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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Unexpectedly acidic nanoparticles formed in dimethylamineammonia-sulfuric acid nucleation experiments at CLOUD" *by* Michael J. Lawler et al.

Anonymous Referee #1

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This paper explored the chemical composition of newly formed nanoparticles (2-30 nm) from dimethylamine-ammonia-sulfuric acid using CLOUD chamber experiment. This study used the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) to measure the composition of newly formed nanoparticles (∼10âĂĽnm). The resulting data of this paper reported that the base to acid ratio in the small particles (less than 10âĂĽnm) was lower than thermodynamically predicted values and never reach to entire neutralization of sulfuric acid even with the excess amount of base gases. When particles reached to ∼20âĂĽnm particles, the base to acid ratio accorded with thermodynamic compositions. This paper concluded that the particles less than 10 nm were more acidic than expected as shown in measured aerosol compositions. The authors

suggested that in the small particle size range (∼10âĂĽnm), the rapid heterogeneous conversion of SO2 to sulfate does not need to reach thermodynamic equilibrium with respect to the bases, while it happens to be in the bulk phase (or larger size particles). Overall, no clear conclusion appeared for the new acidic particle formation in the presence of base gas due to the lack of data points and contamination. Although the observation of this paper may not be expected under the ambient conditions of low SO2 and high NOx, the authors also need to provide meaningful implication of the resulting data to the ambient environment. This paper requires major revision. Please find the comments below.

1. Overall, pages 1-10 are related to experimental methods and instrumentations. The actual discussion using laboratory data appeared between pages 11-16. I would like to ask authors to reduce experimental and instrumental sections and focus more on the application of the results to the ambient atmosphere.

2. Introduction section. In general, the amine concentration is much lower than ammonia in ambient air. The authors should provide rationale or hypothesis for why new particle formation experiment from SO2 oxidation has been conducted in the presence of amine. It is difficult to clearly understand the major goal of this paper in the introduction.

3. The effect of humidity on new particle formation should be explained in depth. In page 3, the authors showed that relative humidity (RH) was constant at 38%. Although RH is fixed in this paper, RH is an important parameter to determine the phase of inorganic salt aerosol and liquid water content. Subsequently, the aerosol phase and water content will also influence new particle formation from SO2 oxidation. For example, efflorescent RH (ERH) of ammonium sulfate is near 40%. Is there a specific reason to select RH at 38% ?

4. In Table 1. Ozone was included in the chamber. Ozone is known to influences heterogeneously SO2 oxidation and increase sulfuric acid formation. What is the po-

tential effect of ozone on the new particle formation? Is there a specific reason to fix at 23ppb? Run1047 was operated at the higher ozone concentration but no clear explanation appeared.

5. Figure 4. There were some other peaks from oxalic acid and nitrate (nitrite ?). How do the authors know that the neutralization of nitrate with ammonia can reduce the base-to-acid ratio (amine + ammonia vs. sulfate) ? Page 15, line 31, the author pointed out that the NOx concentration of CLOUD chamber was low. For the Figure 4 and 8, the NOx contamination was not negligible. The NOx effect may source large uncertainty for the final results.

6. Page 6, line 31 and Figure 5. There are limited number of data in the middle range ($0.4\times105 \sim 1.2\times105$) to correlate linearly between acid and base signals.

7. Page 9, line 13-14. What is the source of oxalic acid?

8. Figure 10, it would better to explain ammonium contribution to aerosol compositions in the text. Sentence "...possibly because less contaminant ammonium was required..." in Figure caption should be informed to readers to better understand the results.

9. Page 11, line 10-12. The authors need to discuss more clearly why ammonia becomes abundant at the particle larger than 10 nm. What is the physical state of inorganic salt aerosol (NH4-amine-sulfuric acid) at a given RH? If the inorganic salt aerosol is solid, the heterogeneous reaction of SO2 on the salt aerosol will be less efficient that in the aerosol below the ERH and furthermore uptake of amine and ammonia would be affected by physical state. What is the influence of RH on the chemical compositions of aerosol?

10. Page 12, line 9. Please explain why nanoparticle is liquid. The study by Cheng et al. (2015) suggested that nanoparticles tend to be aqueous phase at room temperature. The temperature of For the CLOUD chamber experiment, was much lower than

room temperature. What is the impact of temperature on aerosol phase ?

11. Page 14, line 13 and Figure 3. The data from Figure 3 are not sufficient to prove that sulfate signals are consistent with sampled particle mass.

12. Page 16, line 8, the authors mentioned about the artifact of DMA on SO2-particle interaction and yielded the factor of 5 for DMA system. The authors need to provide more detailed explanation for how to get the factor of 5.

13. Page 5, line 32, "to obtain agreement of the chamber" should be "to obtain the agreement of the chamber".

14. Page 6, line 1, "determine the sizes and total volume" should be "determine the size and the total volume".

15. Page 6, line 5, "there was" should be "there were".

16. Page 12, line 14, "a more stable salt with sulfuric acid than is ammonia", delete "is".

17. Page 13, line 25, "clusters may is acidic for" should be "clusters may be acidic for"

18. Page 14, line 20, "(Kim et al., 2016)" this citation should belong to next sentence.

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