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Oxidation of SO₂ by H₂O₂ on ice surfaces at 228 K: a sink for SO₂ in ice clouds

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Abstract. The heterogeneous reaction SO₂ + H₂O₂ → H₂SO₄ on ice at 228 K has been studied in a low temperature coated-wall flow tube. With H₂O₂ in excess of SO₂, the loss of SO₂ 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 SO₂. This lowers the surface concentrations of HSO₃⁻, a participant in the rate-determining step of the oxidation mechanism. For a fixed SO₂ partial pressure of 1.4 × 10⁻⁴ Pa, the reaction probabilities for SO₂ loss on a freshly exposed surface scale linearly with H₂O₂ partial pressures between 2.7 × 10⁻³ and 2.7 × 10⁻² Pa because the H₂O₂ surface coverage is unsaturated in this regime. Conversely, the reaction probabilities decrease as the partial pressure of SO₂ is raised from 2.7 × 10⁻⁵ to 1.3 × 10⁻³ Pa, for a fixed H₂O₂ partial pressure of 8.7 × 10⁻³ Pa. This is expected if the rate determining step for the mechanism involves HSO₃⁻ rather than SO₂. It may also arise to some degree if there is competition between gas phase SO₂ and H₂O₂ for adsorption sites. The reaction is sufficiently fast that the lifetime of SO₂ 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. H₂O₂ is the most important oxidant in cloud water but other species such as O₃ 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 SO₂ to snow surfaces, Valdez et al. (1987) found that SO₂ is efficiently converted to S(VI) on snow samples in the field with over 90% of the SO₂ loss due to reaction. To explain these observations, it was speculated that this loss could result from reaction with H₂O₂ which had also been scavenged from the atmosphere. Indeed, H₂O₂ has been detected in freshly fallen snow (Gunz and Hoffman, 1990). Laboratory experiments have confirmed that a reaction occurs between the SO₂ and H₂O₂ 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 SO₂ loss is significantly larger on ice films containing between 0.8 and 3.0 wt% H₂O₂ 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 SO₂ and H₂O₂ 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 SO₂ is driven by the dissociation of the adsorbed form of SO₂ into H⁺ and HSO₃⁻. The uptake of SO₂ 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 H₂O₂. The adsorption of both SO₂ and H₂O₂ were also shown to be completely reversible. In this paper, we extend this earlier study by investigating whether adsorbed SO₂ and H₂O₂ react together on ice, perhaps via a mecha-

1 Introduction

The loss processes for SO₂ in the atmosphere are of considerable importance given the role that the oxidation products play in aerosol and cloud formation. Although SO₂ 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 SO₂ and H₂O₂ 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 SO₂ and H₂O₂ 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. SO₂ (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 SO₂/He reservoir. H₂O₂ 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 ≥ 95 wt% H₂O₂, which had been prepared by bubbling dry nitrogen through commercial H₂O₂ 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 H₂O₂ flow passed through a 10-cm-long pyrex absorption cell which was used to monitor the partial pressure of gaseous H₂O₂ by measuring its absorption at 220 nm where it has a cross section of 2.58×10^{-19} cm² (DeMore et al., 1997).

A kinetics experiment was performed by allowing H₂O₂ 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 H₂O₂. To insure this was the case, some runs were done by monitoring the H₂O₂ mass spectrometer signal at mass 34 after H₂O₂ had been added to the back of the flow tube (see Clegg and Abbatt (2001) for details about mass spectrometric H₂O₂ detection). Then, the movable injector containing SO₂ was pulled back in stages over the ice film. SO₂ 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 SO₂ was

