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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The effect of trimethylamine on atmospheric nucleation involving H_2SO_4" *by* M. E. Erupe et al.

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This paper investigates the effect of trimethylamine (TMA) on the nucleation rate of sulfuric acid water in a flow tube. Sulfuric acid concentrations in the atmospherically relevant concentration range are used (10E6 to 10E7 molecules per cm3), with TMA concentrations in the ppt and low ppb range. A CPC with a detection limit of 3 nm is used for the detection of the particles.

RE: We thank the reviewer for helpful comments. Below we provide our point to point response to the comments.

I have a fundamental problem with these studies: According to Figure 1 in Nieminen et al. (2010) a sulfuric acid concentration of 10E7 molecules per cm3 results in a growth rate of less than 1 nm per hour. The critical cluster size is somewhere below 2 nm. This means that at this concentration the growth of a newly formed particle to the size of 3 nm (where the particle is detected with the available instrumentation) requires well over 1 hour. Accordingly, a residence time of up to 50 seconds is by far not sufficient to grow the particle to this minimum size of 3 nm. Addition of bases (ammonia or, as in this case, TMA), will only enhance the growth at most to the extent that the particle is constantly neutralized); i.e., this will enhance the growth rate by certainly less than a factor of 2. Also in this case the growth rate is by far too small to allow for significant particle formation within less than 1 minute. This is very clear evidence that one of the following points is true: either you only look at the extreme lower end of the detection efficiency curve of your CPC, which may result in an underestimation of the measured number concentration by several orders of magnitude. Or, as the most probable explanation, the system is heavily contaminated with other species, which contribute the major part to this growth. This contamination is not just a minor effect, but fully dominates the observation of new particle formation, as can be easily seen from a comparison of the actual (<1 minute) and required (>1 hour) residence time.

RE: While the current manuscript focuses on the relative effects of TMA in nucleation, in direct comparison to NH3, we also have discussed growth in another two ACPD manuscripts in detail ([Benson et al., 2010a; Benson et al., 2010b] and please also review their interactive discussions with regard to this comment). Briefly, the growth rates in our flow tube (28 nm hr-1) are much larger than can be explained by H2SO4 condensation alone (e.g., 1 nm hr-1 at 10ˆ7 cm-3 H2SO4). Therefore it is possible that the background NH3 present (e.g., 20 – 100 pptv at RH from 6 - 40% in our case) contributes to this growth even for the BHN case. At similarly low H2SO4 of 7x10ËĘ6 cm-3, Berndt et al. (2005, 2006) have also seen roughly 13 nm hr-1 growth rate in their nucleation reactor. This could have been also due “in part” to NH3 or amine impurities in the system. As eliminating background NH3/amine is unavoidable, on the other hand, any EF values found or given will actually be an underestimation due to pptv level NH3 being present. Another possibility is that not every collision results in the formation of a critical cluster [Kuang et al., 2010]. In a study showing the dependence of the nucleation rate on H2SO4 in various atmospheric locations [Kuang et al., 2008], it was found that the kinetic prefactor values were 1-4 orders of magnitude below the hard-sphere collision frequency. If values closer to the collision frequency are used, growth rates would be at least 40 nm hr-1, which could explain growth in our flow tube. At present, however, only a limited number of growth theories exist, none of which incorporate a third species or take into account chemical interactions that occur between precursors.

Therefore, unless the authors have a valid explanation for their observations, this paper cannot be accepted for publication and needs to be rejected. The same is true for any papers that report similar flow tube experiments with these low sulfuric acid concentrations and short residence times.

RE: To our knowledge, we are the first group that has provided a quantitative investigation of TMA in aerosol nucleation of sulfuric acid. TMA is the most abundant amine in the atmosphere. We also provided systematic measurements of impurity ammonia concentrations (at tens to hundreds of pptv level depending on RH) at different experimental conditions, which is extremely important when understanding the relative roles of each precursor in nucleation and growth. All precursors (H2SO4, NH3 and TMA) reported in our study were directly measured with CIMS – rather than estimated indirectly in other studies. [Berndt et al., 2010] have provided a qualitative study of another amine molecule (tert-butylamine), but the precursor concentrations (both sulfuric acid and amine) were 2-3 orders of magnitude higher; and, amine concentrations were not measured directly. NH3 impurities in the system were also reported to be < 100 pptv, roughly; similarly, for [Brus et al., 2010], NH3 impurities <500 pptv. [Sipila et al., 2010] have used these two instruments. Note that [Berndt et al., 2005; Berndt et al., 2006] were also conducted at very similar conditions: low H2SO4 concentration (10ˆ6-10ˆ7 cm-3) with nucleation time < 300 s, and also used conventional CPC or SMPS. Ammonia and amines always exist as impurities form water vapor in the nucle-

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ation system – and it is unavoidable. While this is an inherent limitation of nucleation experiments, there are also differences in this aspect; some studies try to have lowest ammonia contamination (using TFA material vs. stainless steel) and some provide direct measurements of these impurity concentrations (as opposed to roughly estimate). Different experiments have different advantages and disadvantages, but there is no perfect ideal experiment – like there is no perfect theoretical model. And yet, controlled experiments (that reduce the impurities and systematically detect them) are critically needed to understand how these base species can contribute to nucleation, especially relative effects of amines vs. ammonia and the chemical composition of critical clusters containing these bases. These experiments with a unique experimental design and valuable results can complement with other studies. These data together will be the basis to test and improve theories.

The paper has a number of additional weaknesses and errors, and I am willing to address these once the authors have provided convincing evidence that the data are valid and my conclusion is wrong.

Reference: Nieminen, T., Lehtinen, K. E. J., and Kulmala. Sub-10nm particle growth by vapor ondensation – effects of vapor molecule size and particle thermal speed. Atmos. Chem. Phys., 10, 9773–9779, 2010.

Additional references:

Benson, D., et al. (2010a), Ternary homogeneous nucleation of H2SO4, NH3, and H2O under conditions relevant to the lower troposphere, Atmos. Chem. Phys. Discuss., 10(9), 22395-22414.

Benson, D. R., et al. (2010b), Atmospheric homogeneous nucleation of H2SO4 and H2O, Atmos. Chem. Phys. Discuss., 10, 29051-29073.

Berndt, T., et al. (2005), Rapid formation of sulfuric acid particles at near atmospheric conditions, Science, 307, 671-698.

Berndt, T., et al. (2006), Formation of atmospheric H2SO4/H2O in the absence of organics: A laboratory study, Geophys. Res. Lett., 33, L15817, doi:15810.11029/12006GL026660.

Berndt, T., et al. (2010), 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, Atmos. Chem. Phys., 10(15), 7101-7116.

Brus, D., et al. (2010), Homogenous nucleation of sulfuric acid and water mixture: experimental setup and first results, Atmospheric Chemistry and Physics, 10, 2631-2641.

Kuang, C., et al. (2008), Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, Journal of Geophysical Research, 113.

Kuang, C., et al. (2010), Measurements of newly formed 1-3 nm nanometer particles using a high-time resolution nanparticle size spectrometer, in AAAR 29th Annual Conference, edited, Portland, Oregon.

Sipila, M., et al. (2010), The Role of Sulfuric Acid in Atmospheric Nucleation, Science, 327, 1243-1246.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27673, 2010.

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