Response to the comments of Reviewer #1

The manuscript entitled "Effects of OH radical and SO_2 concentrations on photochemical reactions of mixed anthropogenic organic gases" presents new findings of the atmospheric processing of the anthropogenic pollutants, represented by n-dodecane, 1,3,5-trimethylbeneze, which are associated with the vehicular traffic pollution. The paper is scientifically sound; for the most part, methods and experimental details are adequately presented. The equipment and methodology used in the simulation chamber experiments are adequate and provide valuable information about the reactions under investigation. The length of sections 1 and 2 is well balanced, providing sufficient details and discussion without adding too much volume to the final manuscript.

Response: We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. We have fully considered the comments and responded to these comments below in blue text. The revisions in the manuscript are highlighted in yellow color. The response and changes are listed below.

Major Comments

1. *At the same time, the article would benefit from major revisions. Generally, the use of the English language should be improved because it is frequently awkward, even from the point of view of a non-native speaker of English.*

   We thank the reviewer for pointing this out. The use of the English language has been polished.

2. *My technical comments are provided below. Regarding the scientific comments, I believe that the article would benefit greatly from a more in-depth analysis of the results. The is a lack of a broader context in the presented discussion. The discussion in section 3 discusses the data but without providing any broader insights into the processes under investigation. In connection with this comment, there is no quantitative information presented in section 4, which almost reads like a literature review section. I would recommend constructing a kinetic model (perhaps MCM can be utilized in some way) and attempting to reproduce the experimental temporal profiles of the reactants from the chamber experiments and the measured yields of SOAs. All of the elements are here; rate coefficients for the two molecules under investigation are available or can be estimated with SAR parameter if needed. The author should attempt to construct a mechanism explaining the*

experimental observations and the use of this mechanism to discuss and explain the atmospheric implications of their findings in section 4 (Atmospheric Implications).

See also:

Environ. Sci. Technol. 2001, 35, 1394-1405

https://acp.copernicus.org/articles/22/215/2022/acp-22-215-2022.pdf

We thank the reviewer for this comment. We agree that a kinetic model (e.g., MCM) reproducing the time series could help to improve this paper. However, modeling SOA formation is very complex, which needs not only the reaction mechanism in the gas phase, but also complex gas–particle partitioning process which is related to volatility, phase, and mixing state. Therefore, modeling SOA formation, in our opinion, is greatly beyond the scope of this study, and might be a separate paper itself. Nonetheless, we have applied the MCM model to simulate the experimental temporal profiles of the reactants and ozone, and a mixture experiment was selected for comparison with the simulated results. (Page 9-10, line 228-238, Figure 3)

"Figure 3 shows the concentration-time profiles of measured and simulated ozone and ozone formation and loss rates in H-HONO-Mix-4 experiment. The experiment was simulated with Master Chemical Mechanism MCM version3.3 (http://mcm.leeds.ac.uk/MCM/). The model was constrained with measured NO, NO_2, and HONO concentration. As shown in Figure 3a, the ozone production is well represented by the model in the first 0.5 h, however the model starts to over-predict the O_3 concentration in the after 5.5 h. This phenomenon is similar to a study about 1,3,5-TMB, the experiment of which was performed with an outdoor chamber (Metzger et al., 2008). Meanwhile, the ozone photochemical budget cycle was simulated with MCM model. The two major reactions of HO_2 + NO and RO_2 + NO control the photochemical generation of ozone; NO_2+OH, NO_2+ RO_2, and VOCs + NO_3 reactions control the ozone consumption."

