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THE IMPORTANCE OF SOOT PARTICLES AND NITROUS ACID IN OXIDIZING SO$_2$
IN ATMOSPHERIC AQUEOUS DROPLETS

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Abstract

Soot particles catalyze the oxidation of SO$_2$$\cdot$H$_2$O, HS$_3$O$_5^-$, and SO$_4^{2-}$ species at the same rate; however, the rate of production of sulfate is not constant at a constant partial pressure of SO$_2$. The rate decreases as the pH decreases because the total concentration of S(IV) in aqueous droplets decreases as the pH decreases. The sulfate production rate has a complex dependence on the concentration of S(IV) and is not very sensitive to a change in SO$_2$ concentration at normal atmospheric conditions.

The oxidation of SO$_2$ by HNO$_2$ in atmospheric water droplets first produces hydroxylamine disulfonate, which undergoes acid-catalyzed hydrolysis to form sulfate and hydroxylamine monosulfonate. The latter can react with HNO$_2$ and would then end up as nitrous oxide and sulfate.

Model calculations have been made comparing the relative importance of the sulfate production mechanism by soot particles and nitrous acid with other mechanisms involving liquid water. The results indicate that both soot and HNO$_2$ mechanisms can be very important when the lifetime of the atmospheric aqueous droplets is long.
Introduction

Atmospheric sulfate, a major constituent in ambient aerosol particles, is presumably formed by the oxidation of SO₂. The dominant mechanisms responsible for this transformation have not yet been established. One set of mechanisms thought to be important involves the dissolution of SO₂ in water droplets. When liquid water is present—as in clouds, fog, and plumes—the atmospheric SO₂ can dissolve in the droplets and be oxidized to sulfate. Aqueous oxidation mechanisms involving trace metal catalysts such as Fe³⁺ and Mn²⁺ and oxidizing species like O₂, O₃, and H₂O₂ have been studied and compared (Beilke and Gravenhorst, 1978; Chang et al., 1978; Hegg and Hobbe, 1978; Middleton et al., 1980; Penkett et al., 1979). We have recently identified two previously unrecognized mechanisms which could play an important role in terms of sulfate aerosol formation: 1) oxidation of SO₂ in water droplets containing soot particles (Chang et al., 1978; Brodzinsky et al., 1980), and 2) oxidation of SO₂ by HNO₂ in water droplets (Oblath et al., 1980).

This paper discusses the implications of the kinetic results of these two systems on atmospheric aerosol formation and presents the results of a model calculation which compares the relative importance of various sulfate production mechanisms involving liquid water.

Review of Previous Results

1. Oxidation of SO₂ in water droplets containing soot particles. Soots that were produced by the combustion of acetylene and natural gas and from a diesel engine were used in the kinetic study and showed the same reaction characteristics as those obtained by suspensions of similar concentrations of activated carbon (Nuchar C-190). Since it is difficult to reproducibly prepare soot suspensions, suspensions of Nuchar were used as a model system. The majority of results are therefore obtained from the model system. The kinetic
data indicate that catalytic oxidation of SO$_2$ on soot in aqueous solution has the following characteristics: 1) the reaction rate is independent of pH (pH < 7.6), and therefore SO$_2$·H$_2$O, HSO$_3^-$, and SO$_2^{2-}$ are indistinguishable in terms of oxidation on carbon surfaces; 2) the reaction rate is first order and 0.69$^{th}$ order with respect to the concentration of carbon and dissolved oxygen respectively; 3) the reaction rate has a complex dependence on the concentration of S(IV), ranging between a second and zeroth order reaction as the S(IV) concentration increases; and 4) the activation energy of the reaction is 11.7 kcal/mole. The reaction rate law can be expressed by the following equation:

$$\frac{d[S(IV)]}{dt} = k[C_x][O_2]^{0.69} f[S(IV)]$$

where $f[S(IV)] = \left( \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} \right)$,

$[C_x] = \text{grams of carbon particles/L}$,

$[O_2] = \text{moles of dissolved oxygen/L}$, and

$[S(IV)] = \text{total moles of S(IV)/L}$.

