Comment on acp-2022-294
Anonymous Referee #2

Referee comment on "Effects of OH radical and SO$_2$ concentrations on photochemical reactions of mixed anthropogenic organic gases" by Junling Li et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-294-RC2, 2022

Review of acp-2022-294 manuscript

Effects of OH radical and SO$_2$ concentrations on photochemical reactions of mixed anthropogenic organic gases

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The manuscript presents smog-chamber studies of the photooxidation of $n$-dodecane, 1,3,5-trimethylbeneze, and their mixture in the presence of OH, NO$_x$, HONO, and SO$_2$. 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 NO$_x$, SO$_2$, O$_3$, HONO, and HNO$_3$ 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 SO$_2$. On the other hand, SO$_2$ 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.

**Introduction**

The authors might cite a recent review (Srivastava et al. 2022) to support the relevance of their work.

The authors name several groups of compounds investigated by researchers (e.g., long-chain alkenes and aromatic hydrocarbons). They may consider explicitly naming a few examples that were studied in the cited works.

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).

Line 44. What is "S/IVOCs"?

**Section 2.1. Smog chamber experimental conditions.**

Line 74. Was there any particular reason for carrying out the experiments only in winter?
Section 2.2. Online and offline measurements

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.

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).

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

Section 2.3. Calculation methods of SOA yields and OH concentration

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

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 \( k[OH] \)

\[ d \ln ([TMB])/dt = -k [OH] \]  

- Line 120. The authors should specify how they averaged the slope and \([OH]\).
- 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?

Section 3.1. General results of the experiments

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

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.

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.

Section 3.2. Ozone formation and gas phases products

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.

Line 178. Write explicitly “concentrations similar to those in NO experiments.”

Section 3.3. Effect of NO\textsubscript{x} and SO\textsubscript{2} on particle formation
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?

The OH concentration in HONO experiments was higher than in NO experiments only in the initial hours.

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.

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

Section 3.4. Chemical composition of particles

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.

Correct to “Organic chemical composition.”

The authors might compare the FTIR observations with literature e.g., (Holes et al. 1997).

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).
References

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

Supporting information

Tables S1 and S2. Explain “Mo” in table headings.

Table S3. Explain “RDB” in table heading.

Figures S2 and S3 are illegible even after magnification in the pdf file and must be improved.

English language

The authors should polish the English language of the manuscript using either an external service like Copernicus English copy-editing service or an AI proofreading tool like Grammarly. Some advice follows.

Line 19 and many other. Do not use “It is found”. Skip or use “We found.”

Lines 22-23 and throughout the manuscript. Replace “organo-sulfates” and “organo-nitrates” with “organosulfates” and “organonitrates,” respectively.
Line 33. Replace “a mixture of multiple precursors” with “a mixture of many precursors”.

Lines 41-42. Replace “long-chain alkanes as one of the species” with “long-chain alkanes as the species.”

Line 50. Replace “could be > 100 ppb” with “could exceed 100 ppb”.

Line 55. Do not use “It should be noted that.” Use “Notably, “ remarkably,”, “Interestingly, “ or so.

Line 61. Do not use “The results in this work are helpful to...”. Use “The results help ....”.

Line 165. Do not use “It is also shown in Figure 2 that ...”. Use “Figure 2 shows ...”.

Lines 204, 206. Do not use “It can be seen that ...”. Skip.


and LC/MS analyses of SOA from the photooxidation of benzene and
1,3,5-trimethylbenzene in the presence of NO$_x$ effects of chemical
structure on SOA aging. Atmos Chem Phys 12, 4667-4682. 10.5194/acp-12-4667-2012

aerosols from anthropogenic precursors in laboratory studies. npj Climate and
Atmospheric Science 5, 22. 10.1038/s41612-022-00238-6