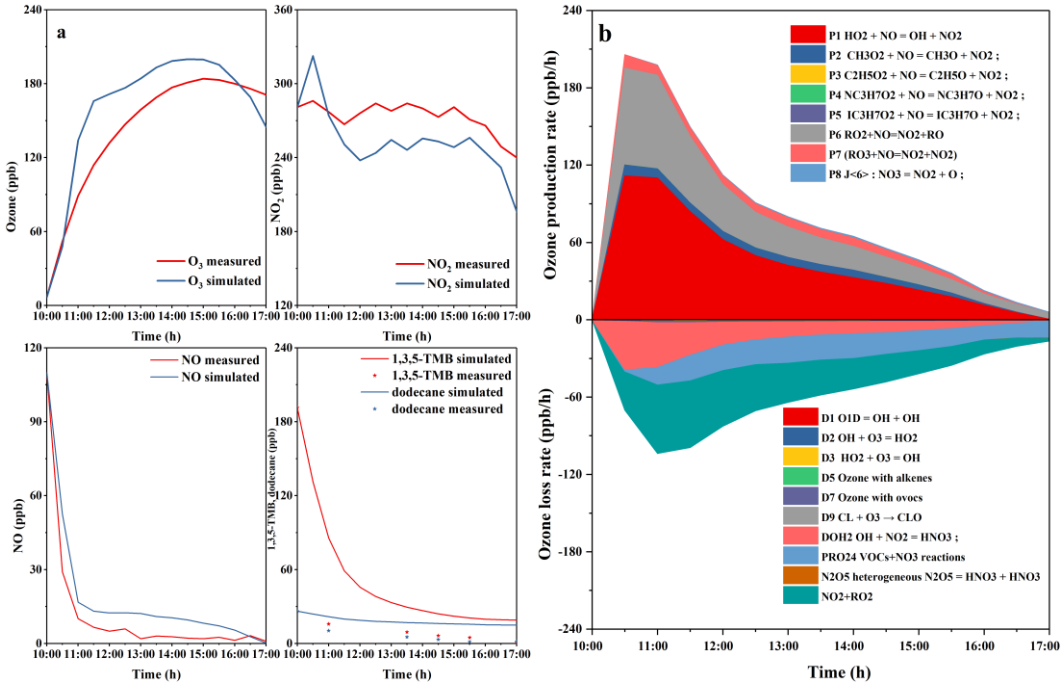

Figure 3. Concentration-time profiles of monitored and simulated (a) ozone, NO, NO_2, and 1,3,5-TMB and dodecane, and (b) ozone formation and loss rates in the H-HONO-Mix-4 experiment.

According to literature and experiment results, the reaction mechanism is proposed, and it has been added in the manuscript. (Page 15-16, line 356-367, Figure 8).