The rate constants for Nuchar C-190 were determined as follows:

$$k = 9.04 \times 10^3 \ e^{-5888/T} \ \text{moles}^{-1} \text{L} \cdot \text{mol}^{-1} \cdot \text{g} \cdot \text{sec} \ (T \text{ is temperature in Kelvin})$$

$$\alpha = 1.50 \times 10^{12} \ \text{L}^2/\text{mole}^2$$

$$\beta = 3.06 \times 10^6 \ \text{L/mole}.$$

The dependence of the rate of formation of sulfate on the partial pressure of SO$_2$ ($P_{SO_2}$) in the atmosphere can be obtained from Eq. (1). Because the effect of $P_{SO_2}$ on the rate is contained in $f[S(IV)]$, we illustrate the relationship of $f[S(IV)]$ with $P_{SO_2}$ and pH of the aqueous droplets as shown in Figs. 1 and 2. The rate of production of sulfate (because the rate is linearly proportional to $f[S(IV)]$), decreases as the pH decreases at a given $P_{SO_2}$. The magnitude of $f[S(IV)]$'s changing per unit pH change is much
larger at a lower $P_{SO_2}$. Also $f[S(IV)]$ (or the rate) depends only slightly on $P_{SO_2}$ under most atmospheric conditions when $P_{SO_2}$ is between 1 and 10 ppb and the pH ranges between 5 and 6. $f[S(IV)]$ increases only 1/10 and twofold respectively at pH of 6 and 5 when $P_{SO_2}$ increases from 1 to 10 ppb. However, $f[S(IV)]$ depends strongly on $P_{SO_2}$ when the pH is low.

The catalytic oxidation of sulfurous acid on carbon particles of different origins shows the same kinetic behavior. However, the rate constants of several different types of carbon particles were studied and found to differ from type to type. In principle, the reaction rate should be proportional to the concentration of active sites on the carbon particles, rather than to the concentration of carbon particles. The number of active sites per unit mass of carbon particles is different from type to type and is not necessarily proportional to the surface area. Sidelewski (1965) has shown, by means of the electron paramagnetic resonance method, that free electrons on carbon particles can serve as active centers for the adsorption of oxygen molecules and for the oxidation of $SO_2$. The concentration of free electrons is related to the origin and thermal history of the carbon particles.

It is therefore erroneous to conclude a rate constant for atmospheric soot particles in general because these particles may arise from the combustion of different types of fossil fuel under different combustion conditions and thus possess a different catalytic activity. The rate constants used in these calculations represent the average value between the values of natural gas and of acetylene soot particles produced under rich flame conditions. This value (pre-exponential factor in Eq. [1]) is five times larger than that determined for Nuchar C-190.

2. Oxidation of $SO_2$ by $HNO_2$ in water droplets. Many concurrent and consecutive chemical reactions can occur as a result of the interaction between
nitrous acid and sulfurous acid (Raschig, 1924; Latimer and Hildebrand, 1951; Duecker and West, 1959). Hydroxylamine disulfonate (HADS) is the first stable product under most atmospheric conditions:

$$\text{HNO}_2 + 2\text{HSO}_3^- \rightarrow \text{HON(SO}_3)_2^- + \text{H}_2\text{O}.$$  (a)

The formation kinetic of HADS has been studied in our lab and consists of three concurrent processes. The reaction rate law can be expressed as:

$$\frac{d[\text{HADS}]}{dt} = k_0[H^+][\text{NO}_2^-] + k_1[H^+][\text{NO}_2^-][\text{HSO}_3^-] + k_{II}[\text{NO}_2^-][\text{HSO}_3^-]^2,$$  (2)

where

$$k_0 \approx 8 \times 10^5 \text{ liters}^2/\text{mole-sec (at 295}^\circ\text{K)},$$

$$k_1 = 3.7 \times 10^{12} \text{ e}^{-6100/T} \text{ liter}^2/\text{mole}^2\cdot\text{sec},$$

$$k_{II} = 9.0 \times 10^{-4} \text{ e}^{2.1(\mu)^{1/2}} \text{ liter}^2/\text{mole}^2\cdot\text{sec (T is temperature in Kelvin, and } \mu \text{ is ionic strength in moles/liter).}$$

