

# Oxidation of SO<sub>2</sub> by H<sub>2</sub>O<sub>2</sub> on ice surfaces at 228 K: a sink for SO<sub>2</sub> in ice clouds

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**Abstract.** The heterogeneous reaction SO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>SO<sub>4</sub> on ice at 228 K has been studied in a low temperature coated-wall flow tube. With H<sub>2</sub>O<sub>2</sub> in excess of SO<sub>2</sub>, the loss of SO<sub>2</sub> on an ice surface is time dependent with the reaction most efficient on a freshly exposed surface. The deactivation of the surface arises because the protons formed in the reaction inhibit the dissociation of adsorbed SO<sub>2</sub>. This lowers the surface concentrations of HSO<sub>3</sub><sup>-</sup>, a participant in the rate-determining step of the oxidation mechanism. For a fixed SO<sub>2</sub> partial pressure of 1.4 × 10<sup>-4</sup> Pa, the reaction probabilities for SO<sub>2</sub> loss on a freshly exposed surface scale linearly with H<sub>2</sub>O<sub>2</sub> partial pressures between 2.7 × 10<sup>-3</sup> and 2.7 × 10<sup>-2</sup> Pa because the H<sub>2</sub>O<sub>2</sub> surface coverage is unsaturated in this regime. Conversely, the reaction probabilities decrease as the partial pressure of SO<sub>2</sub> is raised from 2.7 × 10<sup>-5</sup> to 1.3 × 10<sup>-3</sup> Pa, for a fixed H<sub>2</sub>O<sub>2</sub> partial pressure of 8.7 × 10<sup>-3</sup> Pa. This is expected if the rate determining step for the mechanism involves HSO<sub>3</sub><sup>-</sup> rather than SO<sub>2</sub>. It may also arise to some degree if there is competition between gas phase SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> for adsorption sites. The reaction is sufficiently fast that the lifetime of SO<sub>2</sub> within ice clouds could be controlled by this heterogeneous reaction and not by the gas-phase reaction with OH.

(e.g. Finlayson-Pitts and Pitts, 2000). This is particularly true in the boundary layer and lower free troposphere where liquid water clouds are common, as opposed to the upper part of the troposphere where ice is more prevalent. H<sub>2</sub>O<sub>2</sub> is the most important oxidant in cloud water but other species such as O<sub>3</sub> and transition metal ions can play significant roles as well, depending on the cloud droplet pH and chemical composition.

By studying the dry deposition of SO<sub>2</sub> to snow surfaces, Valdez et al. (1987) found that SO<sub>2</sub> is efficiently converted to S(VI) on snow samples in the field with over 90% of the SO<sub>2</sub> loss due to reaction. To explain these observations, it was speculated that this loss could result from reaction with H<sub>2</sub>O<sub>2</sub> which had also been scavenged from the atmosphere. Indeed, H<sub>2</sub>O<sub>2</sub> has been detected in freshly fallen snow (Gunz and Hoffman, 1990). Laboratory experiments have confirmed that a reaction occurs between the SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in the presence of ice (Mitra et al., 1990; Conklin et al., 1993), most recently in a flow tube study of Chu et al. (2000) which demonstrated that SO<sub>2</sub> loss is significantly larger on ice films containing between 0.8 and 3.0 wt% H<sub>2</sub>O<sub>2</sub> than on pure ice films. Chu et al. (2000) also showed that sulfate is a major product of the reaction.

