

Interactive comment on “Oxidation of SO₂ by H₂O₂ on ice surfaces at 228 K: a sink for SO₂ in ice clouds” by “S. M. Clegg and J. P. D. Abbatt”

Anonymous Referee #3

Received and published: 29 October 2001

General Comments

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

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contribution of this reaction to SO_2 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 HNO_3 , and a reduced capacity to oxidize SO_2 due to the retention of the H_2SO_4 product on the ice surface. For this reason, the last sentence in the abstract that claims that the lifetime of SO_2 within ice clouds may be controlled by reaction with H_2O_2 seems to be inappropriate.

Specific Comments

Page 81, Line 4. The uptake of SO_2 onto the surfaces is enhanced by the presence of adsorbed H_2O_2 . 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.

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 ?

Page 81, Line 24. Does the standard approach mean use of the geometric surface area, the BET surface area or is a pore diffusion correction applied to the "smooth" films ?

Page 82, Line 8-10. The dependence of the uptake coefficient of SO_2 on the gas-phase H_2O_2 concentration is described as linear at partial pressures of H_2O_2 below 3×10^{-2} Pa. It would be interesting to see error bars on these data points to see whether an extrapolation to atmospherically relevant H_2O_2 concentrations is justified by the present data set. Some indication of the reproducibility of the data (and the ice surfaces) is required.

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 H_2O_2

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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 ?

Page 84, Line 5. The coincidence of the deviation from linearity in the plot of SO_2 uptake coefficient versus H_2O_2 with the calculated value of the extrapolated vapor pressures of H_2O_2 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 SO_2 would decrease when a thermodynamically stable H_2O_2 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 !)

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

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

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

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