$k_1[H^+][\text{NO}_2^-][\text{HSO}_3^-]$ and $k_{II}[\text{NO}_2^-][\text{HSO}_3^-]^2$ are two major processes under the conditions of the experiment (nitrite concentration, $10^{-2}-10^{-3}$ M; sulfite concentration, $10^{-2}-10^{-1}$ M; and pH, 4-7. The determination of these two processes has clarified the disagreement of previous kinetic results among Seel and Knorre (1961), Seel and Degener (1956), and Yamamoto and Kaneda (1959). In addition to these two processes, a third process, $k_0[H^+][\text{NO}_2^-]$ has been identified not only by us but also by Seel and Degener (1956), and Yamamoto and Kaneda (1959). This third process was found to be independent with respect to the sulfite concentration. We tentatively assumed that this rate law will still hold in an atmosphere where concentrations of both nitrite and sulfite are several orders of magnitude lower than the concentrations used when this rate equation was derived. Therefore, a rate law which includes all three terms (Eq. 2) is used in our model calculations.
HADS can undergo further reaction, either hydrolysis or sulfonation. Hydrolysis of HADS (Naiditch and Yost, 1941) produces hydroxylamine monosulfonate (HAMS) and sulfates:

\[
\text{HON(SO}_3\text{)}^\text{-2} + \text{H}_2\text{O} \rightarrow \text{H}^+ \rightarrow \text{HONOHSO}_3^- + \text{HSO}_4^- \quad \text{(b)}
\]

Sulfonation of HADS (Yamamoto and Kaneda, 1959; Seel and Knorre, 1961) yields amine trisulfonate:

\[
\text{HON(SO}_3\text{)}_2^\text{-2} + \text{HSO}_3^- + \text{N(SO}_3\text{)}_3^\text{-3} + \text{H}_2\text{O} \quad \text{(c)}
\]

The extent to which HADS will undergo hydrolysis (H) and sulfonation (S) can be represented by the following equation:

\[
\frac{H}{S} = \frac{2.10 \times 10^{11} e^{-17600/RT}[H^+] + 1.67 \times 10^{11} e^{-23000/RT}}{3.4 \times 10^{10} e^{-19200/RT}[\text{HSO}_3^-]} \quad \text{(3)}
\]

Figure 3 shows the \(\frac{H}{S}\) ratio against the pH of the solution at three different partial pressures of \(\text{SO}_2\) at 25°C. Hydrolysis is more favorable at higher solution acidity, whereas sulfonation becomes more important at higher concentrations of \(\text{SO}_2\). It is obvious that the major fraction of HADS undergoes hydrolysis under most atmospheric conditions.

If we let the rate of formation (Eq. 2) equal the rate of destruction (hydrolysis), we can calculate the steady-state concentration of HADS in aqueous droplets at 295 K by the following equation:

\[
[HADS]_{s.s.} = \frac{8 \times 10^5 [H^+]^2 [\text{NO}_2^-] + 3.87 \times 10^3 [H^+] [\text{NO}_2^-] [\text{HSO}_3^-] + 9.0 \times 10^{-4} [\text{NO}_2^-] [\text{HSO}_3^-]^2}{\{1.92 \times 10^{-2} [H^+] + 1.52 \times 10^{-6}\}} \quad \text{(4)}
\]
This steady-state concentration is the upper limit of HADS in aqueous droplets, because the rate of destruction by way of hydrolysis will become larger than the rate of formation if the concentration of HADS is larger than this steady-state concentration. Figure 4 shows the steady-state concentration of HADS as a function of pH at two atmospheric conditions.

HAMS, a product resulting from the hydrolysis of HADS, can either undergo further hydrolysis,

$$\text{HONH}^+\text{SO}_3^- + \text{H}_2\text{O} \rightarrow \text{NH}_3\text{OH}^+ + \text{SO}_4^{2-},$$  \hspace{1cm} (d)

or react with nitrous acid to produce nitrous oxide and sulfates,

$$\text{HONH}^+\text{SO}_3^- + \text{HNO}_2 \rightarrow \text{N}_2\text{O}^+ + \text{HSO}_4^- + \text{H}_2\text{O}.$$  \hspace{1cm} (e)

