate from the phase-mixed situation, because of aqueous-phase mass-transport limitation of NO_2; this is for a cloud droplet of 10 μm diameter. Mass-transport limitation becomes more significant for larger drop diameter, greater rate constant, or greater SO_2 concentration.

A.W. GERTLER: You depend on a pH probe response to determine the rate of H^+ formation (or change). The time frame you are working in is on the order of seconds (i.e., Figs. 3 and 6). The response of the probe may affect the absolute value of the rate measurement since you are not operating in steady state or equilibrium conditions.

Y.-N. LEE: I think perhaps you are mis-interpreting these figures. The abscissa of these figures is the characteristic time of mixing of the reactor, not time in the course of a kinetic run. In fact pH changes are quite slow--see Table 2, in which the fastest rate reported is $1.7\text{x}10^{-9}$ M(H^+) sec^{-1}. The pH electrode rapidly responds to pH changes induced by the reaction, as does the entire servo system of the pH-stat.

A.W. GERTLER: You depend on measurement of characteristic times (τ_r and τ_m) for evaluating the reaction kinetics. τ_r depends on H_{NO_2} which is not well known since it is difficult to determine for the case where you have simultaneous dissolution and reaction. This is evidenced by the observed variation of H_{NO_2} during this study. This in turn leads to uncertainties in your earlier results for H_{NO_2} using this technique.

Y.-N. LEE: Actuallly we feel that the agreement between the several values for H_{NO_2} that result from analysis of these data and the value reported earlier was rather good, considering the present rudimentary understanding of the chemical mechanism of the NO_2-S(IV) reaction.

A.W. GERTLER: Not knowing the reaction mechanism - you suggest some intermediate species may be involved. I wonder if the platinum electrode of the conductivity meter could play a role in the observed rate.

Y.-N. LEE: We are confident this is not the case. The observation of continued reaction after NO_2 was turned off was observed by both conductivity and pH-stat detectors and was not observed for other systems we have studied, e.g., reactive dissolution of NO_2 and the reaction of NO + NO_2 to produce HNO_2.

J.D. SINCLAIR: Why did you use ion chromatography to analyze for sulfate but not for nitrate? They are analyzed on the same column and nitrate has a shorter retention time.

Y.-N. LEE: Since the retention times for NO_3^- and $SO_4^=$ are rather close to each other, ion chromatography would not be sensitive for the detection of NO_3^- when $SO_4^=$ is present in much larger amounts.

W.L. CHAMEIDES: Would you speculate on the elementary kinetics of this reaction?

Y.-N. LEE: We would speculate that NO_2 forms an intermediate with a S(IV) species, which breaks down to give products upon reacting with either another intermediate or a NO_2 molecule. Also, we suspect that $SO_3^=$ may be the dominant reacting species from our limited pH dependence study.

T. MILL: Could nitrous acid be an intermediate and the actual oxidizing species?

Y.-N. LEE: We don't think so, because the formation of nitrous acid or nitrite from NO_2 would require the concomitant production of nitrate, which is excluded as a product of reaction.

P. GRENNFELT: Please, can you comment on the consequences of the NO_2^- formation in the droplets? Will this give significant concentrations of HNO_2 in the atmosphere?

Y.-N. LEE: Nitrite concentration would build up comparably to sulfate to the extent that reaction [2] is occurring in the atmosphere and, depending on pH, might exert a significant vapor pressure as HNO_2. At pH 6 the partial pressure of HNO_2 above a 10^{-5} M NO_2^- solution would be 0.5 ppb. However it should be noted that NO_2^- and/or HNO_2 would also be subject to oxidation (e.g., by O_3 and H_2O_2) or reduction (e.g., by organic compounds) as well as to photolysis. The absence of NO_2^- in cloud or rain water therefore might not be a sufficient argument against the occurrence of reaction [2] in the atmosphere.

W.G.N. SLINN: Can you speculate on the applicability of your study to the interpretation of Grennfelt's results?

Y.-N. LEE: The potential for NO_2-S(IV) reaction in liquid water exists in any situation where these materials coexist, including plant tissues and fluids. However we do not know at the present time the nature of other reactions of these gases with other substances present in plant tissues and fluids that would compete with this reaction.

W.G.N. SLINN: Can you tell us physicists what the Henry's law coefficient of NO_2 is in dimensionless units, and why do you use the unit molar per atmosphere?

Y.-N. LEE: I would turn the question back to you: Why do you use dimensionless units? The conversion factor is RT, where R is the universal gas constant and T is the absolute temperature. But you must be careful, since frequently the dimensionless quantity is inverted, though it is often hard to tell because it is dimensionless. Use of a Henry's law coefficient with dimension removes this ambiguity. The unit molar per atmosphere corresponds to the standard states of 1 atm pressure and 1 molar solution. The Henry's law coefficient in these units is thus related, in the usual way for any equilibrium constant, to the free energy of dissolution.

The Henry's law coefficient of NO_2, *ca.* $7\text{x}10^{-3}$ M atm^{-1}, is characteristic of a rather insoluble gas, somewhat more soluble than O_2 ($1.3\text{x}10^{-3}$ M atm^{-1}) and somewhat less soluble than CO_2 ($4.0\text{x}10^{-2}$ M atm^{-1}). It must be emphasized that this represents the reversible physical solubility and not any enhanced solubility due to chemical reaction.

Erratum

Fig. 6, left axis label should read: $10^{-2} \times \left((d[\mathrm{H}^+]/dt)/p_{\mathrm{NO}_2} \right)^{-1}$, atm s M^{-1}

Erratum

Equation 4 should read:

$$k^{(2)} = \frac{k_0 + k_1 K_1/[\mathrm{H}^+] + k_2 K_1 K_2/[\mathrm{H}^+]^2}{1 + K_1/[\mathrm{H}^+] + K_1 K_2/[\mathrm{H}^+]^2}$$

Erratum

Table 2, col. 4, column head should read 4×10^{-8} atm

KINETICS OF OXIDATION OF AQUEOUS SULFUR(IV) BY NITROGEN DIOXIDE

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