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Reply on RC2

Jacky Yat Sing Pang et al.

Author 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-AC2, 2022

We thank the reviewer for the useful comments improving our manuscript.

Line 138: Is there an estimate for the "small" fraction of limonene-RO_2 that is converted and measured as HO_2 in the LIF detection cell during these experiments? Has this fraction been determined specifically for limonene-RO_2 and the NO concentrations used in detection cell or is it possible that this RO_2 interference is more significant than anticipated? If so, could this at least partially explain the discrepancies between measured and modeled HO_2 concentrations, especially during the ozonolysis experiment when measured RO_2 concentrations were highest?

Authors response:

A potential interference was only once explicitly tested, when the first experiments were performed. Results showed that the upper limit of an interference would be around 15%, but data were too noisy to derive an accurate number. We added in Line 144 to 146: "The upper limit of such an interference would be around 15% as indicated by characterization experiments, which unfortunately did not allow to determine an accurate number due to the limited precision of results."

Line 143: Are the RO_2 concentrations reported from all experiments derived from calibrations with methylperoxy radicals? If so, does this imply that the reported RO_2 concentrations, which are largely due to limonene-RO_2, represent a lower limit? Or have adjustments been made that take the RO_x-LIF system's reduced sensitivity to limonene-RO_2 into consideration?

Authors response:

RO_2 concentrations reported here are derived from the calibrations with methyl peroxy radicals. The RO_x-LIF measurement sensitivity of limonene-RO_2 relative to CH_3O_2 was determined in laboratory experiments to be 0.85±0.05. No correction is applied to account for the lower sensitivity, because this would require knowledge of the exact distribution of RO_2 radicals in the experiments. Corrections would be smaller than the discrepancies between modeled and measured RO_2 concentrations.

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.

Authors response:

The fluctuation in NO mixing ratios is mainly driven by the fluctuation in the photolysis frequencies that are affected by cloud cover. In order to illustrate the effect, the photolysis frequency of HONO (j_{HONO}) is now added to the overview plots in photooxidation experiments (Figure 4, 5, 6, S3, S4, and S5).

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 RO_2 concentrations prior to the CH_4 addition likely due to the oxidation of some VOC produced in the chamber? It is interesting that, after the CH_4 injection, the measured RO_2 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 CH_3O_2 and limonene-RO_2? Similarly, the model agrees with the HO_2 measurements during the CH_4 injection but underpredicts the measurements after the limonene injection. While these trends could again indicate a limonene-RO_2 interference in the HO_2 measurement, they could also support the later claims of missing RO_2 loss processes, whether isomerization or RO_2 + RO_2 recombination reactions, that are much faster for large complex monoterpene peroxy radicals (and produce HO_2), but do not occur for smaller RO_2 species like CH_3O_2. A short discussion on this particular experiment could be useful but is not absolutely necessary.

Author response:

The observed RO_2 concentration before the injection of CH_4 is indeed likely due to the oxidation of unidentified background sources. The presence of these unidentified background sources is also seen in the background OH reactivity. Our model treats these unidentified background species as having the same chemical properties as CO to match the background OH reactivity. Therefore, RO_2 produced from the oxidation of the background source cannot be reproduced by our model calculations. The high measured HO_2 concentration right after the limonene injection would require that half of the RO_2 is detected in the HO_2 cell, which would be inconsistent with our characterization experiments, which determined an upper limit of the interference of 15%. Overall results from this experiment are consistent with results discussed for the experiment on 01 September 2012 in the main paper, so that we do not think that there is additional discussion needed.

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

Author response:

The sentence is corrected as suggested by removing "concentrations". (Line 561)

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."

Author response:

The sentence is changed as suggested by the reviewer. (Line 647 – 649)

Line 659: Delete "-" after OH

Author response:

The sentence is corrected as suggested. (Line 689)

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.

Authors response:

Thanks for the suggestion. Figures 9 to 11 and S8 to S12 are now labeled with case name in each subplot. For Figure 12, experiment cases are now labeled separately (Medium NO: Figure 12; Low NO: Figure 13; Ozonolysis: Figure 14) similar to that of Figures S10 to S12. The Figures of the autooxidation mechanism of limonene-RO_2 are now Figure 15 and 16 (Line 934, 940). The labels in the text are also changed accordingly.

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.

Authors response:

CH_3O_2 is mainly produced from the oxidation of HCHO that is produced from the oxidation of limonene in most of the experiments. In the low-NO experiment on 13 June 2015, CH_3O_2 was mainly produced from the oxidation of CH_4 that was added before the injection of limonene. The caption in Figure S8 is now changed to: "Methylperoxy radicals (CH3O2) are mainly produced from the oxidation of HCHO in most of the experiments or from the oxidation of CH_4 during the experiment on 13 June 2015" in Line 135 in the supplementary material.

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

Authors response:

The sentences are corrected. (Lines 750, 754, 765, 1035)

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.

Authors response:

The sentence is changed as suggested and the missing reference is added. (Line 798 –

799)

Line 893: One example instead of one examples.

Authors response:

The sentence is corrected as suggested. (Line 934)

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

Authors response:

The sentence is corrected as suggested. (Line 1050)