Although a complete rate law has not been determined for both reactions, indications from the kinetic study (Naiditch and Yost, 1941; Seel and Pauschmann, 1962) are that the reaction with nitrous acid is much more important than the hydrolysis. Therefore, it appears that the reaction between SO$_2$ and HNO$_2$ in atmospheric water droplets will first produce HADS (a), which undergoes acid-catalyzed hydrolysis to form HAMS and sulfate (b). HAMS then reacts with nitrous acid and ends up as nitrous oxide and sulfate (e). The total stoichiometric equation can be expressed as

$$2\text{HNO}_2 + 2\text{HSO}_3^- \rightarrow \text{N}_2\text{O}^+ + 2\text{HSO}_4^- + \text{H}_2\text{O}.$$  \hspace{1cm} (f)

If the reaction is at steady-state condition, then two moles of sulfate will be produced (b and e) for every mole of HADS consumed (or produced), assuming that the reaction rate between HAMS and nitrous acid is very large.
Comparison of Sulfate Production Mechanisms

We have carried out a box-type calculation to compare the relative importance of sulfate production mechanisms by soot particles and nitrous acid with other mechanisms involving liquid water. The systems considered in the batch reactor include the \( \text{SO}_2-\text{CO}_2-\text{H}_2\text{O}(\%) \)-air and any of the oxidizing agents such as \( \text{O}_2, \text{O}_3, \text{HNO}_2 \), or catalysts such as \( \text{Fe}^{+++}, \text{Mn}^{++} \), and soot. The role of \( \text{NH}_3 \) is investigated in these reactions. The kinetics of each of these processes other than soot-catalyzed and \( \text{HNO}_2 \) reactions have been studied by many investigators. The results of Beilke et al. (1975), Erickson et al. (1977), Freiberg (1975), and Matteson et al. (1969) for oxygen, ozone, iron, and manganese systems respectively were used in this calculation.

All the oxidation mechanisms considered except \( \text{Mn}^{++} \) are pH dependent. Most of these mechanisms have lower oxidation rates at a lower pH, but some are more sensitive to the change in pH than others. The \( \text{HNO}_2 \) mechanism shows a larger oxidation rate when the solution is more acidic, however. The following initial conditions were used in the calculation: liquid water, 0.05 g/m\(^3\); \( \text{SO}_2 \), 0.01 ppm; \( \text{O}_3 \), 0.05 ppm; and \( \text{CO}_2 \), 0.000311 atm. Concentrations of particulate Fe and Mn of 250 ng/m\(^3\) and 20 ng/m\(^3\) respectively were assumed. However, only 0.13% of the total iron and 0.25% of the manganese are water soluble, according to Gordon et al. (1975). The concentrations of soot and \( \text{HNO}_2 \) were taken as 10 \( \mu \text{g/m}^3 \) and 8 ppb respectively. The latter corresponds to 25 ppb of \( \text{NO} \) and 50 ppb of \( \text{NO}_2 \) at equilibrium conditions (Schwartz and White, 1980). For \( \text{NH}_3 \) a concentration of 5 ppb was used, which is higher than the highest equilibrium partial pressure of \( \text{NH}_3 \) over the United States as calculated by Lau and Charlson (1977). Tables 1 and 2 list the equilibrium equations and oxidation rate equations used for this comparative study.

The following assumptions were made in the calculations:

1. The size of liquid water drops suspended inside the box is so small
that the absorption rate of gaseous species (SO$_2$, NH$_3$, and HNO$_2$) is governed by chemical reactions.

2. There is no mass transfer of any species across the box during the reaction; therefore, the SO$_2$ (and NH$_3$ or HNO$_2$) in each box is depleted with time. The mass balance of the SO$_2$, CO$_2$, NH$_3$, and HNO$_2$ is always maintained (i.e.,

\[ \Delta [SO_2]_g = \Delta [SO_2 \cdot H_2O] + \Delta [HSO_3^-] + \Delta [SO_3^{2-}] + \Delta [SO_4^{2-}]; \Delta [CO_2]_g = \Delta [CO_2 \cdot H_2O] + \Delta [HCO_3^-] + \Delta [CO_3^{2-}]; \Delta [NH_3]_g = \Delta [NH_3 \cdot H_2O] + \Delta [NH_4^+] + \Delta [HNO_2] + \Delta [NO_2^-] + 2\Delta [N_2O]_g; \] all units are in mole).

