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Atmospheric
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Discussions

Interactive comment on "Oxidation of SO_2 by H_2O_2 on ice surfaces at 228 K: a sink for SO_2 in ice clouds" *by* "S. M. Clegg and J. P. D. Abbatt"

S. M. Clegg and J. P. D. Abbatt

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Anonymous Referee #3

"This is an experimental study of the uptake and reaction of SO2 on ice surfaces that contain H2O2, and has bearing on the rate and mechanism of SO2 oxidation in the upper troposphere. It extends previous flow tube studies of this heterogeneous reaction by the same authors, which used ice surfaces that were not in equilibrium with H2O2 present in the gas-phase.

Constrained by the experimental sensitivity to SO2, the authors were forced to conduct experiments with H2O2 and SO2 at concentrations that are orders of magnitude greater than those found in the upper troposphere. As the uptake coefficients measured show dependence on both concentration of H2O2 and SO2 the extrapolation to the real atmosphere is problematic, and weakens any arguments for a significant contribution of this reaction to SO2 oxidation in the UT. The authors are well aware of these problems, and indeed discuss them in sufficient detail. They even present other arguments against an important role, including the passivation of ice surfaces due to uptake of acids such as HNO3, and a reduced capacity to oxidize SO2 due to the retention of the H2SO4 product on the ice surface. For this reason, the last sentence in the abstract that claims that the lifetime of SO2 within ice clouds may be controlled by reaction with H2O2 seems to be inappropriate."

We feel the last sentence in the Abstract is appropriate because we are only saying that the reaction 'could' control the lifetime of SO2 and not that it necessarily 'will' control the lifetime.

Specific Comments

"Page 81, Line 4. The uptake of SO2 onto the surfaces is enhanced by the presence of adsorbed H2O2. An examination of Figure 1 (upper panel) appears to show that the uptake onto a pure ice surface is in any case not fully reversible, as the adsorption peaks are all smaller than the desorption peaks. The authors should comment on this."

The results reported in Clegg and Abbatt 2001 indicate that the areas of the uptake and desorption peaks for both SO2 and H2O2 are the same within experimental uncertainty. That is, the uptakes are reversible. (Refer to the lower frame of Figure 2 in Clegg and Abbatt 2001 which illustrates this point.) We will make this point explicitly in the new version for ACP.

"Page 81, Line 26/27 The data were analyzed using the method of Brown. What was the size of the correction applied to the raw data to take into account radial and axial concentration gradients ? What was the source of the diffusion constants used to make this correction, and what are the associated errors ? "

The correction is very small, on the order of 15% for reaction probabilities close to 0.01, i.e. pretty much the largest reported here. The diffusion coefficients were estimated using the standard kinetic theory of gases approach but given the relative unimportance of this correction, we don't feel it is necessary to include details.

"Page 81, Line 24. Does the standard approach mean use of the geometric surface

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area, the BET surface area or is a pore diffusion correction applied to the "smooth" films ?"

We use the geometric surface area. However, for arguments presented in Arora et al. (GRL, 26, 3621-3624, 1999), we believe the films are smooth at the molecular level.

"Page 82, Line 8-10. The dependence of the uptake coefficient of SO2 on the gasphase H2O2 concentration is described as linear at partial pressures of H2O2 below 3x10-2 Pa. It would be interesting to see error bars on these data points to see whether an extrapolation to atmospherically relevant H2O2 concentrations is justified by the present data set. Some indication of the reproducibility of the data (and the ice surfaces) is required."

The reviewer's criticisms regarding the lack of error bars associated with the data in Figures 3 and 4 are justified and uncertainties have been added to the Figures in the new ACP version. The tightness of the data points to the line-of-best-fit is a measure of the reproducibility of the data.

"Page 82, Line 10. The section in which the results are compared to those of Chu et al is particularly weak. Even if it is difficult to know what surface coverages of H2O2 prevail in the Chu et al experiments, some comment on the values of uptake coefficient obtained would be useful. Did Chu et al reach the same conclusions regarding the atmospheric relevance of this process ?"

We feel it is not fruitful to extensively compare reaction probabilities measured by Chu et al. to those we measure in this work primarily because the H2O2 surface compositions in the former experiments were not well defined, but also because their experiments were done at significantly lower temperatures than ours (around 200 K) and the films may have a significantly different degree of roughness. In particular, Chu et al. prepared their films by condensing gas-phase H2O2/H2O flows onto cold flow tube walls. The concentration of the film that formed was determined by UV absorption. However, because it is not known whether the H2O2 is distributed uniformly through the film or whether it is at the surface, their estimates of the surface coverage vary by close to three orders of magnitude. Nevertheless, for comparison sake, in the ACP version of the paper we will state that Chu et al. have "observed reaction probabilities on the order of 10-4 at close to 200 K on 3.0 wt% H2O2 ice films".

Motivated by their data Chu et al. also suggested that the adsorption and heterogeneous oxidation of SO2 by H2O2 on ice particles could lead to loss of gas phase SO2. This will be mentioned in the ACP version of the paper.

"Page 84, Line 5. The coincidence of the deviation from linearity in the plot of SO2 uptake coefficient versus H2O2 with the calculated value of the extrapolated vapor pressures of H2O2 over aqueous solutions may be fortuitous. The authors should inform the reader about the range of temperatures actually covered in the work of Schumb et al, and the errors associated with the extrapolation to 228 K. Also, is there any reason to expect that the uptake coefficient of SO2 would decrease when a thermodynamically stable H2O2 solution is formed on the surface as the authors observe ? (in the absence of error bars it is not possible to say whether this decrease in uptake coefficient is real!)"

Given the error bars, the deviation of the data points at high peroxide partial pressures from those at lower pressures does seem to be real. Our suggestion is that the nature of the surface at the high pressures, i.e. a liquid solution, is very different from that at low pressures, i.e. a solid. A priori, it is hard to predict what effect this change in surface structure would have on the reaction probability. The error in the extrapolation of the Schumb et al. data (which extends from 273 to 303 K) is less than a factor of two, so it is unlikely that the agreement between the partial pressures at which we observe this deviation in the behavior from the pressure predicted for the phase transition from the Schumb et al. data is entirely fortuitous (unless, of course, there are systematic errors in the Schumb et al. data set).

"Figure 2. This is the data from the 4 experiments shown in Figure 1. What do the error bars represent here. Is the data aquisition rapid enough to resolve the initial value of the uptake coefficient ?"

The data points represent Sout/Sin where Sout is the SO2 signal immediately after the injector is withdrawn and Sin is the baseline signal just before the injector is

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withdrawn. The uncertainties in the measured Sout and Sin were determined from the noise associated with the measurement of those values. The uncertainties in Sout and Sin were propagated through the ratio which generated the error bars displayed in Figure 2.

The reviewer alludes to an important point, namely that our experimental technique is sensitive to timescales of a second or so, i.e. which is both the time it takes to withdraw the injector and our data acquisition sampling time. We will add a caveat to the ACP paper that the 'initial' uptake coefficients that we measure may be lower limits to values that could be measured on a shorter timescale.

"Figures 3 and 4. Error bars on the data points please."

This reviewer's comments regarding the lack of error bars for the data in Figures 3 and 4 are justified and uncertainties have been added to the Figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 1, 77, 2001.

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