In a recent study we have measured the uptake and surface coverages of SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> on ice surfaces a functions of the partial pressure of the gas, temperature and surface acidity (Clegg and Abbatt, 2001). These studies indicate that the uptake of SO<sub>2</sub> is driven by the dissociation of the adsorbed form of SO<sub>2</sub> into H<sup>+</sup> and HSO<sub>3</sub><sup>-</sup>. The uptake of SO<sub>2</sub> increases with temperature suggesting that the surface has a substantial amount of disorder or perhaps even a liquid-like surface. On the other hand, H-bonding most likely drives the uptake of H<sub>2</sub>O<sub>2</sub>. The adsorption of both SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> were also shown to be completely reversible. In this paper, we extend this earlier study by investigating whether adsorbed SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> react together on ice, perhaps via a mecha-

## 1 Introduction

The loss processes for SO<sub>2</sub> in the atmosphere are of considerable importance given the role that the oxidation products play in aerosol and cloud formation. Although SO<sub>2</sub> can be oxidized by a gas-phase reaction involving OH, a condensed-phase process which occurs via reactions with a variety of oxidants dissolved in cloud droplets can be more significant

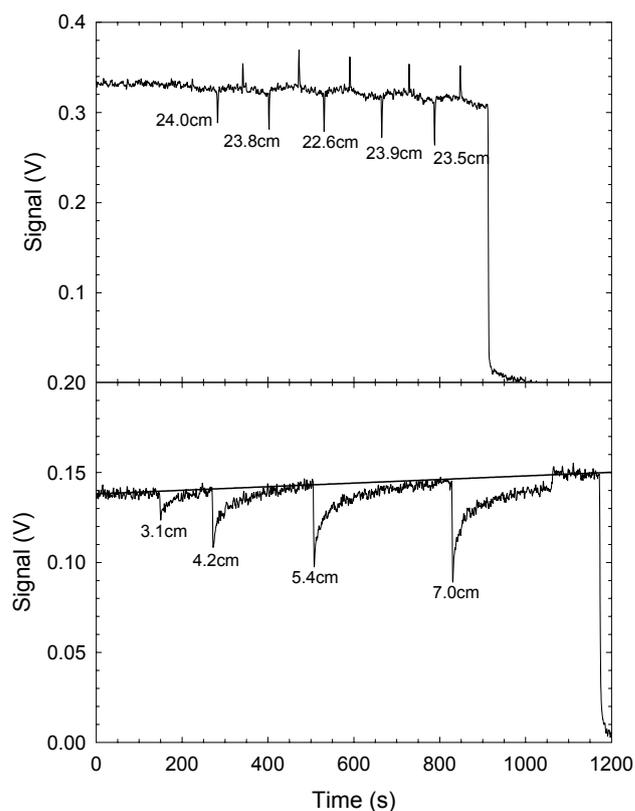
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nism similar to that which occurs in cloud water. Our work is distinguished from previous studies by the fact that we deliver both reagents from the gas-phase. Thus, we are able to study the kinetics of the reaction as functions of reagent partial pressure and surface coverage. This approach allows us to make the first estimates of the rate of this heterogeneous reaction as a function of the gas-phase abundances of SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in the atmosphere.

## 2 Experimental

The reaction probability measurements were performed at 228 K in a low temperature coated-wall flow tube which was coupled to an electron-impact quadrupole mass spectrometer. Details of the experimental approach as it pertains to SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> have been described previously in Clegg and Abbatt (2001). The ice surfaces were prepared by coating the inner walls of a 2.50-cm-i.d. pyrex reaction tube with distilled water, and inserting the tube into the cold flow reactor. The water quickly froze to form a smooth ice film. By mixing a dry helium carrier gas flow with one which was bubbled through a water trap, the helium carrier gas was humidified so that the film did not evaporate over the course of an experiment. Given that net deposition of water vapor may have been occurring at the upstream end of the flow tube, we only studied kinetics over the downstream three-quarters of the film. SO<sub>2</sub> (Matheson, Anhydrous Grade) was stored in a glass bulb as a dilute mixture in helium and then added to the flow tube via a 0.6-cm-o.d. movable injector. Its partial pressure in the flow tube was determined by monitoring in time the change of pressure of the SO<sub>2</sub>/He reservoir. H<sub>2</sub>O<sub>2</sub> vapor was delivered to the back of the flow tube in a small flow of helium (10's of standard cubic centimeters per minute (sccm)). The source was a bubbler filled with  $\geq 95$  wt% H<sub>2</sub>O<sub>2</sub>, which had been prepared by bubbling dry nitrogen through commercial H<sub>2</sub>O<sub>2</sub> solutions (Aldrich, 50 wt%) for weeks. The composition of the liquid solution was determined via density measurements (Washburn, 1926). En route to the flow tube, the H<sub>2</sub>O<sub>2</sub> flow passed through a 10-cm-long pyrex absorption cell which was used to monitor the partial pressure of gaseous H<sub>2</sub>O<sub>2</sub> by measuring its absorption at 220 nm where it has a cross section of  $2.58 \times 10^{-19}$  cm<sup>2</sup> (DeMore et al., 1997).

