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## Reply on RC4

Shijie Liu et al.

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Author comment on "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 Shijie Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-560-AC5>, 2021

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## Response to Reviewers

Ms. Ref. No.: acp-2021-560

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

Dear Editor:

We greatly appreciate the time and effort that the editor and reviewer spent in reviewing our manuscript. After reading the comments from the reviewers, we have carefully revised our manuscript. All the changes we made are marked in red. Our responses to the comments are itemized below. The referee's comments are in black, authors' responses are in blue.

Anything for our paper, please feel free to contact me via [ghwang@geo.ecnu.edu.cn](mailto:ghwang@geo.ecnu.edu.cn).

All the best

Gehui Wang

Oct.14, 2021

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.

#### **Author reply:**

We thank the reviewers for the very important comments.

As calculated, the dissolved SOA in methanol is about 300 milligram per liter, not 3000 here. According to the actual measurement of the collected particulate matter mass, the dissolved SOA is about 100~150 milligram per liter.

As we reply to the comments in RC#2, atmosphere environment is very complicate and the experimental conditions in the chamber cannot be the same as the real environment. Although the VOCs concentration our study is high, the proportion of the key components is comparable to the ambient level. The mean concentration of aromatics VOCs and OH was about 11 ppb (Zou et al., 2015) and  $1 \times 10^6$  molecule  $\text{cm}^{-3}$  (Prinn et al., 1995), respectively, which was consistent with the VOCs/OH ratio ( $\sim 700$  ppb/ $5.9 \times 10^7$  molecule  $\text{cm}^{-3}$ ) in our study. Therefore, our results still have some guidance for actual atmospheric reactions.

To provide a better illustration of the experiment condition, the following sentences have been added in the revised manuscript in line 170:

"In our work, the OH and toluene concentrations were higher than those of urban conditions. The purpose of the high OH and toluene concentrations is to obtain enough particle production samples for off-line collections and accurate measurements. The toluene concentrations remained stable under the different experimental conditions, the variation of toluene-derived SOA mass concentration and yield was only affected by the different NO<sub>2</sub> and/or NH<sub>3</sub> concentrations in this study. Toluene was studied here as the representative of total aromatic VOCs in the urban atmosphere. The concentration ratio of toluene to OH in this study is similar to that under the real atmospheric conditions (Zou et al., 2015; Prinn et al., 1995)."

The follow sentences were also added in line 523 of the revised manuscript:

"It has to be noted that the concentration of reactants used for the experiments is much higher than that observed in polluted areas, the effect of NH<sub>3</sub> and NO<sub>x</sub> on the

photooxidation of toluene with lower concentrations would be checked in the further study.”

- 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.

#### **Author reply:**

We are very grateful to the reviewer for this comment. We measured the toluene concentration with PTR-MS on-line. And the OH concentration was calculated based on the on the first order decay of toluene. In the revised manuscript, the following sentences were added in line 163 “The OH concentration in the chamber was calculated based on the first order decay of toluene concentration. There was no obvious difference of OH concentrations in the different NO<sub>x</sub> and NH<sub>3</sub> levels (Fig. S2).”

The highest OH concentration of  $1.02 \times 10^8$  molecule  $\text{cm}^{-3}$  was observed at the beginning of the reaction. The average OH concentration over the entire reaction period was  $5.87 \times 10^7$  molecule  $\text{cm}^{-3}$ . The calculation of OH concentration was added in the Supporting Information as below:

#### **“S1 OH Concentration Calculation Process**

The OH concentration was calculated based on the decay ratio of toluene concentrations and the known rate constant with respect to OH. The change of toluene concentration over time can be expressed as:

(RS1)

Where,  $K_{\text{OH}}$  is the reaction rate constant of OH radicals with toluene ( $K_{\text{OH}} = 5.7 \times 10^{-12}$   $\text{cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>). Assuming that the concentration of hydroxide did not change during the experiment, then we can get:

(RS2)

