**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$_2$O vapour, NH$_3$ and the amine tert-butylamine on the overall process" *by* T. Berndt et al.

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Received and published: 15 June 2010

The authors thank Fangqun Yu for the constructive comments.

F. Yu:

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 contra-

diction? In some of previous laboratory studies, H2SO4 concentrations were very high (>1E10/cm3, up to _ 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).

Reply: At the moment a comprehensive modelling study is carried out regarding the nucleation experiments given so far in the literature. Preliminary results show that many of them are in reasonable agreement with our experiment when residence time and consequently growth, and CPC detection efficiency are considered adequately. Nothing changed in the text.

F. Yu:

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.

Reply: As stated in the manuscript, we cannot rule out contaminations below a few 10(9) cm(-3). Consequently, we cannot rule out a third component taking part in the nucleation process featuring a concentration below that level. In other words, we don't claim and actually never did claim that BHN models are wrong. However our results are indicative that, for whatever reason, maybe a third component (e.g. an amine), they may not be appropriate to describe what's going on. We will include a respective statement in the text.

F. Yu:

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 _ 0.8 nm. As I understand, field measurements reported in Kulmala 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?

Reply: Considering binary nucleation, the nucleation theorem gives the number of H2SO4 and H2O molecules in the critical cluster from which the cluster size can be calculated. However, assuming e.g. a third component being involved in the nucleation process functioning either as seed (activation) or true third component (ternary nucleation), nucleation theorem would still yield the number of H2SO4 molecules involved in the rate limiting step (e.g. one in case of activation or maybe 2 in the case of ternary nucleation), however determination of critical cluster sizes from the nucleation theorem is not straight forward anymore. We think that the referee's comment points at the still existing lack of understanding concerning the actual nucleation mechanism, and as long as this mechanism is not understood, and consequently the composition of the critical clusters is not known, in our opinion, cluster sizes determined applying nucleation theorem should not be over-interpreted when comparing to experimental data.

F.Yu:

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].

C4026

Reply: Strictly speaking the formula is only valid in the temperature range investigated. Considering a specific temperature, conversion from relative humidity to [H2O] and vice versa, as done here, is straight forward. The referee is correct that from a thermodynamic point of view RH is the more appropriate parameter. In the revised version of the manuscript, we will therefore give the formula in terms of RH. However, this will not automatically enlarge the temperature range it should be used in as at least k and maybe also alpha in eq. 6 should be temperature dependent.

F.Yu:

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?

Reply: In Fig.7 the measured mean particle diameters for r.h.= 22 and 61% are depicted. The growth rate at r.h. = 22% meets that what is expected from the theory. But the relatively strong increase of particle diameter with r.h. is not in line with theoretical predictions. So we cannot exclude the possibility that additional condensing substances could arise from the water saturator. Furthermore, it is not clear whether these possible additional vapors did influence the nucleation process. It could be a source of uncertainty regarding the r.h.-dependence of nucleation. But it is to be noted that all laboratory studies so far observed a very strong r.h. effect on nucleation, mostly much more pronounced than observed in our study. This point will be discussed in the revised manuscript.

C4027

F.Yu:

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?

Reply: If the activation mechanism would be responsible for our observations, the overall kinetics should show 1st order dependence on H2SO4. However, we observe a 2nd order dependence on H2SO4. This suggests the activation of impurities by H2SO4 to be of minor importance. The manuscript will be changed accordingly.

F.Yu:

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.

Reply: An additional figure will be given showing calculated profiles in the tube as well as the corresponding average values for H2SO4 as used in the analysis of the data.

F.Yu:

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).

Reply: In ACP, 2008, our own data using a H2SO4 point source (liquid source) were qualitatively in line with former observations using a similar experimental approach and commercial CPC′s (nucleation for about 10(9) cm(-3) of H2SO4) but clearly contrary to the findings with continuous H2SO4 production via OH+SO2. Explaining the discrepancy, the possible role of HSO5 was discussed. Applying CPC′s with clearly enhanced detection efficiency connected with direct H2SO4 measurements revealed that a mechanistic discrepancy between H2SO4 from bulk and H2SO4 via OH+SO2 does not really exists. Obviously, the most critical points are the growth to detectable sizes and the counting efficiency itself connected accordingly to the residence time and the loss processes. This will be explained more detailed in the revised version.

F.Yu:

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.

Reply: 1. We will state also in Abstract numbers describing the enhancing effect of NH3. 2. An example how condensation of sulfuric acid on the nucleated particles (the condensed amount being derived from the measured size distributions) can account for the missing fraction of H2SO4 will be given. 3. Yes, of course. In each case, particle number is a function of H2SO4. If OH was reduced, SO2 had to be increased accordingly. 4. We can add a figure showing the experimental observations from Heidelberg and Hyytiälä, J vs. [H2SO4], as well as the predictions from the parameterization.