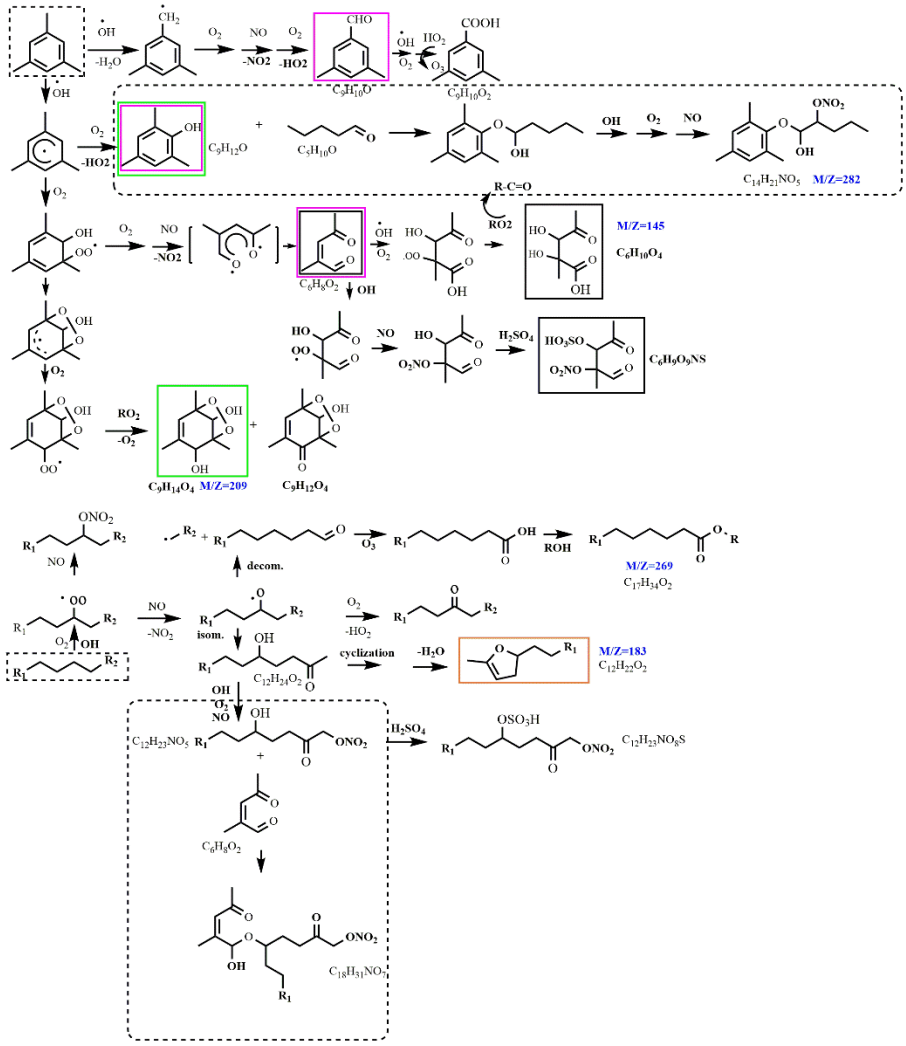

Figure 8. Proposed reaction mechanism of the mixture experiment in the presence of NOx and SO_2 (R1 and R2 are alkyl groups). Blue texted compounds are detected by ESI-Q-ToF-MS in this work; solid boxed compounds are detected by previous studies (black, Yang et al., 2020; purple, Huang et al., 2014; green, Sato et al., 2019; orange, Yee et al., 2013). The reactions in the dotted boxes are the proposed reaction paths of the mixture experiment.

Yang, Z., Tsona, N. T., Li, J., Wang, S., Xu, L., You, B., and Du, L.: Effects of NOx and SO_2 on the secondary organic aerosol formation from the photooxidation of 1,3,5-trimethylbenzene: A new source of organosulfates, Environmental pollution, 264, 114742, 10.1016/j.envpol.2020.114742, 2020.

Huang, M., Hu, C., Guo, X., Gu, X., Zhao, W., Wang, Z., Fang, L., and Zhang, W.: Chemical composition of gas and particle–phase products of OH–initiated oxidation of 1,3,5–trimethylbenzene, Atmos. Pollut. Res., 5, 73-78, 10.5094/apr.2014.009, 2014.

Sato, K., Fujitani, Y., Inomata, S., Morino, Y., Tanabe, K., Hikida, T., Shimono, A., Takami, A., Fushimi, A., Kondo, Y., Imamura, T., Tanimoto, H., and Sugata, S.: A study of volatility by composition, heating, and dilution measurements of secondary organic aerosol from 1,3,5-trimethylbenzene, Atmos. Chem. Phys., 19, 14901-14915, 10.5194/acp-19-14901-2019, 2019.

Yee, L. D., Craven, J. S., Loza, C. L., Schilling, K. A., Ng, N. L., Canagaratna, M. R., Ziemann, P. J., Flagan, R. C., and Seinfeld, J. H.: Effect of chemical structure on secondary organic aerosol formation from C12 alkanes, Atmos. Chem. Phys., 13, 11121-11140, 10.5194/acp-13-11121-2013, 2013.

Technical comments.

3. *Line 36-37, 41-45 These sentences are not well constructed and read awkwardly, please revise.*

   Thank you for this comment. These sentences have been revised. (Page 2, line 36-38, line 42-46)

4. *etc. is used a little bit too much in the introduction, please avoid such abbreviations in the scientific writing.*

   This has been revised in the introduction.

