Atmos. Chem. Phys. Discuss., 8, S5338–S5342, 2008
www.atmos-chem-phys-discuss.net/8/S5338/2008/

Atmospheric Chemistry and Physics 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.

T. Berndt et al.

Received and published: 28 July 2008

The authors thank this reviewer for the comments. Replies are given below:

Reviewer: "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 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."

Reply:

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Payne, Stief and Davis (JACS, 95, 1973, p.7614) published for HO2 + SO2 a rate coefficient of 8.7x10(-16) cm3/s determined in an indirect way. This data is far away from the results of other researchers. E.g., Burrows et al. (Proc.R.Soc.Lond., 368, 1979, p.463) deduced from direct measurements an upper limit for k(HO2+SO2) of 2x10(-17) cm3/s. The IUPAC recommendation for atmospheric chemistry states k(HO2+SO2) $<$ 10(-18) cm3/s. But nevertheless, if there is an effective catalytic effect of H2O, HO2(H2O) + SO2 (Payne et al. measured in presence of 20 torr H2O, the other studies have been done under dry conditions), the impact of HO2 + SO2 -$>$ SO3 + OH in our extended ideal plug model using the rate coefficient by Payne et al. was investigated. The extended ideal plug model considers all reactions of OH, HO2, O3, CO, H2O2, SO2 (and for NOx if needed) and reactions (1) - (4) in this manuscript represent the most important steps describing this system soundly. The modelling showed that there is a 26% increase of H2SO4 at the end of the irradiated section using k(HO2+SO2) = 8.7x10(-16) cm3/s (reaction conditions as given in fig.2 and fig.4). For k(HO2+SO2) = 2x10(-17) cm3/s (upper limit of Burrows et al.) the effect of H2SO4 increase is lower than 1%. Even HO2(H2O) + SO2 with k = 8.7x10(-16) cm3/s cannot explain the discrepancy between the different H2SO4 threshold concentrations.

Reviewer: "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?" - and some points from the "Details"paragraph

Reply:

The three different models used, i) extended ideal plug ii) simple ideal plug (pathways (1) - (4)) and iii) CFD model with pathways (1) - (4) yield results in good agreement. E.g., for the conditions mentioned before (cf. fig.4) calculated H2SO4 concentrations at the end of the irradiated section are: model i): 2.63x10(8) 1/cm3, model ii): 2.58x10(8) 1/cm3) and for model iii) 2.58x10(8) 1/cm3 at centre line and 2.00x10(8) 1/cm3 in the middle between centre line and wall. This comparison shows clearly that application of

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the "simple ideal plug model" is reasonable.

Reviewer: "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."

Reply:

According to our opinion occurrence of large scale eddies is unlikely as the flow tube is kept at a constant wall temperature using a high precision thermostat. Influences of the UV-lamps are very unlikely as a) their thermal emission is low, and b) the lamps are located outside of the thermostated water jacket. Furthermore, large eddies, due to their inherent instability, would result in significant fluctuations in the number concentrations and size distributions measured at the tube outlet. Such fluctuations were never observed during our experiments.

Reviewer: "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 tubes 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."

Reply:

Fluid mechanics suggests that a laminar flow develops after approx. 5 time the diameter of the tube, i.e., after 40 cm. After that a fully developed laminar flow, and the corresponding convective diffusion and source/sink controlled concentration profiles do exist. Therefore measuring at the tube's centre line, which is by the way impossible due to space limitations, will give no additional information. In addition, particles $<=$ 2 nm particles have a pretty high diffusion coefficient causing particles to be dispersed over the tube cross section.

Reviewer: "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."

Reply:

Regarding particle growth for [H2SO4] from bulk of about 10(9) 1/cm3: Primary, the intension of this experiment was to accelerate the growth process for particles from OH + SO2 with the help of H2SO4 from bulk and to perform sensitivity studies with regard to the growth rate depending on H2SO4 in the system, but it does not work. And H2SO4 from bulk was measured directly at the end of the outlet tube from the saturator (identical to the point where H2SO4 from bulk was introduced in the flow tube). And for more than diffusion controlled wall loss (parameterisation via pathway (4) in the models i) and ii); in the CFD model with axial and radial diffusion each collision of H2SO4 with the wall is a loss) there are no arguments.

Reviewer: "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- ergy changes."

Reply:

We agree to the referee‘s statement regarding the Gibbs free energy change. Text will be changed accordingly.

Reviewer: "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."

Reply:

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High purity carrier gas (99.9999999%) is used in these experiments. At the outlet of the flow tube we attempted to measure impurities (memories from experiments with organics or evaporations from gaskets etc.) using a cryo-focusing unit with subsequent GC analysis allowing detection limits better than 10(10) 1/cm3. No impurities were detectable.

Reviewer: "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."

Reply:

In both ideal plug models i) and ii) diffusion controlled wall loss for H2SO4 using parameterisation via pathway (4) according to Hanson and Eisele, JPC, 104, 2000, p.1715, is assumed. In the CFD model iii) axial and radial diffusion is considered and each collision of H2SO4 with the wall is assumed to be a loss out of the gas phase. For comparison of modelling results please see the example given above.

In summary, we feel that a lot of the referee's comments and concerns are connected to the issue of the actual H2SO4 concentration during nucleation. According to our opinion, even if all the referee's concerns would be valid, which is very unlikely according to our conviction, these effects could never explain the 3 order of magnitude H2SO4 concentration difference observed when comparing nucleation for H2SO4 generated via OH + SO2 and taken from bulk.

Finally we would like to state that a) we have done our very best to perform our experiments as carefully and accurately as possible, b) we appreciate any constructive and helpful comments, but c) we think that its time for other researchers to repeat our experiments and to continue the discussion at the level of peer reviewed publications.

Torsten Berndt and Frank Stratmann

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

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