A kinetics experiment was performed by allowing H<sub>2</sub>O<sub>2</sub> to flow over the ice film for a sufficiently long time that the entire length of the film surface was at equilibrium with the gaseous H<sub>2</sub>O<sub>2</sub>. To insure this was the case, some runs were done by monitoring the H<sub>2</sub>O<sub>2</sub> mass spectrometer signal at mass 34 after H<sub>2</sub>O<sub>2</sub> had been added to the back of the flow tube (see Clegg and Abbatt (2001) for details about mass spectrometric H<sub>2</sub>O<sub>2</sub> detection). Then, the movable injector containing SO<sub>2</sub> was pulled back in stages over the ice film. SO<sub>2</sub> was detected at mass 64 by the mass spectrometer. Typical conditions in the flow tube were 67 Pa total pressure and 300 sccm total gas flow. The detection limit for SO<sub>2</sub> was

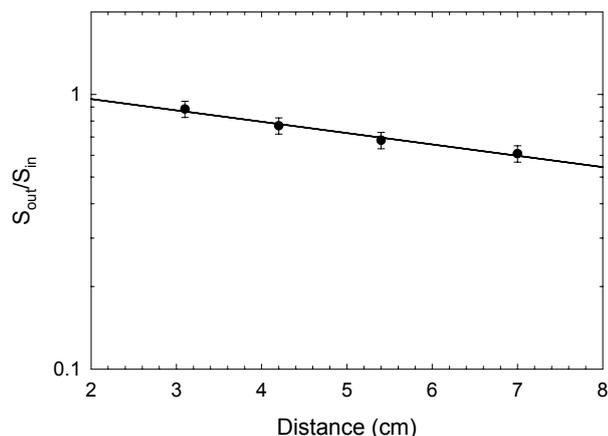


**Fig. 1.** Typical SO<sub>2</sub> uptake profiles in a 228 K ice-coated flow tube in the absence (upper frame,  $P(\text{SO}_2) = 8.1 \times 10^{-5}$  Pa) and presence of H<sub>2</sub>O<sub>2</sub> (lower frame,  $P(\text{SO}_2) = 7.1 \times 10^{-5}$  Pa,  $P(\text{H}_2\text{O}_2) = 1.0 \times 10^{-2}$  Pa). The distances the injector was withdrawn are indicated. In the upper frame the injector is withdrawn and pushed back in five times over the same ice surface. In the lower frame, the injector is incrementally withdrawn over a fresh ice surface and not pushed back into its starting position until the end of the experiment at 1100 seconds.

between  $0.7$  and  $1.3 \times 10^{-5}$  Pa, for S/N=1 and 3 second integration times. Only one SO<sub>2</sub> decay was measured on an individual ice film.

