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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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The authors thank this reviewer for the constructive comments.

Referee 1:

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 =3.1×1012 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 NOx dependency mentioned above this could point to a systematic uncertainty in the data! P 6458 line 10-26: In this respect 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!?

Reply: In Berndt et al., ACP 2008, the old idea dating from the eighties was discussed that HSO5 as an intermediate from OH initiated SO2 oxidation could trigger new particle formation. The experimental finding that high NO concentrations can suppress nucleation was taken as an argument supporting the potential role of HSO5. Recently, experiments using high efficiency particle counters with simultaneous H2SO4 measurements showed that there exists no clear discrepancy between a point H2SO4 source (liquid) and continuous H2SO4 formation via OH+SO2 pushing back the importance of HSO5 for nucleation. The critical points are obviously the different profiles in the tube in connection with significant wall losses and the efficiency of the growth process, cf. Sipilä et al., Science 2010. It remains speculative what′s the reason for the observed NO effect is. Unfortunately, in these experiments H2SO4 was not measured directly, the acid was determined from titrated OH and known concentrations of SO2. The paper by Sorokin, ACP 2010, deals with possible, additional pathways for H2SO4 caused by UV irradiation as used in the photolysis experiments. A couple of photo-induced reactions are discussed, but their relevance for the resulting H2SO4 concentration is highly uncertain. If correctly understood, the final conclusion of this paper is that additional H2SO4 arising from excited O2 cannot represent more than the "normal" H2SO4 concentration produced via OH+SO2. The good agreement between measured H2SO4 and modelled H2SO4 (using OH chemistry) at the output of the flow tube supports the fact that OH chemistry is dominating. Differences at higher H2SO4 concentrations can be explained by cluster/particle formation consuming H2SO4. From our view point, generally, the agreement between the H2SO4 measurements and the results of modelling do not point at other, significant H2SO4 sources not accounted for in the model (beyond the stated uncertainty for H2SO4). Starting for H2SO4 concentrations of (3-5) 10(7) cm(-3) the measurements show lower concentrations as expected from the model. That′s the range where cluster/particle formation becomes important representing a significant sink for H2SO4 beside the wall loss. Initially, the curvature can be described by a 2nd order process. With further increasing H2SO4 concentration, the H2SO4-consuming processes gain importance and the overall process seems to have an order higher than 2. That′s why it was stated "higher than 1". This topic will be explained more in detail. The daily measurement of O3 photolysis rate is merely

a check for the performance of the OH production. As a result we found that the UV lamps are really stable! CI-MS measurements were possible only for a total flow of 11 l/min. or higher. If the needed gas flow by the analyzers was higher than the carrier flow, the analyzers were connected to the tube one-by-one. We applied no dilution techniques.

Referee 1:

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.)).

Reply: The performance of TGA 310, OMNISENS, was controlled using a NIST NH3 standard. Simultaneously, NH3 concentrations were measured by long-path UV absorption confirming the certification of the standard. There were no indications that the TGA 310 was out of range of factory settings. The detection limit of on-line GC-FID with a cryo-enrichment was determined using known concentrations of 1,3,5-trimethylbenzene (C9H12) and furan (C4H4O). PTR-MS measurements have been done using the pure carrier gas as well as in the presence of H2O and the trace gases. There were no clear hints for the occurrence of organic contamination. Therefore, a limit for organics of a few 10(9) cm(-3) should be a conservative value.

Referee 1:

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

Reply: We agree that water alone is possibly not enough to explain the behavior found. The observed enhancement of growth is more than expected assuming collision limited growth by H2SO4 with a few co-condensing water molecules per H2SO4 molecule. Explanation for this strong enhancement is still unclear and we cannot exclude the possibility that additional condensing vapors were present in the humidified gas. This point will be discussed in the revised manuscript also with respect to the r.h. dependence of nucleation.

Referee 1:

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.

Reply: In Introduction the clearly different predictions from theoretical considerations regarding ternary H2SO4/H2O/NH3 nucleation are given. ". . . theoretical studies pro-

posed that atmospheric mixing ratios of NH3 at pptv-level can stabilize the critical cluster (Coffman and Hegg, 1995, Korhonen et al., 1999). ... . More recently, a re-evaluation at theoretical level shows that even a mixing ratio of 1 - 10 ppbv NH3 is not able to trigger nucleation at 295 K unless the H2SO4 concentration accounts for at least 109 molecule cm-3 (Merikanto et al., 2007)." In the discussion of the results we focussed on a comparison with other experimental work, especially with Benson, et al. 2009. We agree with the referee, that also in this section a comparison with theoretical studies should be dealt with. It should be noted that our experimental findings are closer to predictions by Merikanto et al., 2007, than in earlier work. In the revised version this topic will be discussed. Zhang et al., PNAS 2009, studied the process of particle growth of produced 3 – 30 nm particles in the presence of 3 x 10(14) cm(-3) of NH3 by means of a T-DMA. In our study we observed in a nucleation/growth experiment an overall enhancing effect of NH3. Nothing changed in the text.

Referee 1:

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).

Reply: The referee is right that this interesting topic deserves closer attention. Therefore, in addition to the data presented up to now, we will show in the revised manuscript also data for r.h. = 13%. In a new figure showing particle number vs. amine(NH3) concentration, the enhancing effects of tert-butylamine and NH3 are compared. The figure also gives a good impression concerning the magnitude of the enhancement factors. In the text this topic will be discussed more in detail.

Technical corrections: In the revised manuscript the typos will be eliminated and an additional reference will be included according to referee′s suggestions.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6447, 2010.