Thus, plotting the variation curve of  $\ln([\text{toluene}]_0/[\text{toluene}]_t)$  vs. time  $t$  showed as Fig.S1. The  $\ln([\text{toluene}]_0/[\text{toluene}]_t)$  in Fig.1(b) was not a straight line. This is because the OH is consumed as the reaction goes on. The evolution of OH concentration at experiment conditions was shown in Fig.S2. The different experiment conditions in this study did not

affect the OH concentration obviously. The highest OH concentration of  $1.0 \times 10^8$  molecule  $\text{cm}^{-3}$  was observed at the beginning of the reaction. The average OH concentration over the entire reaction period is  $5.9 \times 10^7$  molecule  $\text{cm}^{-3}$ .

Fig.S2 The evolution of OH concentrations at different experiment conditions”

In this study, 254 nm UV light was used for the  $\text{H}_2\text{O}_2$  photolysis and OH formation. The photolysis of  $\text{NO}_2$  requires 365 nm black light as the light source. We cannot exclude small amount  $\text{O}_3$  formation from the photolysis of  $\text{NO}_2$ .  $\text{O}_3$  concentration observed in Exp. 3 and 4 was lower than 10 ppb.  $\text{O}_3$  does not react with toluene. The formation ratio of  $\text{NO}_3$  through  $\text{O}_3$  with  $\text{NO}_2$  is very slow, only  $3.5 \times 10^{-17}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . And the reaction rate of  $\text{NO}_3$  with toluene is also very low, which is  $2 \sim 6 \times 10^{-17}$   $\text{cm}^3$  molecule $^{-1}$  s $^{-1}$ . At the same time,  $\text{NO}_3$  has a short lifetime under the light conditions because  $\text{NO}_3$  is extremely easy to photolysis. Obviously,  $\text{NO}_3$  oxidation of toluene is negligible here.

The previous study was included here “Liu S. J., Wang Y., Wang G., et al. Enhancing effect of  $\text{NO}_2$  on the formation of light-absorbing secondary organic aerosols from toluene photooxidation [J]. *Sci. Total Environ.*, 2021, 794: 148714.”

- 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, OSC 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?

#### **Author reply:**

Here is a mistake, “quadrupole” has been deleted.

Elemental analysis (O/C, H/C, OM/OC, OSC etc.) later was based on the HR fitting through V-mode data.

We are very grateful to the reviewer for this comment. Nafion dryer is one part of the AMS. The RH was low in this study, but SOA formation with different RH was also be studied in our group. The potential particle loss passing the Nafion dryer is very low (Eatough et al., 1999). Nafion dryer did not cause the potential loss of SOA.

- 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  $\text{NH}_3$ , 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.

#### **Author reply:**

Mass concentrations in Fig. 1 were obtained from SMPS data.

$\text{NH}_4^+$  and  $\text{NO}_3^-$  are inevitably counted in the SOA mass concentration. The concentration variations of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  during the experiments were measured by the AMS. The content of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  is very low in particulate matter. The content of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for each experiment was list in the table below.

**Table S1.** The content of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in the particle-phase for each experiment

	$[\text{NO}_x]_0$	$[\text{NH}_3]_0$	$[\text{NO}_3^-]/[\text{Org}]$	$[\text{NH}_4^+]/[\text{Org}]$
	(ppb)	(ppb)	(%)	(%)
Exp.2	-	~200	-	1.9
Exp.3	62	~200	4.0	2.6
Exp.4	63	-	□0.2	-

