Response to the comments of Reviewer #2

The manuscript presents smog-chamber studies of the photooxidation of n-dodecane, 1,3,5trimethylbeneze, and their mixture in the presence of OH, NOx, HONO, and SO₂. The purpose was to simulate the photooxidation of vehicle exhausts in urban atmospheres. The experiments were carried out in an outdoor chamber illuminated by sunlight. The authors followed NOx, SO₂, O₃, HONO, and HNO₃ concentrations in the chamber and precursor concentrations before and after the reactions. They monitored the number and mass of particles formed and collected them on PTFE filters for subsequent direct-injection ESI-MS and FTIR analyses. Besides, they analyzed inorganic nitrite and sulfate contents in the particles. The results showed that ozone formation during the reactions was enhanced by OH radicals and temperature but not by SO₂. On the other hand, SO₂ increased the number and mass of particles formed. The particles contained many organic compounds, including organosulfates and organonitrates.

The transformation of vehicle exhaust in urban atmospheres, including particulate matter formation and its composition, is a relevant topic of atmospheric chemistry and air quality studies. The authors present and analyze new experimental data on the photooxidation of two components of the exhausts and their mixtures. The presented results and analysis should be interesting for ACP readers and deserve publication in that journal, provided the submitted manuscript is corrected and extended. Below is a list of necessary corrections and extensions before ACP editors may accept the manuscript.

Response: We thank Anonymous Referee #2 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.

Introduction

- The author might cite a recent review (Srivastava et al. 2022) to support the relevance of their work.
 This review has been added in the introduction part of the manuscript. (Page 2, line 35)
- Srivastava, D., Vu, T. V., Tong, S., Shi, Z., and Harrison, R. M.: Formation of secondary organic aerosols from anthropogenic precursors in laboratory studies, npj Climate and Atmospheric Science, 5, 10.1038/s41612-022-00238-6, 2022.
- 2. The authors name several groups of compounds investigated by researchers (e.g., long-chain

alkanes and aromatic hydrocarbons). They may consider explicitly naming a few examples that were studied in the cited works.

Thank you for your suggestion. The corresponding examples have been added in the manuscript. (Page 2, line 38-39; line 47)

3. Lines 59-63. The authors should justify the choice of n-dodecane (DOD) and 1,3,5-trimethylbeneze (TMB) as the model compounds for the study. Besides, they should briefly explain the purpose of comparing NO and HONO experiments (also applies to Section 2.1, lines 73-82).

According to the field observation in China, high concentration of 1,3,5-TMB and *n*-dodecane were observed: the 1,3,5-TMB concentration at rural site could reach 1.447 ppb, and the measured concentration of C_{12} alkanes at rural site was 0.122 ± 0.12 ppb (Chen et al., 2020; Wang et al., 2020a). In addition, 1,3,5-TMB and *n*-dodecane are important components in liquid gasoline and diesel and their vapors (Schauer et al., 2002; Gentner et al., 2012). This has been added in the manuscript. (Page 2, line 61-64)

NO and HONO experiments were designed, as their pathways for generating OH radicals were different. In HONO experiments, the photolysis of HONO could directly generate OH radicals; while for NO experiments, the generation of OH radical was through recycling via NO_x/HO_x chemistry (Ng et al., 2007). Therefore, the OH concentration and exposure are also different in these two experimental setups. This has been added in the manuscript. (Page 3, line 89-92)

- Chen, T., Xue, L., Zheng, P., Zhang, Y., Liu, Y., Sun, J., Han, G., Li, H., Zhang, X., Li, Y., Li, H., Dong, C., Xu, F., Zhang, Q., and Wang, W.: Volatile organic compounds and ozone air pollution in an oil production region in northern China, Atmospheric Chemistry and Physics, 20, 7069-7086, 10.5194/acp-20-7069-2020, 2020.
- Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, Proceedings of the National Academy of Sciences of the United States of America, 109, 18318-18323, 10.1073/pnas.1212272109, 2012.
- Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, Atmospheric Chemistry and Physics, 7, 3909-3922, 2007.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles, Environmental Science & Technology, 36, 1169-1180, 10.1021/es0108077, 2002.
- Wang, C., Yuan, B., Wu, C., Wang, S., Qi, J., Wang, B., Wang, Z., Hu, W., Chen, W., Ye, C., Wang, W., Sun, Y., Wang, C., Huang, S., Song, W., Wang, X., Yang, S., Zhang, S., Xu, W., Ma, N., Zhang, Z., Jiang, B., Su, H., Cheng, Y., Wang, X., and Shao, M.: Measurements of higher alkanes using NO+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmospheric Chemistry and Physics, 20, 14123-14138, 10.5194/acp-20-14123-2020, 2020.

4. Line 44. What is "S/IVOCs"?

S/IVOCs are the abbreviations of semi/intermediate volatile organic compounds. This has been added in the manuscript. (Page 2, line 44-45)

Section 2.1. Smog chamber experimental conditions.

