

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

Anonymous Referee #2

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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.

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

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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.

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.

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 condensation – effects of vapor molecule size and particle thermal speed. *Atmos. Chem. Phys.*, 10, 9773–9779, 2010.

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