5. *Line 61 Consider removing "in combination with the corresponding equipment"*

   This has been removed.

6. *Lines 74-77 Can you please clarify why the temperature inside the chamber during wintertime is within 15-30 °C range?*

   As the bottom of the reactor was made of aluminum, after a period of sunlight exposure, the surface temperature of the aluminum plate will rise. The chamber covered by Teflon film is equivalent to a greenhouse, the internal temperature will rise after the sunlight exposure. The cooling system of the chamber is water-cooled, in order to prevent the cooling pipes from being frozen and cracked, the system is closed. Thus, the temperature inside the chamber during winter is higher than the ambient environment. The corresponding explanation has been added in the manuscript. (Page 3, line 82-86)

7. *Line 80 Consider removing "classics"*

   This has been removed.

8. *Line 80 NO was introduced from a 500 ppm standard gas cylinder, I understand that this cylinder contained a 500 ppm mixture of NO in nitrogen? Similar comment to Line 84 (SO_2 cylinder).*

   Yes, NO cylinder contained a 500 ppm mixture of NO in nitrogen, and SO_2 cylinder contained a 60 ppm mixture of SO_2 in nitrogen. The corresponding text has been added in the manuscript. (Page 3, line 93,96)

9. *Line 82 Consider removing "home-made"*

   This has been removed.

10. *Line 92 Consider removing "solid" and changing adsorbent to sorbent*

    "Solid" has been removed and "adsorbent" has been changed to "sorbent". (Page 4, line 105)

11. *Line 99 Can you provide some more details about the experimental conditions for the ESI-MS measurements? Perhaps in the SI? What was the difference between the measured and expected elemental formula? What was the mass resolution of the used instrument? Note also that the elemental composition provides little information about the molecular structure.*

    The experimental conditions for the ESI-MS measurements have been added in the "2.2 online and offline measurement part" and Supporting Information. (Page 4, line 113-116; Supporting information, Page 1, line 10-17)

    In general, the theoretical molecular mass of a compound refers to the monoisotopic mass of the compound, which is the sum of the masses of its constituent elements, with each element mass choosing the mass of its most abundant isotope. The expected elemental formula means the formula with the theoretical molecular mass. However, due to the error/interference of the instrument, the measured molecular mass is usually slightly different from the expected molecular mass, and this difference is indicated as mass accuracy (in ppm). The mass resolution of this used instrument is $>$ 20000. In order to explain the detected compounds in depth, we have compared the detected substances with the existing literatures, and this has been added in the manuscript.

12. *Line 111 Referring to OH as the hydroxyl free radical is rather uncommon.*

    This has been revised in the manuscript.

13. *Lines 271-272 more as a higher number or larger concentration?*

    "More" has been changed to "larger concentration". (Page 14, line 347)

14. *Figures S2 and S3 – the labels on these plots are completely unreadable, can you please make the fonts larger?*

    The labels on Figure S2 and S3 have been revised. (Supporting information, Page 7-9, line 51-67)

15. *Figures 2 and 4 are difficult to read, perhaps consider presenting some of these results in a form of a bar plot?*

    Thank you for your comment. Figure 2 and 4 have been revised, now as Figure 2 and Figure 5. The color-coding of shaded areas in the plot have been removed. In addition, the corresponding traditional plots (one variable vs. one factor) have been added in the Supporting Information as Figure S4 and S7. (Supporting Information, Page 9-10, line 68-70; Page 12, line 85-87)

