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Atmospheric
Chemistry
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Discussions

Interactive comment on “SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation – Part 1: Laboratory investigations” *by* T. Berndt et al.

Anonymous Referee #2

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The author’s assert that there is an oxidation pathway for SO2 that is not in their model. They clearly show that their model is unable to explain the particles that are formed with conventional chemistry. But the question remains, despite their first three publications on this subject, is their calculated H2SO4 representative of that in the experiment? This reviewer is still unable to ascertain the answer to this question and thus has reasonable doubts. It is desirable that the model be fully explained and given a thorough examination

It may turn out that further speculation regarding new SO2 oxidation pathways may be warranted. However, this reviewer suggests that HO2 + SO2 as Davis et al. measure

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should also be considered. This would take place in a kind of chaperone mechanism involving water vapor: HO2.H2O + SO2 (Davis et al. had water vapor present, the conflicting experiments did not.) It seems that this channel has not been given full consideration for the atmosphere. It may be particularly important in this experiment.

Their model apparently assumes that the flow is fully developed laminar, i.e., a parabolic radial velocity profile. How dependent are the calculations on assumed flow profiles? If plug-flow is assumed, what is the effect on the calculated H2SO4 centerline concentration? This reviewer is also concerned about the possibility of large scale eddies due to temperature gradients in the flow reactor. These temperature gradients can appear when the UV lamps are turned on, thus comparing particle formation from bulk H2SO4 with UV initiated H2SO4 is problematic. Even though the agreement of UV results and O3 + alkenes results in earlier papers argues against this, the latter has its own set of problems: high oxidation rates can occur during initial mixing of ozone and alkenes.

Apparently, H2SO4 and 'H2SO4', and thus particles, are concentrated along the centerline of the reactor. Particles can be sampled as a function of the sampling tube's radial position within the reactor. The particles should be present in a narrow radial region near the center. This would address somewhat the concerns of the preceding paragraphs.

They observed no effect on particle size when ˜109 cm-3 of H2SO4 vapor was added from bulk (p9768.) This seems to indicate that these particles do not take up H2SO4, a most surprising result. Or it could mean that they were not adding as much H2SO4 as they thought they were. A concern that they overestimate H2SO4 from the bulk reservoir source does not inspire confidence that they know how much H2SO4 is present during oxidation experiments.

The authors seem to have forgotten (p 9770) about entropy changes in their comments about thermodynamically favored reaction channels. What counts are Gibbs free en-

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ergy changes.

Details: To say it again: in the previous work, is there any direct verification of H2SO4 model values? 9764. l 17 upper limit comment must mean they assume that nucleation occurs only in the fastest portion of the flows. How do they know this? l 18 Many types of mass flow controllers have elastomers or plastics exposed to the gas and thus could introduce impurities, especially, for slightly corrosive gases such as SO2. 9765. l 12 Quoting a first order wall loss rate for H2SO4? In what way is that value incorporated into the model? The model should have H2SO4 diffusing in a known axial flow velocity and a diffusion coefficient is the pertinent variable. Assuming some sort of laminar flow profile, there must be large radial gradients in [OH], which leads to large radial gradients in H2SO4 produced as well as large radial gradients in SO2 consumed. Also, what is the radial profile of the photolysis rate (i.e., is the UV fluence independent of radius?) The explanation and confirmation of the model is lacking, in this paper and in all of their previous work. l 20-23. The ratio of 0.5 quoted here confirms only that the major loss for OH is reaction with furan. 9767. l 13 'cannot exceed the modeled data considerably.' It can exceed it by a factor of 2.3, using this data as a measure. Also, what is average in this context? The radial average concentration? A mixing cup average concentration? What is the calculated centerline H2SO4 concentration? Maybe the authors should quote centerline values primarily. 9771. l 21. Adding NO or NO2 reduces particle formation. It also seems to increase the model calculated H2SO4 values which seems to be due to increases in modeled OH inferred from increases in furan/CO losses. However, the effects of NO and NO2 on OH and HO2 etc. can also be modeled. Does such modeling help or hinder their arguments?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9761, 2008.