

Interactive comment on “Direct contribution of ammonia to CCN-size alpha-pinene secondary organic aerosol formation” by Liqing Hao et al.

Anonymous Referee #1

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This manuscript reports new findings on the role ammonia in the formation of SOA from photooxidation of alpha-pinene. Neutralization of carboxylic acid by ammonia in the gas phase is reported as a process of CCN-sized SOA formation. PTR-MS and AMS were mainly used to measure relevant species in gas and particle phase, respectively, and to interpret the measured data for the neutralization. Although this manuscript is unique and concise, there are several main questions to be clarified. 1) In this manuscript key data used to support the process are correlations between organic acids and particulate ammonium. Mixing ratio of ammonia might be a critical factor in the photooxidation of smog chamber. It is not clear about the introduction to a reactor bag and mixing ratio of ammonia in the bag. The authors report N/C ratio remained consistent, implying negligible formation of organonitrogen via particle phase

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reaction. Reaction pathways might be largely dependent on the mixing ratio of ammonia. 2) For seeded experiments alpha-pinene concentration was too low compared to nucleation experiments. It is uncertain why such low concentration was used for seeded cases. It makes difficult to clearly show the temporal variation of organic acids. In seeded experiments correlation of organic acids with ammonium are not apparent as much as in nucleation experiments, probably due to lower concentration of alpha-pinene. A result stated in P5, line 181-183 (48.6 times lower concentration of CO₂+ for seeded experiment) might be just due to lower initial α -pinene concentration for seeded condition (23 times lower). 3) Figure 3 apparently show the difference in a lag time of CO₂+NH₄. It was partly explained that nitric acid delayed its accumulation in high NO_x condition. More explanation might be necessary for the delay in low NO_x conditions. Very limited amount of CO₂+NH₄ was formed roughly at 1/100 of SOA in mass both in nucleation and seeded experiments. Is it caused by limit in the available low MW carboxylic acids, ammonia, or other factors? It is probably associated with the contribution of neutralization and its atmospheric implication due to the omnipresence of NO_x and nitric acids. 4) Although a previous paper (Friedman and Farmer, 2018) also reported the formation of low molecular weight organic acids as observed in this manuscript, little information is available about the formation mechanism of those species. Even a brief introduction of the formation mechanism would be very useful in the understanding of neutralization process. Overall, I would recommend the publication of the manuscript if the authors can address my questions and comments. Minor comments are show below.

P3, line 89-91: H₂O₂ was introduced as a source of OH radical. Although OH exposure is presented in Table 1, H₂O₂ concentration itself is informative for readers.

P5, line 173, 179: It is curious why chloride ion was added in the estimation of NH₄⁺, since there was no source of chloride in the smog chamber experiments.

P6, Line 228: “Fig. 4” might a typo of “Fig. 6”.

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P7, line 270-274: Diacids such as malonic and succinic acids have vapor pressure similar to pinonic acid. Differently from pinonic acid, those diacids showed good correlation with ammonium. This might mean continuous formation of those diacids. It is not clear how these nonvolatile diacids could form in the gas phase until the later part of photooxidation.

P9, Line 316: “affective” might be a typo of “effective”.

P15, Table 1: α -Pinene might be a typo of “alpha-Pinene”.

P18, Figure 3: In the caption, “SOA” needs to be deleted in “... (B) SOA seeded experiments ...”

P20, Figure 5: In the caption, “the AMS NH_4^+ is the difference between $\text{NH}_4^+,_{\text{pre}}$ and $\text{NH}_4^+,_{\text{mea}}$, refer to the text for details.” needs to be clarified. In the text $\text{NH}_4^+,_{\text{pre}}$ and $\text{NH}_4^+,_{\text{mea}}$ are defined, whereas “AMS NH_4^+ ” is not defined. It should be defined clearly in the caption, e.g., $\text{NH}_4^+,_{\text{mea}} - \text{NH}_4^+,_{\text{pre}}$. It should be clarified in the caption of figures 6 and 7. It might be better to move the position of “ $\times 10^{-3}$ ” to improve the readability in the figure. It is same in figures 6 and 7.

P21, Figure 6: Readers might expect to see plots of AMS data also as Figure 5.

P22, Figure 7: Readers might expect to see plots of AMS data also as Figure 5.

It is worthy to clearly note in the text that all particulate data were not corrected to wall loss of particulate.

In the figure, axis titles need to be checked to properly note “ NH_4^+ ”, “ SO_4^{2-} ”, and “ NO_3^- ”.

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