5. Line 74. Was there any particular reason for carrying out the experiments only in winter? Temperature of the experiments carried out in winter in this chamber was in the range of 15~30 °C, and this was suitable for studying reactions at room temperature.

Section 2.2. Online and offline measurements

6. Lines 92-95. The concentrations of organic precursors determined before and after the photooxidation do not appear in the manuscript. Tables S1 and S2 show the initial concentrations, but it is not clear if they were measured or calculated.

The concentration of organic precursors was measured before and after the photooxidation. As the concentration of organic precursors after the photooxidation was nearly zero, so the initial concentrations were shown in Table S1 and S2 to represents the organic precursors consumed in the reaction. This has been added in the manuscript. (Page 4, line 107-109)

7. *Lines* 98-99. *The authors should describe how the filter extraction was done exactly (whole filter or punches, volume of methanol, time of extraction, device used for extraction).*

The collected whole PTFE filter was extracted with 5 mL methanol in an ultrasonic bath (KH5200DV, Hechuang Ultrasonic, China) for 30 min. This has been added in the manuscript. (Page 4, line 113-114)

8. *Lines 99-101. The authors should specify the inorganic species they analyzed in the gas and particle phases.*

The measured inorganic species in gases was nitric acid, and the inorganic species measured in aerosols included sulfate and nitrate. This has been added in the manuscript. (Page 4, line 118-119)

Section 2.3. Calculation methods of SOA yields and OH concentration

9. Lines 105-110. The authors should provide more details on the wall-losses analysis. Mere reference to another paper may be insufficient for readers.

Details of the wall-loss analysis have been added in the manuscript. (Page 4-5, line 127-152)

10. Lines 111-121. The calculation of the OH concentration was essential for the analysis of the results presented, so it should be described in better detail. Namely:

The condition of constant OH concentration and integration of Eqn (1) are not necessary since the slope of the logarithmic TMB time profile is always equal to k[OH]

$$d \ln ([TMB])/dt = -k [OH] \qquad (R-1)$$

The calculation of the OH concentration was described in details, and the added and revised parts have been colored in yellow in the manuscript. (Page 5-6, line 153-165)

11. Line 120. The authors should specify how they averaged the slope and [OH].

As mentioned in question 10, this part has been added in the method part. (Page 5-6, line 153-165)

12. In Section 2.2, the authors should describe how TMB concentrations were determined and with what time resolution for [OH] calculations. Besides, how was [OH] determined in n-dodecane experiments in which TMB was absent?

In this work, 1,3,5-trimethylbenzene is chosen as the tracer for the mixture experiments, as it reacts mainly with OH and has no interference with other compounds. Combined with the sampling frequency, the time resolution for [OH] calculation is about 1-1.5 hour. The [OH] concentration is only calculated and compared in the mixture experiments. The corresponding content has been added in the manuscript. (Page 6, line 166-169)

Section 3.1. General results of the experiments

13. Lines 130 and 140 (Figure 1 caption). The authors should explain the term "exposure" and how they calculated it.

The explanation of OH exposure has been added in Section 2.3. (Page 6, line 166-169)

- 14. The manuscript should include time profiles of the organic precursors studied (at least in Figures S2 and S3), which would help readers understand the reaction progress.
 The time profiles of organic precursors have been added in Figures S2 and S3. (Supporting Information, Page 7-9)
- 15. In line 140, Figure 1 should show when the chamber enclosure was opened precisely. Line 76 says the enclosure was opened between 9:00 and 10:00 a.m., but the first experimental points in Figure 1 are at 11:00 a.m. If each point is some average over the time window, that window should also be specified.

The opening time of the chamber enclosure is the time when the photochemical reaction begins, while the points in Figure 1 means the average OH concentration (Figure 1a) and OH exposure (Figure 1b) in the time interval between this data point and the previous data point. For the first

experimental points in Figure 1, they are the average OH concentration (Figure 1a) and OH exposure (Figure 1b) in the time interval between 11:00 a.m. and the opening time of the photochemical reactions. The explanation has been added in the manuscript. (Page 7, line 188-191)

Section 3.2. Ozone formation and gas phases products

16. Line 150. Figure 2 includes several encodings referring to precursors, reactants, and reaction parameters. A reader needs some effort to decipher those encodings, so it would be beneficial to have them explicitly explained in the Figure caption. Besides, the color-coding of shaded areas in the plot seems redundant with other encodings, so that it could be removed for presentation simplicity. The corresponding explanation has been added in the Figure caption, and the color-coding of shaded areas in the plot have been removed. (Page 8, line 199-207)



Figure 2. Ozone formation in the NO and HONO experiments. The temperature (T) and ozone concentration here refers to the maximum value during the reaction process. The yellow circles refer to NO-Dod experiments with low SO₂ concentration, the yellow boxes refer to NO-Dod experiments with high SO₂ concentration; the yellow filled circles refer to HONO-Dod experiments with low SO₂ concentration, and the yellow filled boxes refer to HONO-Dod experiments with high SO₂ concentration. The blue circles refer to NO-TMB experiments with low SO₂ concentration; the yellow filled boxes refer to HONO-Dod experiments with high SO₂ concentration. The blue circles refer to NO-TMB experiments with low SO₂ concentration; the blue filled circles refer to HONO-TMB experiments with high SO₂ concentration, and the blue filled boxes refer to HONO-TMB experiments with low SO₂ concentration, and the blue filled boxes refer to HONO-TMB experiments with low SO₂ concentration.