## 3 Results and discussion

Typical SO<sub>2</sub> uptakes by an ice surface are shown in Fig. 1 for runs when H<sub>2</sub>O<sub>2</sub> is absent from the flow tube (upper frame) and when it is present (lower frame). Note that the distance the injector is pulled back, indicated on the figure, is 3 to 8 times larger for the H<sub>2</sub>O<sub>2</sub>-free case than for the case with H<sub>2</sub>O<sub>2</sub>. This emphasizes that the uptake of SO<sub>2</sub> is very much enhanced by the presence of adsorbed H<sub>2</sub>O<sub>2</sub>. We interpret this enhanced uptake as due to reaction between SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>, based on the observation of sulfate formation in previous ice experiments (Valdez et al., 1987; Conklin et al., 1993; Chu et al., 2000). Furthermore, the SO<sub>2</sub> uptakes on H<sub>2</sub>O<sub>2</sub>-free surfaces like the type displayed at the top of Fig. 1 are

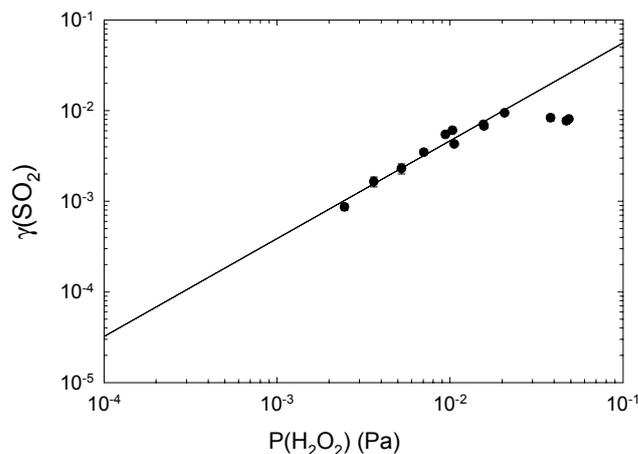


**Fig. 2.** SO<sub>2</sub> decay for the data in the lower frame of Fig. 1, which has been constructed from the ratio of the SO<sub>2</sub> signal immediately after and prior to the withdrawal of the injector over a fresh ice surface ( $S_{\text{out}}/S_{\text{in}}$ ).

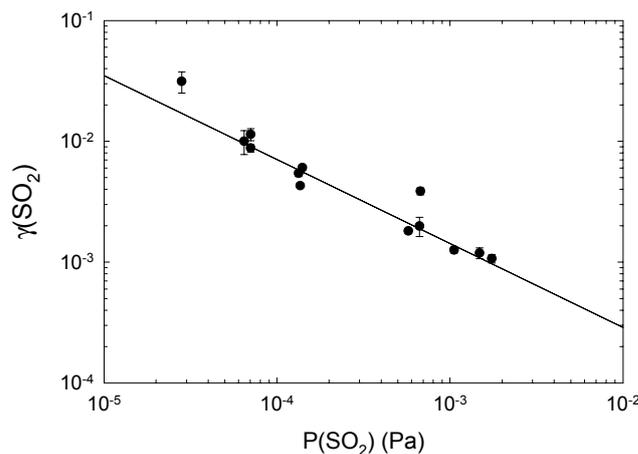
completely reversible. When the injector is pushed back to its starting position in the runs with H<sub>2</sub>O<sub>2</sub> present, there is no surge in the SO<sub>2</sub> signal. This indicates that the loss of SO<sub>2</sub> is irreversible, presumably due to reaction. In all cases the conditions were chosen so that H<sub>2</sub>O<sub>2</sub> was the excess reagent, with the surface coverages of H<sub>2</sub>O<sub>2</sub> at least 2 to 3 times larger than those of adsorbed SO<sub>2</sub> (Clegg and Abbatt, 2001).

The reaction probability for SO<sub>2</sub> loss on a fresh ice surface was determined by taking the ratio of the SO<sub>2</sub> signal before and after the ice has been exposed. The uptake coefficients measured here may be lower limits due to the one-second time resolution of this experimental approach. The logarithm of this ratio vs. the distance the injector was withdrawn generates a straight line to within our experimental uncertainty. Figure 2 contains such a plot for the uptake data in Fig. 1. The equivalent of a traditional pseudo-first-order rate constant is the slope of the best-fit-line in Fig. 2. This rate constant is used to calculate the gas-surface reaction probability using the standard approach which takes into account concentration gradients which arise from both axial and radial diffusion in the flow tube (Brown, 1978). The diffusion coefficients that we used in these calculations were  $259/P$  cm<sup>2</sup>/s for SO<sub>2</sub> in He and  $57/P$  cm<sup>2</sup>/s for SO<sub>2</sub> in H<sub>2</sub>O, with  $P$  in Torr. The water pressure in the flow tube was taken to be the vapor pressure over ice at 228 K.

