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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”

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Anonymous Referee #1

1. "Page 84. H2O2 was in isotherm equilibrium with the ice surface (approximately) (page 80) before SO2 was introduced to the system. Should [H2O2(ad)] be nearly a constant? Also, [H2O2]$>$[SO2], the competition between H2O2 and SO2 should not be a significant factor."

These experiments were designed such that the reaction involved pseudo-first order conditions where [H2O2(ads)]$>$[S(IV)(ads)]. Therefore, even after the addition of SO2, [H2O2(ad)] should be constant during the heterogeneous oxidation of SO2(ads).

It is probably true that there is little competition between H2O2 and SO2 when both are adsorbing to the ice, given that the surface coverages are in the unsaturated portion of the adsorption isotherms for the partial pressures used. Indeed, we have new, unpublished data (O. Sokolov, J. Abbatt, to be submitted to GRL) that demonstrate that little competition occurs when acetic acid and 1-butanol are co-adsorbing at low partial pressures. The text of the revised version will de-emphasize this suggestion that competition may occur.

2. "The semi-quantitative or qualitative mechanism/explanation has some problems. SO2 is efficiently taken by H2O2 covered ice surfaces, but not on H2O surfaces. Reaction 4 was assumed to be the rate determining step. As it was written, Reactions 2-3, the loss of SO2 on H2O surfaces, should be slower steps. Reaction 4 is a reversible reaction and a rate expression in Equation 6 should have both forward and backward terms. Equation 7 was from isotherms of SO2 on H2O surfaces. The expression for [HSO-3 (ad)] may not be that simply as it was given in Equation 7 if one applies the steady-state approximation to Reactions 1-5."

It should be pointed out that the reaction mechanism we present in Reactions 1 to 5 is only a postulate, based in part on the observation of Chu et al. 2000 that the exposure of SO2 to ice surfaces containing H2O2 yields S(VI). At present it agrees with the observed kinetics. Specifically: 1. We know that the overall extent of SO2 adsorption, as determined by Reactions 2 and 3, is low. However, no experimental studies have quantified the kinetics of adsorption under these conditions and so one can not say, conclusively, that these will be the slower steps. Generally, mass accommodation coefficients to surfaces are quite large whereas the reaction probabilities that we measured were as small as 10-3. 2. The reviewer is quite correct that some of the reactions are equilbria, and they will be written as such in the ACP versoin of the paper. (In fact, the reactions were written as equilbria in our submitted text but they were not transcribed properly when the manuscript was published in ACPD). Our general assumption here is that Reactions 1 to 3 are established as rapid equilbria, whereas Reaction 4 progresses only in the forward direction (or, at least, the reverse reaction is slow in a relative sense). Our motivation in choosing Reaction 4 as the rate-determining step and not Reaction 5 is our inference that acidity, from the reaction product H2SO4, slows down the reaction. The rate constant for Reaction 5 will clearly be very large, being an anion-cation reaction.

3. As pointed out above, since both SO2 and H2O2 are adsorbing in the unsaturated portion of the adsorption isotherm, it is unlikely that there is significant competition between the two. And so, we feel justified in assuming the equilibria of reactions 2 and 3 which prevail on clean ice are not significantly perturbed by reaction 1.

3." Equation 11 was obtained by a semi-quantitative approach. The discussion in the last paragraph on page 83 perhaps stretched the conclusion of Equation 11 beyond its limit. The difference between -0.5 and -0.7 can also be an uncertainty of the semiquantitative approach."

We stated that one explanation for the difference between the observed slope of -0.7 and the predicted slope of -0.5 could be a consequence of experimental uncertainty. In addition to the other potential explanations described in the paper, it is possible that the discrepancy may be explained by an inadequacy in the postulated reaction mechanism. This will now be stated in the ACP paper.

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

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Interactive Discussion

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