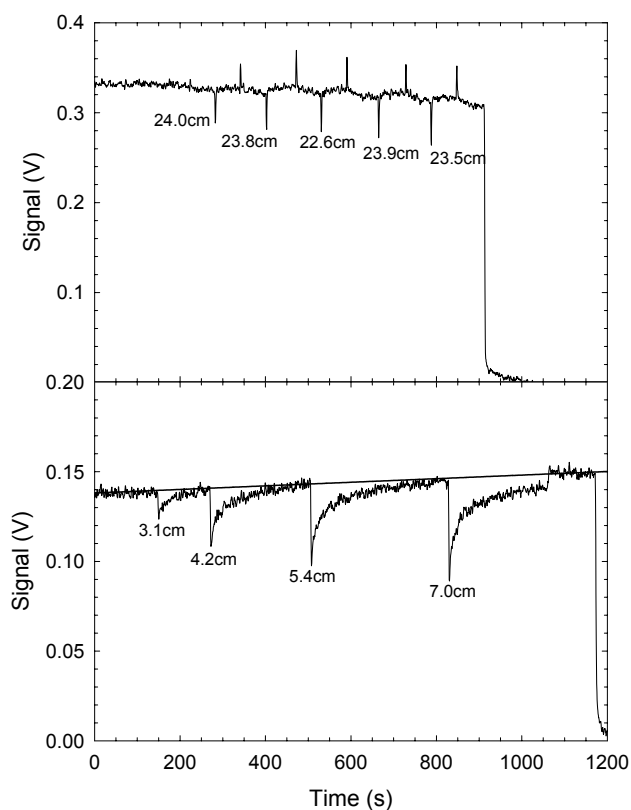


Fig. 1. Typical SO₂ uptake profiles in a 228 K ice-coated flow tube in the absence (upper frame, $P(\text{SO}_2) = 8.1 \times 10^{-5}$ Pa) and presence of H₂O₂ (lower frame, $P(\text{SO}_2) = 7.1 \times 10^{-5}$ Pa, $P(\text{H}_2\text{O}_2) = 1.0 \times 10^{-2}$ Pa). The distances the injector was withdrawn 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 1.3×10^{-5} Pa, for S/N=1 and 3 second integration times. Only one SO₂ decay was measured on an individual ice film.

3 Results and discussion

Typical SO₂ uptakes by an ice surface are shown in Fig. 1 for runs when H₂O₂ 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 H₂O₂-free case than for the case with H₂O₂. This emphasizes that the uptake of SO₂ is very much enhanced by the presence of adsorbed H₂O₂. We interpret this enhanced uptake as due to reaction between SO₂ and H₂O₂, 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 SO₂ uptakes on H₂O₂-free surfaces like the type displayed at the top of Fig. 1 are

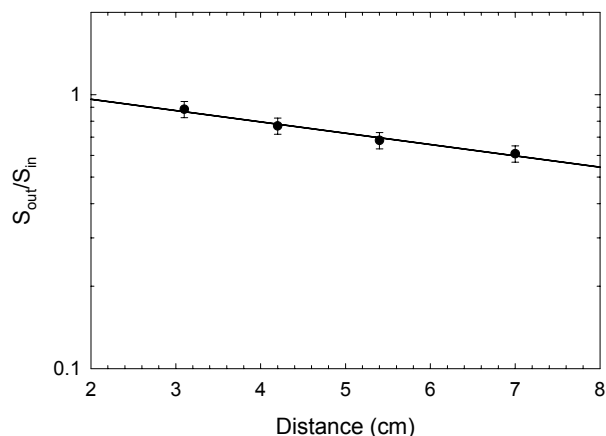


Fig. 2. SO₂ decay for the data in the lower frame of Fig. 1, which has been constructed from the ratio of the SO₂ signal immediately after and prior to the withdrawal of the injector over a fresh ice surface ($S_{\text{out}}/S_{\text{in}}$).

completely reversible. When the injector is pushed back to its starting position in the runs with H₂O₂ present, there is no surge in the SO₂ signal. This indicates that the loss of SO₂ is irreversible, presumably due to reaction. In all cases the conditions were chosen so that H₂O₂ was the excess reagent, with the surface coverages of H₂O₂ at least 2 to 3 times larger than those of adsorbed SO₂ (Clegg and Abbatt, 2001).