To determine the reaction mechanism and allow us to extrapolate our experimental conditions to atmospheric conditions, we studied the dependence of the reaction probabilities on the partial pressures of one of the two reactant gases, keeping the partial pressure of the other gas fixed. The results are shown in Figs. 3 and 4 for variable partial pressures of H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub>, respectively. For partial pressures below  $3 \times 10^{-2}$  Pa, the dependence of the reaction probability on the partial pressure of H<sub>2</sub>O<sub>2</sub> is linear with a slope for the



**Fig. 3.** Plot of SO<sub>2</sub> reaction probabilities on ice as a function of  $P(\text{H}_2\text{O}_2)$ , at 228 K and  $P_{\text{SO}_2} = 1.5 \times 10^{-4}$  Pa. Line-of-best fit does not include the three points at highest partial pressures (see text).

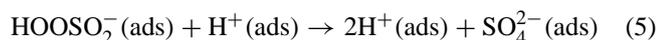
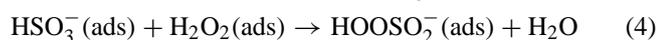
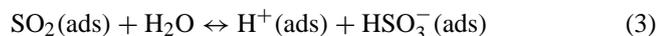


**Fig. 4.** Plot of SO<sub>2</sub> reaction probabilities on ice as a function of  $P(\text{SO}_2)$ , at 228 K and  $P_{\text{H}_2\text{O}_2} = 8.7 \times 10^{-3}$  Pa.

log-log plot of 1.08. There is also a dependence of the reaction probabilities on SO<sub>2</sub> partial pressure with a slope in the log-log plot of  $-0.70$ . It should be noted that Chu et al. (2000) observed a similar but weaker trend of decreasing reaction probability with increasing  $P_{\text{SO}_2}$  in some of their experiments as well. Chu et al. observed reaction probabilities on the order of  $10^{-4}$  at close to 200 K on 3.0 wt% H<sub>2</sub>O<sub>2</sub> ice films. However, absolute comparison to the Chu et al. results is difficult given that their surfaces were different from ours, consisting of relatively concentrated mixtures of ice and H<sub>2</sub>O<sub>2</sub>, i.e. it is difficult to know what H<sub>2</sub>O<sub>2</sub> surface coverages are present.

To interpret these observations, we consider a possible mechanism for the reaction, i.e. one analogous to that which operates in aqueous solutions (e.g. Finlayson-Pitts and Pitts,

2000):



The terms '(g)' and '(ads)' refer to the gas and adsorbed phases, respectively. If Reaction 4 is the rate-determining step in this mechanism (see below), then the overall rate will be proportional to the concentrations of the two reactants HSO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub>:

$$\text{Rate} = k_4[\text{HSO}_3^-(\text{ads})][\text{H}_2\text{O}_2(\text{ads})] \quad (6)$$

where the concentration terms refer either to surface coverages or to the concentrations of the species in the uppermost few monolayers of the ice film. In our study of the surface coverages on ice we observed that there is a square root dependence on the partial pressure of SO<sub>2</sub> (Clegg and Abbatt, 2001):

$$[\text{HSO}_3^-(\text{ads})] \propto P_{\text{SO}_2}^{1/2} \quad (7)$$

and a linear dependence for H<sub>2</sub>O<sub>2</sub>:

$$[\text{H}_2\text{O}_2(\text{ads})] \propto P_{\text{H}_2\text{O}_2} \quad (8)$$

