

Atmos. Chem. Phys. Discuss., referee comment RC2
<https://doi.org/10.5194/acp-2022-239-RC2>, 2022
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Comment on acp-2022-239

Anonymous Referee #2

Referee comment on "Investigation of the limonene photooxidation by OH at different NO concentrations in the atmospheric simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber)" by Jacky Yat Sing Pang et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-239-RC2>, 2022

This manuscript presents a series of chamber studies that investigate the OH initiated oxidation of limonene at various NO_x mixing ratios and also presents an additional experiment that investigates the ozonolysis of limonene in a dark chamber with near-zero NO_x mixing ratios. Although only a handful of experiments were performed, the manuscript is built around an extensive dataset including measurements of limonene, formaldehyde, HONO, NO_x, O₃, and photolysis frequencies in addition to the important and technically challenging measurements of OH, HO₂, RO₂, and OH reactivity. The measured radical concentrations are compared to results from a box model featuring MCM v3.3.1 chemistry which typically suggests RO₂ concentrations that are much higher, and HO₂ concentrations that are lower than measured values. As suggested by reviewer 1, the discrepancies between measured and modeled RO₂ concentrations, particularly during the low-NO_x and zero-NO_x experiments, are significant results that highlight a gap in our understanding of this type of oxidation chemistry. The paper also examines the formaldehyde and organic nitrate yield to further aid in understanding the fate of limonene RO₂ species.

Overall, the paper is well written and is particularly effective at merging the results and discussion of several different experiments, which were performed across a number of years, into a cohesive manuscript with a unified conclusion.

Specific comments:

Line 138: Is there an estimate for the "small" fraction of limonene-RO₂ that is converted and measured as HO₂ in the LIF detection cell during these experiments? Has this fraction been determined specifically for limonene-RO₂ and the NO concentrations used in detection cell or is it possible that this RO₂ interference is more significant than anticipated? If so, could this at least partially explain the discrepancies between measured and modeled HO₂ concentrations, especially during the ozonolysis experiment when measured RO₂ concentrations were highest?

Line 143: Are the RO₂ concentrations reported from all experiments derived from calibrations with methylperoxy radicals? If so, does this imply that the reported RO₂ concentrations, which are largely due to limonene-RO₂, represent a lower limit? Or have adjustments been made that take the RO_x-LIF system's reduced sensitivity to limonene-RO₂ into consideration?

line 207: Are the fluctuations in NO mixing ratios (and ultimately measured and modeled radical concentrations) during the low and medium NO experiments (Figures 3 and 4) caused by changes in HONO production from the chamber source that are driven by changes in solar radiation? If so, these fluctuations may be easier for readers to interpret if measured or parameterized HONO mixing ratios or measurements of photolysis frequencies were shown.

Figure S3: This figure is not discussed in the context of the low NO experiments. This is understandable since only a small portion of this experiment involves limonene oxidation, but since the figure is shown – are the observed RO₂ concentrations prior to the CH₄ addition likely due to the oxidation of some VOC produced in the chamber? It is interesting that, after the CH₄ injection, the measured RO₂ concentration increases as expected (at least relative to the established background), but the measurement/model agreement quickly reverses after limonene addition. Could this difference in measurement/model response to the different VOCs be related to the previously mentioned RO_xLIF sensitivities to CH₃O₂ and limonene-RO₂? Similarly, the model agrees with the HO₂ measurements during the CH₄ injection but underpredicts the measurements after the limonene injection. While these trends could again indicate a limonene-RO₂ interference in the HO₂ measurement, they could also support the later claims of missing RO₂ loss processes, whether isomerization or RO₂ + RO₂ recombination reactions, that are much faster for large complex monoterpene peroxy radicals (and produce HO₂), but do not occur for smaller RO₂ species like CH₃O₂. A short discussion on this particular experiment could be useful but is not absolutely necessary.

Line 533: "concentration" can be removed, or this sentence should be otherwise rephrased.

Line 619: This sentence is a bit awkward. Perhaps "In the ozonolysis experiment, prior to the addition of CO as an OH scavenger (Fig. 8d) OH is only produced by the ozonolysis of limonene."

Line 659: Delete "-" after OH

Figures 9, 12, and others in supplement: When data from multiple experiments are presented in one figure it would be useful to also label each panel (or group of panels) with "low NO" or "ozonolysis" instead of just the date. Figures 8 and S6 are good

examples.

Figures 9 and S8: The caption in Figure 9 suggests that CH_3O_2 is mainly produced from the oxidation of HCHO while the caption in Figure S8 suggests that CH_3O_2 is mainly produced from the oxidation of limonene.

Lines 716, 720, 731, 1003: Some commas are unnecessary.

Line 764/765: This sentence is a bit awkward. Consider "These reactions could involve an unknown reaction partner X, as used in Hofzumahaus et al. (2009), or could be unimolecular reactions." Also, this reference may be missing from the reference list.

Line 893: One example instead of one examples.

Line 1018: Second "in the model" is unnecessary.