The reaction probability for SO₂ loss on a fresh ice surface was determined by taking the ratio of the SO₂ 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 $259/P$ cm²/s for SO₂ in He and $57/P$ cm²/s for SO₂ in H₂O, 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 H₂O₂ and SO₂, respectively. For partial pressures below 3×10^{-2} Pa, the dependence of the reaction probability on the partial pressure of H₂O₂ is linear with a slope for the

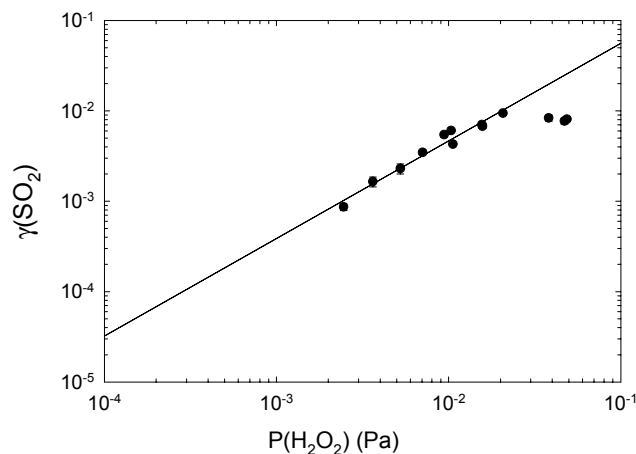


Fig. 3. Plot of SO₂ reaction probabilities on ice as a function of $P(\text{H}_2\text{O}_2)$, at 228 K and $P_{\text{SO}_2} = 1.5 \times 10^{-4}$ Pa. Line-of-best fit does not include the three points at highest partial pressures (see text).

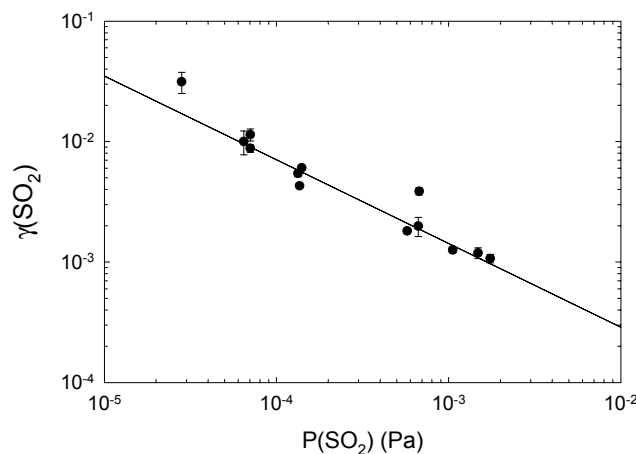
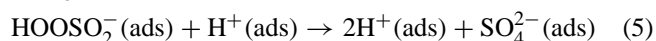
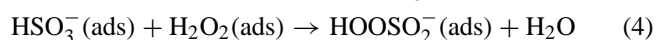
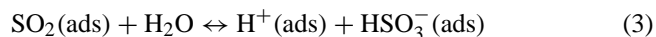


Fig. 4. Plot of SO₂ reaction probabilities on ice as a function of $P(\text{SO}_2)$, at 228 K and $P_{\text{H}_2\text{O}_2} = 8.7 \times 10^{-3}$ Pa.

log-log plot of 1.08. There is also a dependence of the reaction probabilities on SO₂ 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_{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% H₂O₂ 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 H₂O₂, i.e. it is difficult to know what H₂O₂ 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 HSO₃⁻ and H₂O₂:

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

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 SO₂ (Clegg and Abbatt, 2001):

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

and a linear dependence for H₂O₂:

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

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, γ^{SO_2} , in terms of pseudo first-order kinetics:

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

where γ^{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 H₂O₂ in the gas phase lead to greater surface coverage of H₂O₂ and to a higher probability that SO₂ 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 4×10^{-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 H₂O₂ vapor pressures of aqueous solutions measured at higher temperatures to 228 K (Schumb et al., 1955). For the solution concentration of H₂O₂, 42.5 wt%, which is in equilibrium with ice at 228 K (Schumb et al., 1955), the extrapolation yields a partial pressure of 4×10^{-2} Pa. That is, we predict that at H₂O₂ partial pressures of this value and higher, the ice surface melts to form a thermodynamically stable solution. The 'saturation' of the SO₂ reaction probabilities at this partial pressure may reflect the change in surface composition at this partial pressure. In our measurements of the uptake of H₂O₂ 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 4×10^{-3} Pa but were unable to operate at higher partial pressures because H₂O₂ 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 H₂O₂ 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 SO₂ 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 H₂O₂ and SO₂ for adsorption sites on the surface so that more H₂O₂ is allowed to adsorb to the surface as the partial pressure of SO₂ goes down, thus increasing the SO₂ 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 SO₂, otherwise there would have been no dependence. This arises because it is not adsorbed SO₂ but HSO₃⁻ 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 SO₂ 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 SO₂ loss is time-dependent with the most efficient reaction on fresh surfaces. Does the formation of the H₂SO₄ 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 SO₂ and H₂O₂ on ice surfaces (Clegg