TMB experiments with high SO_2 concentration. The red circles refer to NO-Mix experiments with low SO_2 concentration, the red boxes refer to NO-Mix experiments with high SO_2 concentration; the red filled circles refer to HONO-Mix experiments with low SO_2 concentration, and the red filled boxes refer to HONO-Mix experiments with high SO_2 concentration.

17. Line 178. Write explicitly "concentrations similar to those in NO experiments." This has been revised in the manuscript. (Page 10, line 247-248).

Section 3.3. Effect of NO_x and SO₂ on particle formation

- 18. Line 188. Figures S4 and S5 show that in some cases, a banana-like formation of particles occurred, while in other cases not. Could the authors discuss that observation briefly?
 When the max number concentrations are above 10⁵ #/cm³, the banana like-formation particles occur, especially in experiments with high SO₂ concentration. The corresponding explanation has been done in the manuscript. (Page 10, line 256-258)
- 19. Line 200. The OH concentration in HONO experiments was higher than in NO experiments only in the initial hours.

This expression has been revised in the manuscript. This phenomenon can be explained by higher OH exposure in HONO experiments, as shown in Figure 1b. Higher OH exposure causes the higher consumption rate of the precursors and the subsequent faster particle generation rates. (Page 11, line 267-270)

20. Lines 202-205 and 210 (Figure 4). I like the encoding concept of Figures 2 and 4 but inferring some relations from them is not easy. For instance, the influence of temperature on particle mass mentioned in line 204 seems not monotonous. For such comparisons, I would like to see traditional plots (one variable vs. one factor) in the Supplementary Information.

For Figure 2 and 4, the corresponding traditional plots have been added in the Supporting Information, as shown in 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.

21. Line 210 (Figure 4). I have comments on encoding, same as for Figure 2 (Line 150).

The explanations of the encodings have been added in the Figure caption, the color-coding of shaded areas in the plot have been removed. (Page 11-12, line 277-286)

Section 3.4. Chemical composition of particles

22. Line 217 (Figure 5). In the caption, mark what SA is. The sulfate and nitrate bars would be more visible if the mass axis in panel (a) was broken, say between 20 and 90 or 90 and 300.



Figure 5 (now is Figure 6) has been revised according to your suggestion. (Page 12, line 289-292)

Figure 6. (a) The measured mass concentration of sulfate, nitrate, and total secondary aerosol (SA) in the particle phase. The data used in this plot are the average of the hour in which the mass concentration was the greatest. (b) The concentration of gas-phase nitric acid in the mixture system.

23. Line 240. Correct to "Organic chemical composition."

This has been corrected in the manuscript. (Page 13, line 313)

24. Lines 240-254. The authors might compare the FTIR observations with literature e.g., (Holes et al. 1997).

Thank you for this suggestion, the FTIR observations have been compared with literature, and corresponding part has been added in the manuscript. (Page 13, line 319-324)

- Holes, A., Eusebi, A., Grosjean, D., and Allen, D. T.: FTIR analysis of aerosol formed in the photooxidation of 1,3,5trimethylbenzene, Aerosol Sci. Technol., 26, 516-526, 10.1080/02786829708965450, 1997.
- 25. Lines 255-280. Proper mass spectrometric analysis of particulate matter should include the separation of analytes, e.g., by chromatography. The direct-injection method used by the authors is less informative, challenging to interpret, and may serve only as "a first glance approach." The authors might compare the list of ions observed (Table S-3) with literature, e.g. (Praplan et al. 2014; Sato et al. 2012).

Thank you for this comment. We compare the list of ions observed with literature, and the proposed reaction mechanism has been added in the manuscript. (Page 15-16, line 356-367)



Figure 8. Proposed reaction mechanism of the mixture experiment in the presence of NOx and SO₂ (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 SO2 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.

References

26. Line 501. Correct "Tadeusz E. Kleindienst" to "Kleindienst, Tadeusz E." and move the reference to the correct place on the list.

This reference has been revised and moved to the correct place on the list. (Page 21, line 509-511)

Supporting information

27. Tables S1 and S2. Explain "Mo" in table headings.

"Mo" has been changed to "M", which is the mass concentration of formed secondary aerosol. The explanation has been added in table headings. (Page 2-3, line 29-35)

28. Table S3. Explain "RDB" in table heading.

Now Table S3 is Table S4, RDB is the abbreviation of ring and double-bond equivalent, this has been added in table heading. (Page 5, line 41)

29. Figures S2 and S3 are illegible even after magnification in the pdf file and must be improved. Figure S2 and S3 have been improved. (Page 6-9)