3. The growth of liquid water droplets due to the vapor pressure lowering effect of the sulfuric acid formed in the droplets is neglected.

The rate of sulfate production is determined by a calculation scheme involving a combination of equilibrium and kinetic steps. Equilibrium between SO$_2$ in the gas phase and sulfur (IV) in the droplet is several orders of magnitude faster than oxidation of sulfur (IV) to sulfate (Beilke and Gravenhorst, 1977). Similar assumptions were made regarding NH$_3$ and CO$_2$ gases. Therefore, initially gases are taken to be in equilibrium with the aerosols. Then the formation of sulfate proceeds by the given time-dependent production rate. The increase in the sulfate level in the small time step $\Delta t$ causes the reduction in pH of the solution, which in turn disturbs the equilibrium between the aerosol and its surrounding gaseous environment. More gases are dissolved in the aerosol to maintain the equilibrium. At the same time, these gases are depleted in the surrounding atmosphere. After each calculation, the time step is adjusted and the process is repeated until a 24-hour period is completed. The results are shown in Fig. 1.

Fig. 4 indicates that O$_3$, soot, and HNO$_2$ can be important mechanisms for sulfate aerosol formation. In general the O$_3$ mechanism is more important under high pH and/or photoactivity conditions when the concentration of
of O$_3$ is high, whereas both soot and HNO$_2$ processes are more important when
the lifetime of fog or clouds is long (Toossi et al., 1980) and the pH of
the droplets is low. Both soot and HNO$_2$ processes can be dominant processes
close to sources and in heavily polluted urban areas, where the concentrations
of soot and NO/NO$_2$ are high and the pH of aqueous droplets is low.

The rate constant for atmospheric soot particles varies depending on the
nature and history of particle production as discussed previously. In a fog
chamber study, Benner et al. (1979) have recently found that the reaction rate
of soot particles from a natural gas diffusion flame can be considerably
faster than the reaction rate reported here. More determination of rate con-
stants of soot from different types of fuel is therefore warranted.

The chemistry of reactions between SO$_2$ and HNO$_2$ in aqueous solution is
very complicated. Many concurrent and consecutive chemical reactions can
occur as indicated previously. Because of the unavailability of a complete
kinetic study, we have ignored the sulfate contribution from at least two
additional concurrent pathways that can occur as a result of the reaction
between HNO$_2$ and sulfites. These two pathways are 1) the hydrolysis of
nitrosulfonic acid (Latimer and Hildebrand, 1951), an intermediate resulting
from the interaction of HNO$_2$ and sulfites to hyponitrous acid and sulfate;
and 2) the reaction of nitrosulfonic acid with HNO$_2$ (Raschig, 1924) to produce
NO and sulfate. A complete understanding of the kinetics of these two
pathways and a confirmation on the validity of rate equation (2) of hydroxyl-
amine disulfonate formation at a much lower concentration of nitrites and
sulfites are needed before one can finally assess the extent of contribution
this system can make in terms of atmospheric sulfate aerosol and acid rain
formation.

