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Atmospheric
Chemistry
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Discussions

Interactive comment on “Ternary homogeneous nucleation of H_2SO_4, NH_3, and H_2O under conditions relevant to the lower troposphere” *by* D. Benson et al.

Anonymous Referee #2

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Nucleation of sulfuric acid particles and the effects of different additional compounds to nucleation have been investigated by numerous laboratory studies within past two decades. However, the results have shown significant divergence and the detailed understanding of nucleation mechanisms even in controlled laboratory systems has been pending. Effect of ammonia on sulfuric acid water nucleation has been studied previously but the results from the different experiments have been, to some extent, conflicting and more work is required before the potential role of ammonia in atmospheric new particle formation can be decoded. Thus, the topic of the present study suits well within the scope of ACP, but there are several crucial issues mainly related to the quality of data, that authors should answer before this manuscript can be published.

Nucleation rates J are measured in the [H2SO4] range 2x10ˆ6 - 2x10ˆ7 cm-3 (which is equivalent to a mean [H2SO4] in the growth region of below 1x10ˆ6 - 1x10ˆ7 cm-3, after accounting for wall losses). This corresponds to a growth rate due to sulfuric acid condensation of about 0.1 - 1.0 nm/hr (see e.g. Nieminen et al., 2010, Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10, 9773-9779.). Even at the maximum residence time (240 s), the mean particle growth (by sulfuric acid) is therefore only 0.007 - 0.07 nm. Please explain how you can measure any meaningful nucleation rate in your experiment using a CPC with a $\sim$3 nm threshold, when the mean time to grow from nucleation size (1-2nm) to detection size is at least 1-10 hours. How significantly particle undercounting affect the measured slopes? This is a highly fundamental question, to which the authors should be able to provide a satisfactory answer.

Related to above comment, authors refer to their earlier studies (Benson et al., 2008; Young et al., 2008; Benson et al., 2009) for description of the experimental setup. However, authors have modified the way that sulfuric acid is introduced into the flow tube. My concern is that if sulfuric acid is introduced from the center of the flow reactor, diffusion is not fast enough that concentration near the tube wall (where CIMS inlet is located according to cited studies) would be representative for the concentration in the nucleation region. This might yield in serious underestimation of sulfuric acid concentration. Authors should discuss their experimental setup in more detail, potentially with help of a drawing. Same comment applies for ammonia measurements.

How is sulfuric acid CIMS calibrated? And what is the calibration coefficient used to convert measured m97/m62 ratio to sulfuric acid concentration?

After addressing the above mentioned points, I presume that numbers and/or accuracy of the numbers given in the text might need to be revised. At present, no conclusions on the composition of critical cluster in the experiment can be drawn from the data.

Abstract: l.3: “..laboratory experiments have failed to reproduce atmospheric obser-

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vations". This is not completely true as Berndt et al. (2010) and Sipilä et al. (2010) reproduced atmospheric J vs. [H2SO4] even in absence of added ammonia and Metzger et al. (2010) by adding organics in the system. Berndt et al. (2010) observed a promoting though not strong effect of ammonia on nucleation rate.

Determining the critical cluster composition from the measured slopes has been discussed by referee 1 and I will not repeat it here.

l.12: "..threshold for of H2SO4 concentrations . . . do not vary in the presence or absence of NH3." This is too strong statement and not even correct. Certainly, it does not vary orders of magnitude but it still varies.

Experiments, l.23.: It is unclear why changing [H2SO4] by adjusting [OH] is an "improvement" in comparison to adjustment of [SO2]. By adjusting [OH] also reaction products from any trace species present in the gas capable of reacting with [OH] will change. These species can potentially participate in nucleation or growth.

Discussions l.17. and Conclusions l.22.: "using the same instrument used in field studies to measure particles (TSI CPC 3876)" It sounds that use of same instrument in laboratory experiment is somehow an advantage and makes the results more representative for the ambient atmosphere. Fact is, though, that in ambient air the particles grow and the particles are detected after their growth above some ∼3 nm. In lab system, if particles do not have time to grow above 3 nm they just are not detected. Formation rate at 3 nm in flow tube is not comparable to formation rate at 3 nm in atmosphere.

Data presented in this paper are conflicting with earlier data reported by the authors (Benson et al., 2008; Benson et al., 2009; Young et al., 2008): 1) Onset sulfuric acid concentrations are clearly lower, and 2) EF's reported in the present work are clearly smaller as could be expected based on Benson et al., (2009) with exponentially increasing EF with lowering SA, and 3) the slopes are different. These differences and reasons for differences are not yet discussed appropriately.

technical comments: monomer cannot evaporate, in references/citations: Antilla->Anttila, Boge -> Böge, Vehkamaki/Vekhamaki -> Vehkamäki, Plass-Dulmer-> Plass-Dülmer,. . .

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 22395, 2010.