Substituting (7) and (8) into (6) gives:

$$\text{Rate} \propto P_{\text{SO}_2}^{1/2} P_{\text{H}_2\text{O}_2} \quad (9)$$

But, we have defined our reaction probability,  $\gamma^{\text{SO}_2}$ , in terms of pseudo first-order kinetics:

$$\text{Rate} = k P_{\text{SO}_2} \quad (10)$$

where  $\gamma^{\text{SO}_2}$  is proportional to  $k$ . Equating (9) and (10) yields the predicted dependence of the reaction probability on the partial pressures of the two gases for the above mechanism:

$$\gamma^{\text{SO}_2} \propto P_{\text{SO}_2}^{-1/2} P_{\text{H}_2\text{O}_2} \quad (11)$$

Thus, the dependence on  $P_{\text{H}_2\text{O}_2}$  shown in Fig. 3 is consistent with the mechanism. In particular, larger amounts of H<sub>2</sub>O<sub>2</sub> in the gas phase lead to greater surface coverage of H<sub>2</sub>O<sub>2</sub> and to a higher probability that SO<sub>2</sub> will be irreversibly lost if it collides with the surface. The points at high  $P_{\text{H}_2\text{O}_2}$  ( $\approx 4 \times 10^{-2}$  Pa) that do not lie on the line-of-best-fit shown in Fig. 3 may indicate that a thermodynamically stable solution of hydrogen peroxide in water is forming on the ice surface at partial pressures of  $4 \times 10^{-2}$  Pa and above. In studies of the uptake of HCl by ice, it was found that melting occurred when HCl was exposed to an ice surface at partial pressures equal to or greater than those corresponding to the vapor pressure of HCl at the solid-liquid coexistence curve

(Abbatt et al., 1992). To determine whether the same phenomenon may have occurred in these experiments, we extrapolated H<sub>2</sub>O<sub>2</sub> vapor pressures of aqueous solutions measured at higher temperatures to 228 K (Schumb et al., 1955). For the solution concentration of H<sub>2</sub>O<sub>2</sub>, 42.5 wt%, which is in equilibrium with ice at 228 K (Schumb et al., 1955), the extrapolation yields a partial pressure of  $4 \times 10^{-2}$  Pa. That is, we predict that at H<sub>2</sub>O<sub>2</sub> partial pressures of this value and higher, the ice surface melts to form a thermodynamically stable solution. The 'saturation' of the SO<sub>2</sub> reaction probabilities at this partial pressure may reflect the change in surface composition at this partial pressure. In our measurements of the uptake of H<sub>2</sub>O<sub>2</sub> by clean ice surfaces (Clegg and Abbatt, 2001), we observed a linear dependence on  $P_{\text{H}_2\text{O}_2}$  up to a partial pressure of  $4 \times 10^{-3}$  Pa but were unable to operate at higher partial pressures because H<sub>2</sub>O<sub>2</sub> began condensing in the movable injector in this regime. In the work described here, we were able to operate at the higher partial pressures because H<sub>2</sub>O<sub>2</sub> is added directly to the back of the flow tube and not through a movable injector.

Equation 11 also accounts for a significant fraction of the dependence of the reaction probability on the partial pressure of SO<sub>2</sub> at low partial pressures where the surface is unsaturated. The difference between the predicted slope of  $-0.5$  and the observed slope of  $-0.7$  may be due to experimental uncertainties or assumptions made in the above reaction mechanism. Another unlikely possibility is that there is competition between H<sub>2</sub>O<sub>2</sub> and SO<sub>2</sub> for adsorption sites on the surface so that more H<sub>2</sub>O<sub>2</sub> is allowed to adsorb to the surface as the partial pressure of SO<sub>2</sub> goes down, thus increasing the SO<sub>2</sub> reaction probability. However, Clegg and Abbatt demonstrated that adsorption of these molecules only accounts for a small fraction of the total surface area far removed from saturation effects. Furthermore, we have new, unpublished data which indicates that there is little competition between acetic acid and 1-butanol adsorbing in the low partial pressure, unsaturated regime. Whatever the case, it is important to note that the reaction is strictly not first order in SO<sub>2</sub>, otherwise there would have been no dependence. This arises because it is not adsorbed SO<sub>2</sub> but HSO<sub>3</sub><sup>-</sup> which is the reactive species in the rate-determining step of the reaction. From an experimental perspective, it is very difficult to differentiate a first-order reaction from one of reaction order 0.5, especially if a reaction is relatively slow - as this is - and reactant decays over many orders of magnitude are difficult to observe.