Acknowledgment

This work was supported by the Biomedical and Environmental Research
References


Table 1. Chemical equilibrium constants at 25°C.\(^a\)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>equilibrium (\text{constant} \quad \text{at } 25^\circ\text{C} \quad \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O} \neq \text{H}^+ + \text{OH}^-)</td>
<td>(K = 1.0008 \times 10^{-14})</td>
</tr>
<tr>
<td>(\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \neq \text{CO}_2\cdot\text{H}_2\text{O})</td>
<td>(K_c = 3.4 \times 10^{-2})</td>
</tr>
<tr>
<td>(\text{CO}_2\cdot\text{H}_2\text{O} \neq \text{HCO}_3^- + \text{H}^+)</td>
<td>(K_{1c} = 4.45 \times 10^{-7})</td>
</tr>
<tr>
<td>(\text{HCO}_3^- \neq \text{CO}_3^{2-} + \text{H}^+)</td>
<td>(K_{2c} = 4.68 \times 10^{-11})</td>
</tr>
<tr>
<td>(\text{NH}_3(\text{g}) + \text{H}_2\text{O}(\ell) \neq \text{NH}_3\cdot\text{H}_2\text{O})</td>
<td>(H_a = 57)</td>
</tr>
<tr>
<td>(\text{NH}_3\cdot\text{H}_2\text{O} \neq \text{NH}_4^+ + \text{OH}^-)</td>
<td>(K_a = 1.774 \times 10^{-5})</td>
</tr>
<tr>
<td>(\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\ell) \neq \text{SO}_2\cdot\text{H}_2\text{O})</td>
<td>(H_s = 1.24)</td>
</tr>
<tr>
<td>(\text{SO}_2\cdot\text{H}_2\text{O} \neq \text{HSO}_3^- + \text{H}^+)</td>
<td>(K_{1s} = 1.7 \times 10^{-2})</td>
</tr>
<tr>
<td>(\text{HSO}_3^- \neq \text{SO}_3^{2-} + \text{H}^+)</td>
<td>(K_{2s} = 6.24 \times 10^{-8})</td>
</tr>
<tr>
<td>(\text{HSO}_4^- \neq \text{H}^+ + \text{SO}_4^{2-})</td>
<td>(K_{3s} = 1.2 \times 10^{-2})</td>
</tr>
<tr>
<td>(\text{HNO}_2(\text{g}) + \text{H}_2\text{O} \neq \text{HNO}_2\cdot\text{H}_2\text{O})</td>
<td>(H_N = 5.1 \times 10^{-4})</td>
</tr>
<tr>
<td>(\text{HNO}_2\cdot\text{H}_2\text{O} \neq \text{H}^+ + \text{NO}_2^-)</td>
<td>(K_N = 5.1 \times 10^{-4})</td>
</tr>
<tr>
<td>(\text{O}_2 + \text{H}_2\text{O} \neq \text{HO}_2\cdot\text{H}_2\text{O})</td>
<td>(H_{\text{O}_2} = 1.08 \times 10^{-3})</td>
</tr>
<tr>
<td>(\text{O}_3 + \text{H}_2\text{O} \neq \text{HO}_3\cdot\text{H}_2\text{O})</td>
<td>(H_{\text{O}_3} = 1.23 \times 10^{-2})</td>
</tr>
</tbody>
</table>

\(^a\)Concentrations in moles/\(\ell\) and gas pressure in atm.
Table 2. Rate of $\text{SO}_2$ oxidation by various mechanisms in aqueous droplets.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Reaction rate law&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>$\text{Rate} = \frac{H_S {k_2+k_{10} K_W/[H^+]} K_{2S} k_3}{k_2[H^+]^2+k_{10}[H^+]K_{2S} k_3} P_{\text{SO}_2}$</td>
</tr>
<tr>
<td>$\text{O}_3$</td>
<td>$\text{Rate} = {k_4[\text{HSO}_3^-]+k_5[\text{SO}_3^-]} [\text{O}_3 \cdot \text{H}_2\text{O}]$</td>
</tr>
<tr>
<td>$\text{Fe}^{+++}$</td>
<td>$\text{Rate} = \frac{k_0 k_S^2 H_S^2 \text{SO}_2^2 [\text{Fe}^{+++}]}{[H^+]^3}$</td>
</tr>
<tr>
<td>$\text{Mn}^{++}$</td>
<td>$\text{Rate} = 3.67 \times 10^{-3} [X] - 1.17 {[\text{HSO}_4^-] + [\text{SO}_4^{2-}]}^2 {[\text{Mn}^{++}] - [X]} \times [\text{H}_2\text{O}([\ell])]^{-2}$</td>
</tr>
</tbody>
</table>

where $X = \frac{k_{1H_S \text{PSO}_2 [\text{Mn}^{++}]}{k_1 \{H_S \text{PSO}_2 + [\text{H}_2\text{O}([\ell])][\text{Mn}^{++}]\} + 0.17}$

| Soot | $\text{Rate} = k_6[C_x][O_2]^{0.69} \frac{\alpha[S^4]^2}{1 + \beta[S^4] + \alpha[S^4]^2}$ |
| $\text{HNO}_2$ | $\text{Rate} = k_7[H^+]^2[\text{NO}_2^-] + k_8[H^+] [\text{NO}_2^-][\text{HSO}_3^-] + k_9[\text{NO}_2^-][\text{HSO}_3^-]^2$. |

