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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Laboratory study on new particle formation from the reaction OH + SO_2: influence of experimental conditions, H_2O vapour, NH_3 and the amine tert-butylamine on the overall process" *by* T. Berndt et al.

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In this paper, the authors presented laboratory results showing the dependence of observed new particle formation rates on a number of important factors: counting efficiency of particle counting instruments, residence time, H2SO4 vapor concentration, relative humidity, and presence of different additives (H2, CO, 1,3,5- trimethylbenzene, NH3, tert-butylamine). The authors demonstrate the critical importance of particle counting efficiency and particle sizes in the interpretation of the experimental results. The authors also obtained some quantitative results about the effects of relative humid-

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ity (RH), ammonia, and tert-butylamine on the nucleation. A parameterization of the experimental data was derived using power law equations for H2SO4 and H2O vapor. The work is a useful addition to the previously published work on the laboratory studies of SO2+OH nucleation and provides new insight into the issue. The paper is well written and the topic is suitable for ACP. However, I have a number of concerns which should be properly addressed before the publication of this manuscript in ACP.

Major comments:

1. Page 6462, first paragraph. As the authors pointed out, the presence of one or two H2SO4 molecules in the critical cluster under the conditions is in clear contradiction to those reported in a number of previous laboratory studies. What are the possible explanations? Can the difference in the counting efficiency fully account for the contradiction? In some of previous laboratory studies, H2SO4 concentrations were very high (>1E10/cm3, up to $\sim$ 1E12/cm3 in the nucleation zone) and thus the growth rates of nucleated particles should be quite faster and the resulting particles might be substantially larger than the instrument cut-off sizes (and thus counting efficiency might not be an issue).

2. If H2SO4-H2O binary homogeneous nucleation (BHN) (without any involvement of other species) did happen under the conditions shown in this study, then the results of this study are also in clear contradiction to previously well established thermodynamic data (vapor pressures, surface tension, etc.) of H2SO4-H2O binary solution. Based on the recent kinetic BHN model constrained by multiple laboratory data (Yu, JCP, 2007), there is no way that BHN occurs under the condition. This should also be pointed out and discussed.

3. The authors argued that their results indicate one or two sulfuric acid molecules in the critical clusters and that this is in agreement with atmospheric measurements. A cluster composed of two sulfuric acid molecules and three water molecules has a mass diameter of $\sim$ 0.8 nm. As I understand, field measurements reported in Kulmala

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et al. (Science, 2007) suggest critical cluster in the range of ∼1.5 nm diameter (which contains ∼ 7 H2SO4 molecules and some water molecules). In addition, ion mobility distributions reported in Hirsikko et al. (ACP, 2007) clearly indicate the presence of small ion mode around 1 nm. If the neutral critical cluster is only ∼ 0.8 nm, why these ion clusters around 1 nm did not nucleate before the smaller 0.8 nm neutral clusters were activated?

4. Equation 6a. Based on hydration and binary nucleation thermodynamics, relative humidity (RH) rather than [H2O] should affect the nucleation. Does your formula expect to hold under a different temperature? If not, such formula is not very useful. I think that it will be more useful if you can express the formula in term of RH instead of [H2O].

5. Figure 6. Based on laboratory results presented in this study at T=293 K and RH=61%, nucleation rate can reach 5 cm-3s-1 when [H2SO4]=1E6/cm3 and exceed 100 cm-3s-1 when [H2SO4]=1E7/cm3. If this is what will happen in the real atmosphere, one would expect significant and frequent nucleation in the summer in the boreal forest region. However, as I understand, nucleation events are infrequent and weak during the summer season in the boreal forests. In addition, your formula will also predict significant nucleation and very high particle number concentration over the tropical oceans which will be inconsistent with ship- and aircraft- based measurements (Yu et al., JGR, 2010). Could any other factors in addition to [H2SO4] and [H2O] affect the nucleation observed in your study?

6. The authors made great effort in reducing the impurity and showed that the impurity is likely below 1E9 molecule/cm3. Since the nucleation precursor H2SO4 vapor concentration is between 1E6-3E8/cm3, any impurity in the level of below 1E9 molecule/cm3 could still impact the results. Some organic molecules can have size bigger than 1 nm (Zhang et al., Science, 2004). If such organic molecules exist as impurity, could they be activated by H2SO4 condensation and detected by the counting devices?

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7. Page 6457, lines 13-14. Also Fig. 1. The evolution of H2SO4 concentration inside the flow tube is clearly important. The authors discussed the method to calculate H2SO4 concentration and compared the calculated values at the outlet with those measured. It will be helpful if the authors could provide a figure showing profiles of modeled H2SO4 concentrations inside the flow tube and illustrate how the average values were obtained for representative cases.

8. Page 6451, second paragraph. The authors listed a number of reasons that might have caused the differences in various experimental results. In Berndt et al. (ACP, 2008), the authors presented detailed laboratory study and analysis and main conclusions are almost opposite to those of the present paper. For example, Berndt et al. (2008) showed that "H2SO4 from the liquid reservoir, its concentration being at least in the same order or one order of magnitude higher compared to that of in-situ produced "H2SO4" (cf. Fig. 4), does not significantly contribute to particle growth". I don't think many observed phenomena presented in Berndt et al. (ACP, 2008) can be simply explained by counting efficiency, residence time, and H2SO4 loss. The authors should provide more detailed explanations on what happened in the laboratory studies presented in their previous ACP paper (i.e, Berndt et al., 2008).

Other comments:

1. Abstract. Lines 17-18, 20-21. Should be quantitative here (such as the values given in the last sentence of page 6470).

2. Page 6458, lines 19-21. Since the particle size distributions were measured, it will be helpful to integrate particle size distribution to obtain the total mass in measured particles to see how much it can account for the additional H2SO4 consuming step.

3. Page 6459, line 19. Why OH concentration in the given range did not influence the number of particles detected? Was SO2 concentration varied accordingly to give the same H2SO4 concentration?

4. Page 6465, line 24. I think that an example (or case study) showing the good agreement should be given.

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