To this point we have only been addressing the initial decline in the SO<sub>2</sub> signal when the injector is pulled back over a fresh surface. The other noteworthy feature of the uptake profile in Fig. 1 is that the SO<sub>2</sub> loss is time-dependent with the most efficient reaction on fresh surfaces. Does the formation of the H<sub>2</sub>SO<sub>4</sub> product poison the surface and shut the reaction off at long times? To answer this we can examine the effects which we observed protons and sulfate ions to have on the uptake of SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> on ice surfaces (Clegg

and Abbatt, 2001). Specifically, the H<sub>2</sub>O<sub>2</sub> uptakes on ice films formed by freezing sulfuric acid solutions (pH 4) were the same as those on pure ice, indicating that neither H<sup>+</sup> nor SO<sub>4</sub><sup>2-</sup> inhibits the uptake. On the other hand, considerably less SO<sub>2</sub> adsorbs to an H<sub>2</sub>SO<sub>4</sub>/ice surface than to a pure ice surface. This is not due to the presence of sulfate ions because Na<sub>2</sub>SO<sub>4</sub>/ice surfaces do not have the same effect. Instead, we believe the protons inhibit Reaction 3, the dissociation of adsorbed SO<sub>2</sub>. This leads to a lower fraction of gas-phase SO<sub>2</sub> adsorbing to the ice surface and a lower reaction probability.

Note that the dependence of the reaction rate upon acidity is different from that exhibited when the reaction occurs in liquid cloud water. In particular, in aqueous systems acidity can accelerate the process through Reaction 5 and decelerate it through Reaction 3, leading to no net effect on the rate over a pH range from roughly 1 to 7. On the other hand, our observations that acidity on an ice surface slows down the overall rate supports our assumption made above that Reaction 4 is rate determining. That is, as soon as the HOOSO<sub>2</sub><sup>-</sup> intermediate is formed, it very easily finds a proton to form products. It should be emphasized that our assumption that the mechanism proceeds through the peroxymonosulfurous acid anion, as it does in cloud water, needs to be tested.

What is the capacity of an ice surface to promote the SO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>SO<sub>4</sub> reaction before the surface is fully poisoned by protons? To address this, we have integrated the time-dependent loss of gas-phase SO<sub>2</sub> due to reaction and referenced this quantity to the exposed ice surface area. Assuming that one molecule of lost SO<sub>2</sub> corresponds to one molecule of H<sub>2</sub>SO<sub>4</sub> product, we find that between 10<sup>14</sup> and 10<sup>15</sup> molecules of H<sub>2</sub>SO<sub>4</sub> are formed per cm<sup>2</sup> of ice before the reaction shuts off.

#### 4 Atmospheric implications

The SO<sub>2</sub> atmospheric lifetime for loss via heterogeneous reaction with H<sub>2</sub>O<sub>2</sub> on ice can be calculated from:

