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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.

T. Berndt et al.

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

(1) In the introduction of Part I paper, the authors have summarized the Berndt et al. 2004, 2005, 2006 results and came to conclusion that the SO2 + OH reaction provides Lower threshold of H2SO4 than those in liquid experiment (Ball et al., 1999; Zhang et al., 2004). We have done experiments with SO2+ OH reaction to produce H2SO4, but our threshold is not as low as Berndt et al. (that is, e8-e9 cm-3, as opposed to e6-e7 in Berndt al.). Our findings are summarized in David R. Benson, Li-Hao Young, F. Rifkha Kameel, Shan-Hu Lee, Laboratory-Measured Sulfuric Acid and Water Homogeneous Nucleation Rates from the SO2 + OH Reaction, Geophys. Res. Lett., 35,

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Interactive Discussion

Discussion Paper

L11801, Doi:2008GL033387 and L.-H. Young, D. R. Benson, F. Rifkha Kameel, Jeffrey R. Pierce, Heikki Juninnen, Markku Kulmala, and Lee, S.-H., Laboratory studies of sulfuric acid and water binary homogeneous nucleation: Evaluation of laboratory setup and preliminary results, Atmos. Chem. Phys. Discuss. 8, 1-47, 2008 (in press for Atmos. Chem. Phys. now). In these two studies, we have used CIMS to directly measure H2SO4 and also took into account wall loss of H2SO4 for our threshold estimation – for some of results presented in Young et al. 2008, we even have used two CIMSs to simultaneously measure both the initial and residual H2SO4 at the beginning and the end of the nucleation reactor. This is so far one of the most constrained data on H2SO4 for BHN studies. I think it would be more appropriate if these two ACPD papers discuss our experimental results – as our results are not entirely supporting these authors' conclusion.

Reply:
In the mentioned Berndt et al. papers it is stated that as a result of IfT-LFT experiments the threshold concentration of H2SO4 or "H2SO4" (stands for all SO2 reaction products) needed for nucleation is in the order of 10(7) molecule cm(-3). (In the atmosphere, new particle formation has been observed for H2SO4 concentrations of 10(7) molecule cm(-3) and below.) The numbers of detected particles and, consequently, the apparent threshold concentration depend on the experimental conditions (e.g. residence time, r.h.) chosen. Therefore, a detailed analysis will show whether or not the experimental findings from the Lee group are significantly different from IfT-LFT results. We agree that H2SO4 analysis by means of a mass spec technique is desirable but do not consider it crucial at this stage. For selected conditions with relatively high SO2 consumption the measured SO2 decay is in good agreement with modelling results. This indicates that H2SO4 or "H2SO4" concentrations in the tube are described well by the modelling approach. In the revised manuscript a paragraph has been added describing in more detail the modelling approach and the role of HO2 + SO2 as a possible source for additional H2SO4.

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(2) While the main conclusion as well as the motivation of these two works are based on the difference in H2SO4 threshold, I am concerned that the Berndt et al.'s H2SO4 has never been measured directly. The kinetic calculation used in Berndt et al. – especially not proven by a calibration with H2SO4 measurements yet – is not a best approach for H2SO4 detection, as this indirect calculation method can introduce large uncertainties in their threshold estimation of H2SO4 and thus their conclusion. Without this issue resolved, any further discussions can be less convincing.

Reply:
Please see the statements given above.

(3) Similarly, the Berndt et al. system especially with SO2, O3, UV, H2O, CO/hydrocarbon and NO/NO2 must be carefully reexamined. This system is in fact very similar to the LA smog chamber condition and the authors' discussion requires comprehensive reexamination to understand the byproducts of their system and their effects on nucleation. This discussion is very important and yet unclear to me in their three previous and current ACPD papers – note that tropospheric chemistry productions are non-linear and sensitive to different NO/NO2 and hydrocarbon concentration regimes.

Reply:
The reviewer should clearly state what the points of criticism are, i.e., what kinds of by- products should have what effect on the nucleation observed in the IfT-LFT experiments. We would appreciate getting valuable hints for an improvement of the experimental approach as well as for data assessment. It should be mentioned that up to now we have investigated the influences of the following substances by adding them to the carrier gas: an alcohol, different carbonyls and an acid in the concentration range 10(10) - 10(12) molecule cm(-3). The observed number of newly formed particles did not show any significant effect. Experiments using alpha-pinene, trans-butene, furan, mesitylene, cyclohexane, or heptane instead of CO as OH scavenger did not show any relevant effects on the number of newly formed particles either. Furthermore, in exper-

iments with H_2SO_4 from the liquid reservoir, cf. fig.2 and fig.6 this ACPD manuscript, detected particle formation is roughly in line with what is to be expected from binary H_2SO_4/H_2O nucleation and there are no indications for additional species enhancing nucleation rate (like aromatic acids, cf. Zhang et al., Science 2004). Switching on UV and starting HOx chemistry (in absence of SO_2!) particle number remains unaffected, i.e. below the noise level. This implies that also oxidation products of any impurities do not enhance H_2SO_4/H_2O nucleation in our experiment. In the revised manuscript a paragraph has been added regarding this topic.

(4) In Part I Figure 2, In this Figure 2, the slopes of Berndt et al. and Zhang et al., and Ball et al. are all in the range 5-8. Our SO_2 + OH reaction experiments also show similar values – please include our SO_2 + OH experimental results (Benson et al., 2008; and Young et al., 2008) in this figure. Please give explanations on these similar slopes from different experiments, especially with regard to the discussion on the authors' new pathway involving $H_2S_2O_8$.

Reply:
Our slopes are clearly influenced by decreasing counting efficiency of the UCPCs used, see also statements in Science, 2005. Therefore, we did not stress any argumentations regarding slops log(N) vs. log([H_2SO_4]) and the resulting number of molecules in the critical cluster. A comparison and discussion should be done on a later time when more reliable data for log(N) vs. log([H_2SO_4]) will be present. And with the knowledge of the "real" slopes the possible role of $HOSO_2O_2$ can be further evaluated.

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