<sup>a</sup> $[\text{H}_2\text{O}([\ell])]$ in cc/m$^3$, concentration in mole/ℓ, gas pressure in atm, and time in sec. $k_0 = 151.69$  ℓ/mole-sec, $k_S = 1.84 \times 10^{-2}$ mole/ℓ, $k_{1H_S} = 8.12 \times 10^4$  ℓ/mole-sec, $k_2 = 3.4 \times 10^6$ sec$^{-1}$, $k_{-2} = 2 \times 10^8$  ℓ/mole-sec, $k_{10} = 2.9 \times 10^5$  ℓ/mole-sec, $k_{-10} = 2.3 \times 10^{-7}$ sec$^{-1}$, $k_3 = 1.7 \times 10^{-3}$ sec$^{-1}$, $k_4 = 1.1 \times 10^5$  ℓ/mole-sec, $k_5 = 7.4 \times 10^8$  ℓ/mole-sec, $k_6 = 1.2 \times 10^{-4}$ mole$^{-3}$·ℓ$^{-7}$/g·sec, $\alpha = 1.5 \times 10^{12}$ ℓ$^2$/mole$^2$, $\beta = 3.06 \times 10^6$ ℓ/mole, $k_7 = 8 \times 10^5$ ℓ$^2$/mole$^2$·sec, $k_8 = 3.8 \times 10^3$ ℓ$^2$/mole$^2$·sec, $k_9 = 9 \times 10^{-4}$ ℓ$^2$/mole$^2$·sec.
Figure 1. The effect of the pH of aqueous droplets on $f[S(IV)]$ at $P_{SO_2} = 100, 10, \text{and } 1 \text{ ppb}$. $f[S(IV)]$ is a function of $S(IV)$ that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 2. The effect of partial pressure of $SO_2$ on $f[S(IV)]$ at pH of 7, 6, 5, 4, and 3. $f[S(IV)]$ is a function of $S(IV)$ that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 3. The ratio of the rate of hydrolysis (H) to sulfonation (S) of hydroxylamine disulfonate as a function of the pH of aqueous droplets at $P_{SO_2} = 1 \text{ ppb}, 10 \text{ ppb}, \text{and } 1 \text{ ppm}$.

Figure 4. The steady-state concentration of hydroxylamine disulfonate in aqueous droplets as a function of pH at two atmospheric conditions: $P_{SO_2} = P_{NO_2} = 2P_{NO} = 10 \text{ ppb}, \text{and } P_{SO_2} = P_{NO_2} = 2P_{NO} = 1 \text{ ppb}$.

Figure 5. Comparison of the relative importance of various sulfate production mechanisms involving liquid water based on a box-type calculation. The following initial conditions were used in the calculation: $P_{SO_2} = 0.01 \text{ ppm}$; $P_{CO_2} = 0.000311 \text{ atm}$; $P_{NH_3} = 5 \text{ ppb}$; $P_{O_3} = 0.05 \text{ ppm}$; $P_{HNO_2} = 8 \text{ ppb}$; $[Fe^{3+}] = 1.2 \times 10^{-7} \text{ mole/\ell}$; $[Mn^{2+}] = 1.8 \times 10^{-8} \text{ mole/\ell}$; soot = $10 \mu g/m^3$; and liquid water = $0.05 g/m^3$. 
Figure 1
Figure 2

The graph shows the relationship between $f [S(IV)]$ and SO$_2$ (ppb) for different pH values. The curves are labeled as follows:

- Curve 7: pH=6
Figure 3
Figure 4

\[ [\text{HADS}]_{\text{s.s.}} = \begin{cases} 10^{-2} & \text{for } P_{\text{SO}_2} = P_{\text{NO}_2} = 10 \text{ ppb} \\ 10^{-3} & \text{for } P_{\text{NO}} = 5 \text{ ppb} \\ 10^{-4} & \text{for } P_{\text{SO}_2} = P_{\text{NO}_2} = 1 \text{ ppb} \\ 10^{-5} & \text{for } P_{\text{NO}} = 0.5 \text{ ppb} \\ 10^{-6} & \text{for } P_{\text{SO}_2} = P_{\text{NO}_2} = 1 \text{ ppb} \\ 10^{-7} & \text{for } P_{\text{NO}} = 0.5 \text{ ppb} \end{cases} \]

pH
Figure 5
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