$$\tau^{\text{SO}_2} = (\gamma v A / 4)^{-1} \quad (12)$$

where  $A$  is the surface area of ice particles in the atmosphere per unit volume and  $v$  is the mean molecular speed. The appropriate reaction probability is determined by the partial pressures of the reactants. For H<sub>2</sub>O<sub>2</sub>, a mixing ratio of roughly 500 pptv has been measured at 8 km in the tropical free troposphere (Cohan et al., 1999). Assuming a linear relationship, extrapolation of the data in Fig. 3 to this partial pressure ( $\approx 1.6 \times 10^{-5}$  Pa) yields a SO<sub>2</sub> reaction probability of  $8 \times 10^{-6}$ . With typical SO<sub>2</sub> amounts in the free troposphere (10's of pptv) considerably lower than the partial pressures used to perform the measurements in Fig. 3, the true reaction probability in the atmosphere may well be larger than  $8 \times 10^{-6}$  when the inverse dependence exhibited in Fig. 4 is taken into account. But, given that we don't

know if the relationship between  $\gamma^{\text{SO}_2}$  and  $P_{\text{SO}_2}$  shown in Fig. 4 necessarily holds for lower partial pressures of H<sub>2</sub>O<sub>2</sub>, we will use the  $8 \times 10^{-6}$  reaction probability estimate as a lower limit to the true value.

Cirrus cloud surface areas range between  $2 \times 10^{-7}$  cm<sup>2</sup>/cm<sup>3</sup>, typical of subvisual cirrus, to  $2 \times 10^{-4}$  cm<sup>2</sup>/cm<sup>3</sup> for anvil-type clouds (O. B. Toon, private communication, 1997). For these surface areas, and for the reaction probability derived above, atmospheric lifetimes for SO<sub>2</sub> calculated from Equation 12 range between 1050 and 1.05 days. For reference, the lifetime for oxidation of SO<sub>2</sub> by gas-phase OH (DeMore et al., 1997) is two weeks, assuming typical conditions at 8 km altitude, i.e. [OH] =  $1 \times 10^6$  molecules/cm<sup>3</sup>, 228 K, [M] =  $9 \times 10^{18}$  molecules/cm<sup>3</sup>. Thus, for moderately thick cirrus clouds the lifetime of SO<sub>2</sub> may be determined by the heterogeneous reaction with H<sub>2</sub>O<sub>2</sub>. The same can be said for ice clouds lower in the troposphere as well. Chu et al. have also suggested that the oxidation of SO<sub>2</sub> on ice particles could lead to loss of gas phase SO<sub>2</sub>.

What additional factors need to be considered to determine whether this is an important atmospheric reaction? One is related to the capacity of the ice surfaces to sustain the oxidation process before enough acidity is deposited on the surface, in the form of sulfuric acid, to shut the reaction off. To address this, consider a cubic centimeter of air at 8 km altitude which contains hundreds of pptv H<sub>2</sub>O<sub>2</sub>, 10 pptv SO<sub>2</sub> and cirrus cloud ice particles (Cohan et al., 1999). Assuming all the SO<sub>2</sub> reacts with the H<sub>2</sub>O<sub>2</sub> to form H<sub>2</sub>SO<sub>4</sub> on the surface of the ice particles, then the surfaces will exceed the 10<sup>14</sup> to 10<sup>15</sup> molecules/cm<sup>2</sup> criterion which was presented above for poisoning the surface if the total cloud surface area is lower than 10<sup>-6</sup> to 10<sup>-7</sup> cm<sup>2</sup>/cm<sup>3</sup>. Thus, it appears that this effect will only be important for the low surface area clouds. However, it is for these clouds that the SO<sub>2</sub> oxidation lifetime is long and gas-phase oxidation will probably dominate.

Another factor to consider is the role that other species may play in affecting the rate of the heterogeneous SO<sub>2</sub> oxidation. There are a number of possibilities, some of which we intend to examine in the laboratory. One is that there is pre-existing acidity on the surface of the cloud particles that could inhibit the SO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> reaction. This acidity could arise from either scavenging of acidic aerosols by the cloud particle or by adsorption of ambient levels of HNO<sub>3</sub> to the ice surfaces (Abbatt, 1997; Zondlo et al., 1997). We are also interested to see if the oxidation of HSO<sub>3</sub><sup>-</sup> by O<sub>3</sub> occurs on ice surfaces, as it does in cloud water.

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