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Comment

Interactive comment on “Laboratory study on new particle formation from the reaction OH + SO₂: influence of experimental conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the overall process” by T. Berndt et al.

Anonymous Referee #1

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General comments: The authors of the current manuscript solved – as it seems – this long standing discrepancy between lab and atmospheric new particle formation. The use of new particle detectors allows them to directly assess the nucleation process (Sipila et al. 2010). They showed that the lab experiments so far were biased by the limited residence time of the experiment and the counting efficiency of the particle detectors. In the follow up study presented here additional information on the experimental setup is presented. The importance of the residence time effect in explaining the discrepancy between existing lab experiments is underscored (e.g. (Berndt, Strat-

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mann et al. 2008) vs. (Young, Benson et al. 2008)). Further the role of water vapor and ammonia for the nucleation process was investigated using the updated experimental setup. A strong positive dependence of the particle formation with increasing relative humidity was observed. A parameterization of the experimental data was developed using power law equations for H₂SO₄ and H₂O. The exponent of water vapor in the nucleation equation was found to be close to 3. Further an increase of particle number with the addition of ~5 and 50 ppb ammonia was observed. Ammonia showed an enhancing effect on particle growth. The authors present also some preliminary results on the role of amines on new particle formation, showing an enhancing impact on nucleation and growth. The paper is well written and is within the scope of ACP. I recommend this paper to be published in ACP. I have a few comments that I would like to be addressed.

Specific (major) comments: 1.) The authors explain the apparent discrepancy between lab and atmospheric measurements with the counting efficiency of the particle detectors and the limited residence time of the experiments (and not with the possible role of HSO₅ products in the nucleation process as suggested before). If this is the case, what is the explanation for the suppression of the particle formation with addition of NO as presented in Berndt et al (2008)? The particle formation for constant SA was reduced by 3 orders of magnitude by addition of nitrogen oxide (NO = 3.1×10^{12} molecule cm⁻³). This effect is much larger than the effect related to the addition of NH₃ presented here (~ one order of magnitude) and needs clearly more attention in the current manuscript! Further, how reliable is the calculation of the sulfuric acid concentration in the nucleation zone of the flow reactor? In a recent paper by Sorokin (ACP 2010) other channels for the formation of sulfuric acid from the UV light induced SO₂ oxidation have been presented. In addition there exists a discrepancy between measured and calculated sulfuric acid concentration (Fig 1 and the cited Figs S1 (Sipila, Berndt et al.)) and between the theoretical and measured wall loss of sulfuric acid (Fig S3 (Sipila, Berndt et al.)). Together with the (so far) unexplained NO_x dependency mentioned above this could point to a systematic uncertainty in the data! P 6458 line 10-26: In this respect

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the discussion on the deviation between the measured and modeled H₂SO₄ concentration needs a significant improvement! Previously a second order loss process was suggested to explain this deviation (H₂SO₄ dimer formation as observed in the CIMS, (Sipila, Berndt et al.))? From the discussion here, it is not clear if the loss is first or second order and/or if the discrepancy could be simply explained by aerosol formation? Since the particle size distribution was measured and hence the aerosol mass is known this needs to be quantified! P6458, line 16: reformulate and clarify the sentence! “This step has to be of an order higher than 1”. P 6458 line 23-26: the paragraph could be omitted since it is simply a repetition of text above P6457 line 2: For each experiment the effective photolysis rate was adjusted to fit the measured O₃ decay. Why? (Instability of the UV-lamps or could this point to an uncertainty in the assumed reaction mechanism?) P6454 line 1: How are the measurements performed in case of lowest flow rates? The total sample flow of the CIMS + 3 CPC + O₃ /SO₂ analyzer is certainly higher than 3.3 or 11 L/min!?

2.) The quality of the gas phase measurements of ammonia as well as organics using GC and PTRMS are not convincing. More details of the measurements are needed! P6453 line 13: “stated” detection limit. The real detection limit might differ significantly from a detection limit “stated” in the manufactures manual. Wasn’t the instrument properly calibrated and characterized? P6459 line 25: “high sensitivity” PTRMS: Details of the measurements are unclear e.g. the sensitivity/ limit of the detection. As I understood, only carrier measurements were performed. However a major source of contamination might be the water (see below) and/or O₃ generator. Thus measurements should be performed at different humidity’s, O₃, SO₂, H₂ and CO concentrations. For a proper setup of the “high sensitivity” PTRMS operation please see (de Gouw and Warneke 2007). In my point of few the comparison of the carrier gas with a zero air generator (which was obviously not properly working) is nonsense (as described in (Sipila, Berndt et al.)).

3.) Section 3.5.2 and Fig 7: Particle growth. This section needs more explanation.

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In a recent paper from Kulmala's group (Nieminen et al., 2010) the theory of particle growth from condensation of H₂SO₄ at different relative humidity's is discussed. While the particle growth at 22% seems to be in accordance with the theory the growth at higher humidity's is much larger than expected from the theory. This points towards the presence of additional condensing vapors at high humidity's and needs to be clarified.

4.) 3.6.1 Ammonia: The results are only discussed with respect to previous lab experiments. I'm a bit surprised that the discrepancy between the new results and theoretical considerations of binary H₂SO₄/H₂O and ternary H₂SO₄-H₂O-NH₃ are not mentioned at all in the manuscript. Especially the fact that existing ternary nucleation theories predict the highest sensitivity to changes in ammonia at concentration levels of a few ppt (e.g Merikanto et al., 2007). In a study by Zhang (Zhang, Wang et al. 2009) no enhancement of the particle growth due to ammonia was observed. This was explained with the larger density of ammonium sulphate compared to sulphuric acid and thus "its formation does not necessarily contribute to a net increase in the particle size". This discrepancy should be discussed in the manuscript.

5.) 3.6.2 Amines: The results are clearly preliminary. But if presented, at least the effect on the cluster composition (number of H₂SO₄ and amines per cluster) should be discussed. Further the discussion of the nucleation enhancement of amines should be extended. It was stated that: "the enhancing effect for nucleation and particle growth was found to be much stronger." Please give some numbers (enhancement factors).

Technical corrections": typing errors, etc.: P 6450, line 5: proper reference for kinetic nucleation: McMurry, P. H. and S. K. Friedlander (1979). "New Particle Formation in the Presence of an Aerosol." Atmospheric Environment 13(12): 1635-1651. P6456, line 24: correct reference: "Petäjä (2008)" should be 2009. P6456, line 20: correct labels of the reaction rates. They are not in line with text on page 6457 line 5-7

References: Berndt, T., F. Stratmann, et al. (2008). "SO₂ oxidation products other than H₂SO₄ as a trigger of new particle formation. Part 1: Laboratory investigations."

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