and Abbatt, 2001). Specifically, the H₂O₂ uptakes on ice films formed by freezing sulfuric acid solutions (pH 4) were the same as those on pure ice, indicating that neither H⁺ nor SO₄²⁻ inhibits the uptake. On the other hand, considerably less SO₂ adsorbs to an H₂SO₄/ice surface than to a pure ice surface. This is not due to the presence of sulfate ions because Na₂SO₄/ice surfaces do not have the same effect. Instead, we believe the protons inhibit Reaction 3, the dissociation of adsorbed SO₂. This leads to a lower fraction of gas-phase SO₂ 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 HOOSO₂⁻ 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 SO₂ + H₂O₂ → H₂SO₄ reaction before the surface is fully poisoned by protons? To address this, we have integrated the time-dependent loss of gas-phase SO₂ due to reaction and referenced this quantity to the exposed ice surface area. Assuming that one molecule of lost SO₂ corresponds to one molecule of H₂SO₄ product, we find that between 10¹⁴ and 10¹⁵ molecules of H₂SO₄ are formed per cm² of ice before the reaction shuts off.

4 Atmospheric implications

The SO₂ atmospheric lifetime for loss via heterogeneous reaction with H₂O₂ 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 H₂O₂, 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 SO₂ reaction probability of 8×10^{-6} . With typical SO₂ 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 8×10^{-6} when the inverse dependence exhibited in Fig. 4 is taken into account. But, given that we don't

know if the relationship between γ^{SO_2} and P_{SO_2} shown in Fig. 4 necessarily holds for lower partial pressures of H₂O₂, we will use the 8×10^{-6} reaction probability estimate as a lower limit to the true value.

Cirrus cloud surface areas range between 2×10^{-7} cm²/cm³, typical of subvisual cirrus, to 2×10^{-4} cm²/cm³ for anvil-type clouds (O. B. Toon, private communication, 1997). For these surface areas, and for the reaction probability derived above, atmospheric lifetimes for SO₂ calculated from Equation 12 range between 1050 and 1.05 days. For reference, the lifetime for oxidation of SO₂ by gas-phase OH (DeMore et al., 1997) is two weeks, assuming typical conditions at 8 km altitude, i.e. [OH] = 1×10^6 molecules/cm³, 228 K, [M] = 9×10^{18} molecules/cm³. Thus, for moderately thick cirrus clouds the lifetime of SO₂ may be determined by the heterogeneous reaction with H₂O₂. The same can be said for ice clouds lower in the troposphere as well. Chu et al. have also suggested that the oxidation of SO₂ on ice particles could lead to loss of gas phase SO₂.

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 H₂O₂, 10 pptv SO₂ and cirrus cloud ice particles (Cohan et al., 1999). Assuming all the SO₂ reacts with the H₂O₂ to form H₂SO₄ on the surface of the ice particles, then the surfaces will exceed the 10¹⁴ to 10¹⁵ molecules/cm² criterion which was presented above for poisoning the surface if the total cloud surface area is lower than 10⁻⁶ to 10⁻⁷ cm²/cm³. Thus, it appears that this effect will only be important for the low surface area clouds. However, it is for these clouds that the SO₂ 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 SO₂ 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 SO₂/H₂O₂ reaction. This acidity could arise from either scavenging of acidic aerosols by the cloud particle or by adsorption of ambient levels of HNO₃ to the ice surfaces (Abbatt, 1997; Zondlo et al., 1997). We are also interested to see if the oxidation of HSO₃⁻ by O₃ occurs on ice surfaces, as it does in cloud water.

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