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## Comment on acp-2021-560

Anonymous Referee #4

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Referee comment on "Synergetic effect of NH<sub>3</sub> and NO<sub>x</sub> on the production and optical absorption of secondary organic aerosol formation from toluene photooxidation" by Shijie Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-560-RC4>, 2021

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Review of "Synergetic effects of NH<sub>3</sub> and NO<sub>x</sub> on the production and optical absorption of secondary organic aerosol formation from toluene photooxidation" by Liu et al.

The authors reported experimental results of secondary organic aerosol (SOA) formation from oxidation of toluene in the absence or presence of NO<sub>x</sub> and NH<sub>3</sub>, or both. They used aerosol mass spectrometry (AMS) and UV/vis spectrometry to characterize the chemical composition and light-absorption property, respectively, of the SOA formed under those conditions. They suggested that the presence of both NO<sub>x</sub> and NH<sub>3</sub> had synergetic effects in both SOA formation and the light-absorption ability. Based on literature and their own indirect results from AMS, they suggested that the efficient formation of secondary imines, which are probably cyclic and aromatic, were responsible for the enhanced SOA formation and light absorption. The work is of a clear objective and of interest to the atmospheric chemistry community, and the data obtained supported the conclusion made. But I do have a few concerns, which are outlined below. The manuscript requires further editing as I found some contradicting descriptions and also difficulty in fully understand the details. I recommend Major Revision before publication in ACP.

Major:

- The first concern is the high concentrations of toluene used and SOA resulted. Even though atmospheric relevancy is always the concern for smog chamber studies, the characterization methods of this study should allow lower concentrations. The AMS should be able to measure SOA in 10s of microgram per cubic meter quite satisfactorily; a rough calculation of the dissolved SOA in methanol (500 microgram per cubic meter, 3 cubic meter, 5 mL methanol) gives a concentration of 3000 milligram per liter, which should be more than enough to get good UV/vis spectra even if only a portion of the SOA is light-absorbing (if this portion is extremely small, then it is not important). Therefore, there is room to reduce the concentrations for the results to be more atmospherically relevant, e.g., for the gas-phase and heterogeneous chemistry as

emphasized by the authors.

- There is a lack in the conditions for the smog chamber experiments. For instance, what was the estimated OH concentration, or OH exposure/equivalent photochemical age, of the experiments? What was the approximate NO/NO<sub>2</sub> ratio given the OH conditions and NO<sub>2</sub> introduced? Is ozone expected to form in significant amount after introducing toluene, or was it measured? If so, would that also convert NO<sub>2</sub> to NO<sub>3</sub> and become another different type of oxidant, and might also lead to the formation of light-absorbing products as well? They authors mentioned in L146 that some details have been described in previous studies. But it would good to include citations here, and better yet to provide some critical details for the readers to apprehend the conditions for the smog chamber experiments.
- The description of the AMS measurements is a bit ambiguous. First, I think there is some inaccuracy in L194: an HR-ToF-AMS normally does not contain a quadrupole, at least not as a mass analyzer. Second, it was stated that the V mode was used to achieve high signal-to-noise ratio, but there are lots of descriptions about elemental analysis (O/C, H/C, OM/OC, OS<sub>C</sub> etc.) later. The question is, were W-mode data acquired together with V-mode data for the high-resolution (HR) analysis or the HR fitting was based on V-mode data? Third, what was the purpose of the Nafion dryer if the RH in all experiments did not exceed 27% (Table 1)? Did it significantly reduce particle bouncing, as compared to the complication of potential particle loss passing the Nafion dryer?
- About the SOA mass. First, were the mass concentrations in Figure 1 from SMPS data or AMS data? If the latter, were there any ammonium signals from the AMS spectra in the presence of NH<sub>3</sub>, and were they "counted" as SOA if any? Maybe whether to call the ammonium ion formed with carboxylic acids (simply neutralization) is a trivial question, but the fragments of m/z 15, 16, 17, 18 etc., which are assigned as inorganic ammonium by default, might come from imines in this study.

Minor:

- L193: "address" to "achieve"? "signal-to-noise" to "signal-to-noise ratio"?

- L277: it might not be good to label the whole SOA as "SV-OOA" just according to the OSc value. And the authors stated in L407 that actually one factor from PMF analysis was very close to LV-OOA based on the O/C ratio.
  
- L313: proper subscript for "OSC".
  
- L337-339: this looks like two sentences.
  
- L427: NOC and NOA are used to refer to more or less the same thing. Please keep it consistent.
  
- L509: "high" to "highly".
  
- Fig. 4: the "relative intensity". It seems it is not relatively to the highest peak, nor the total signal. Then what are they relative to as relative intensities?
  
- Fig. 6: the y-axis title uses different notations as Lo-NOA and Hi-NOA in the legend, and the ratio of the two (as indicated by the y-axis title) should not give a total value of 100%. Should it be just "Percentage in total (%)"?