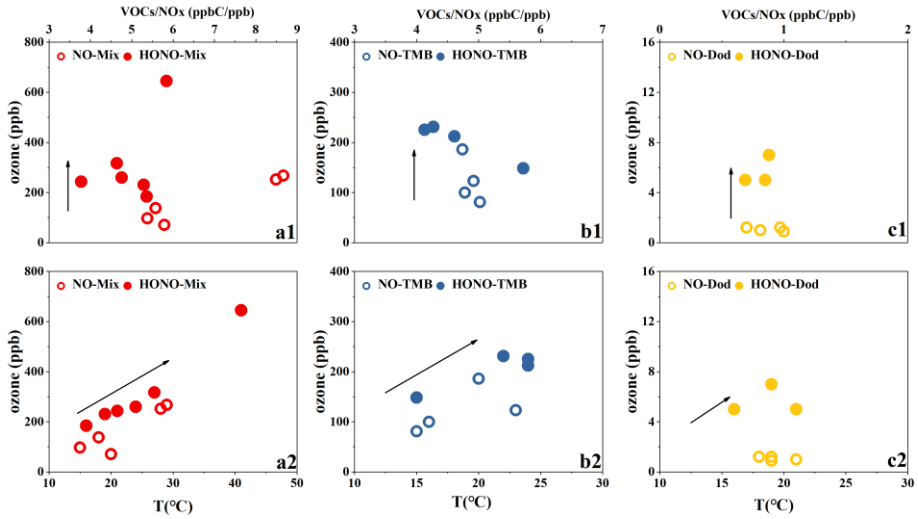

Figure S4. Ozone formation in the NO and HONO experiments. The temperature (T) and ozone concentration here refers to the maximum value during the reaction process.

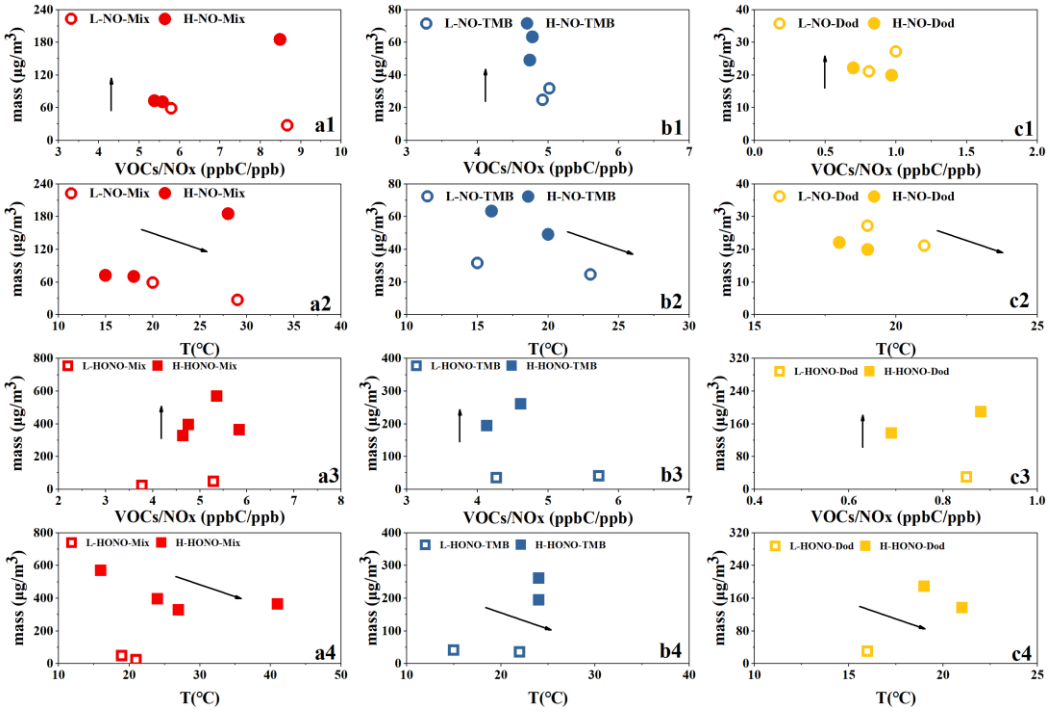

Figure S7. Particle formation of NO and HONO experiments. The temperature (T) and particle mass concentration here refers to the maximum value during the reaction process.