

Interactive comment on “The effect of trimethylamine on atmospheric nucleation involving H₂SO₄” by M. E. Erupe et al.

Anonymous Referee #1

Received and published: 4 January 2011

General comments:

The authors present results of laboratory measurements of the effect of trimethylamine (TMA) on water-sulfuric acid nucleation with atmospherically relevant concentrations of sulfuric acid and TMA. The topic of nucleation participating compounds is a hot topic as quantum chemical calculations has suggested that water-sulfuric acid nucleation can be enhanced by amines or other base molecules. The manuscript is well within the scope of the paper. The results of this kind of experiment can help identifying the compounds involved in the nucleation process. There are some issues that might need considering or revising before publication.

Specific comments:

C11906

1) p. 27678, line 27 is said that this UV-method for productions of sulfuric acid serves as a calibration. What about after adding amine? According to Kurten et al. (2010), CIMS might not be able to measure sulfuric acid if it is bound to base molecule as the charging is not possible. The same should be considered when using other CIMS for measuring the TMA concentration (p. 27680, lines 9-12), because it can be bound to sulfuric acid and though, not be charged in the CIMS.

2) Here is the main issue of the whole manuscript: TMA is seen to enhance nucleation according to the slopes (fig. 2a and p. 27680, results) but no information of the sizes of the nucleated particles is provided. As Sipilä et al. (2010) suggested, the detection efficiency of the particle detector depends greatly on the size of the particles. Here, TSI model 3776 CPC is used which has a d_{50} at 3 nm, so if the mean size of the particles before adding TMA is around 2 nm and assuming a log-normal distribution the tail of the distribution is measured by the CPC. When adding the TMA the particles will grow even if the TMA is not participating on the nucleation, but gets bound on the sulfuric acid molecules, which are condensed on the surface of the particle after nucleation. This also explains the different slopes compared to the ones found in Sipilä et al.. This also would explain the fact that higher sulfuric acid concentrations means lower enhancement due to the larger particles caused by condensed sulfuric acid. The dependence of the EF of the RH in figure 3a) can also be explained with this same issue due to the fact that particles are lot smaller at lower RH. Also the condensed sulfuric acid on the surface of the particles are more accessible for the TMA to get bound to when there is less water molecules shielding the sulfuric acid molecules.

3) The concept of using slopes to determine the number of different molecules in the critical cluster (p. 27680-27681) might not be plausible with multicomponent systems due to the possible local minimums and maximums. This does not mean that the numbers presented here wouldn't be right but this approach should not be used so straight forward without any consideration and justification. 4) Brilliant observation (p. 27681, lines 20-21) that the ammonia will arise always from the water used for BHN and

C11907

though, these measurements are always, as said here, pseudo-BHN. Another good observation is that comparing slopes taken from field measurements and from laboratory measurements are not necessary comparable and these field measurements should always be classified and filtered according to temperature and RH.

5)p. 27683, line 24 is said that "it is commonly believed that species other than sulfuric acid and water is needed to explain aerosol nucleation in the atmosphere...". This might be pretty strongly said, as looking for the third compound has led to very minor advances and it is known (and also mentioned in this manuscript) that sulfuric acid is the key.

references:

Kurtén, T., Petäjä, T., Smith, J., Ortega, I. K., Sipilä, M., Junninen, H., Ehn, M., Vehkamäki, H., Mauldin, L., Worsnop, D. R. and Kulmala M.: Chemical ionization mass spectrometry (CIMS) may not measure all gas-phase sulfuric acid if base molecules are present *Atmos. Chem. Phys. Discuss.*, 10, 30539-30568, 2010.

Sipilä, M., Berndt, T., Petäjä, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin III, Roy L., Hyvärinen, A.-P., Lihavainen, H. and Kulmala, M.: The role of sulphuric acid in atmospheric nucleation, *Science*, 327, 5970, 1243-1246.

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