As seen in Table S1, when only  $\text{NO}_2$  was introduced into the chamber, the content of  $\text{NO}_3^-$  in particulate matter was less than 0.2%. Based on the consumption of  $\text{NO}_2$ , most of the  $\text{NO}_3^-$  was present in the gas phase in the form of nitric acid. When only  $\text{NH}_3$  was introduced in the chamber, the content of  $\text{NH}_4^+$  was about 1.9%. When both  $\text{NO}_2$  and  $\text{NH}_3$  were simultaneously introduced into the chamber, the  $\text{NO}_3^-$  reacted with  $\text{NH}_4^+$  to form ammonium nitrate particles, which accounted for 6.6% of the total mass of particulate matter in the chamber. AMS cannot distinguish whether  $\text{NO}_3^-$  and  $\text{NH}_4^+$  come from organic or inorganic phase, but 6.6% is obviously the upper limit of inorganic components in particulate matter if we assume that both are entirely derived from inorganic phase. The particle mass increased about 59% in the  $\text{NH}_3 + \text{NO}_x$  experiment compared that with no  $\text{NH}_3$  or  $\text{NO}_x$ , which cannot be explained by the formation of inorganic  $\text{NH}_4\text{NO}_3$  but can only be ascribed to the synergetic effect of  $\text{NH}_3$  and  $\text{NO}_x$  on the toluene SOA formation. The following sentences were added in line 253 of the manuscript to explain the possible influence of the smaller amount of the inorganic aerosol on the enhancement in particle mass in the  $\text{NH}_3 + \text{NO}_x$  experiment.

“Although inorganic aerosol was formed from the interaction of  $\text{NH}_3$  and  $\text{NO}_x$  in the

chamber, the upper limit of the inorganic matter only account for 6.6% of the total mass of particulate matter (Table S1) in the NH<sub>3</sub> + NO<sub>x</sub> experiment. Therefore, it was not the main cause of the increase in particulate matter.”

Minor:

- L193: “address” to “achieve”? “signal-to-noise” to “signal-to-noise ratio”?

**Author reply:**

Suggestion taken, we corrected them.

- L277: it might not be good to label the whole SOA as “SV-OOA” just according to the OS<sub>c</sub> 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.

**Author reply:**

“Notably, all the toluene SOA was characterized as semi-volatile oxygenated organic aerosols (SV-OOA)” was fixed as: “Notably, toluene SOA OS<sub>c</sub> values was in the range between -0.5 and 0, which is consistent with that of semi-volatile oxygenated organic aerosols (SV-OOA).”

- L313: proper subscript for “OSC”.

**Author reply:**

Yes, we corrected it.

- L337-339: this looks like two sentences.

**Author reply:**

Yes, we rephrased them.

- L427: NOC and NOA are used to refer to more or less the same thing. Please keep it consistent.

**Author reply:**

We revised all the “NOCs” as “NOA”.

- L509: "high" to "highly".

**Author reply:**

Corrected

- 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?

**Author reply:**

The relative intensity of each m/z mean that it is relative to the total signal. First, we obtained the toluene SOA spectra in both formation stage and stable stage. Then subtract the formation stage SOA spectra from the stable stage mass spectra, and finally we got the differential spectra of Fig. 4.

- 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 (%)"?

**Author reply:**

Suggestion taken. And Fig. 6 was revised as below.

**Reference**

Eatough, D. J., Obeidi, F., Pang, Y., Ding, Y., Eatough, N. L., and Wilson, W. E.: Integrated and real-time diffusion denuder sample for PM<sub>2.5</sub>, *Atmos. Environ.*, 33, 2835-2844, 10.1016/s1352-2310(98)00326-4, 1999.

Prinn, R. G., Weiss, R. F., Miller, B. R., Huang, J., Alyea, F. N., Cunnold, D. M., Fraser, P. J., Hartley, D. E., and Simmonds, P. G.: Atmospheric trends and lifetime of CH<sub>3</sub>CCl<sub>3</sub> and global OH concentrations, *Science*, 269, 187-192, 10.1126/science.269.5221.187, 1995.

Zou, Y., Deng, X. J., Zhu, D., Gong, D. C., Wang, H., Li, F., Tan, H. B., Deng, T., Mai, B. R., Liu, X. T., and Wang, B. G.: Characteristics of 1 year of observational data of VOCs, NO<sub>x</sub> and O<sub>3</sub> at a suburban site in Guangzhou, China, *Atmos. Chem. Phys.*, 15, 6625-6636, 10.5194/acp-15-6625-2015, 2015.