

## ***Interactive comment on* “Evaluation of OH and HO<sub>2</sub> concentrations and their budgets during photo-oxidation of 2-methyl-3-butene-2-ol (MBO) in the atmospheric simulation chamber SAPHIR” by Anna Novelli et al.**

**Anonymous Referee #1**

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This paper presents measurements of OH, HO<sub>2</sub> and OH reactivity during the oxidation of 2-methyl-3-butene-2-ol (MBO) in the SAPHIR chamber. Measurements of OH and HO<sub>2</sub> using a Laser-Induced Fluorescence - Fluorescence Assay by Gas Expansion (LIF-FAGE) instrument. While potential interferences with the OH measurements were not measured, the LIF-FAGE measurements were in good agreement with OH measurements by differential optical absorption spectroscopy (DOAS) in the SAPHIR chamber, suggesting that interferences associated with the FAGE technique were minimal. Measurements of HO<sub>2</sub> were done at relatively low HO<sub>2</sub>+NO conversion efficien-

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cies to minimize potential interferences from RO<sub>2</sub> radicals.

The authors find that modeled concentrations of OH and HO<sub>2</sub> concentrations during the oxidation of MBO using the latest version of the Master Chemical Mechanism were in good agreement with the measurements. The modeled total OH reactivity was also consistent with measurements of total OH reactivity as well as with measured total OH production, suggesting that the sources and sinks of OH were known and accounted for during the experiments. The modeled HO<sub>2</sub> production rate was also found to be in good agreement with the measured HO<sub>2</sub> loss rate, suggesting that the sources and sinks of this radical were accounted for during the oxidation experiments.

The results of these experiments are consistent with ambient measurements of OH and HO<sub>2</sub> in forests where MBO was the dominant biogenic emission, where modeled radical concentrations were found to be in good agreement with the measurements. The results presented here suggest that discrepancies between measurements and models in areas where MBO is not the dominate emission are not due to uncertainties associated with the MBO oxidation mechanism. Rather, the discrepancies may be due to uncertainties in the oxidation of other biogenic emissions such as the oxidation of monoterpenes leading to HO<sub>2</sub> production.

The paper is well written and the results suitable for publication in ACP after the authors have addressed the following:

- 1) The authors state that the largest uncertainty associated with the measurement – model agreement is the uncertainty associated with measurements of the OH reactivity during zero-air measurements, but it does not affect the modeled radical concentrations beyond the calibration accuracy of the measurements (pages 5-6). Unfortunately, Figure 2 does not display the model predictions of OH or HO<sub>2</sub> during the zero measurements after the chamber has been opened. The authors state that (page 5) “Because of the unknown chemical nature of the background reactivity that dominates the loss of OH radicals for the zero air phase of the experiment, agreement between

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measured and modelled radical concentrations cannot be expected during this initial phase. Therefore, no model calculation is shown for this part of the experiment.” However, this unknown background reactivity has been observed previously as referenced in the manuscript (Fuchs et al., 2014; Kaminski et al., 2017) and in these studies the authors were able to demonstrate reasonable agreement of the model with the measurements during the zero-air experiments prior to addition of the reactant of interest. It is unclear why the authors were unable to reproduce the initial OH and HO<sub>2</sub> concentrations in these experiments. Because the OH and HO<sub>2</sub> concentrations depend on radical production from the background production of HONO and HCHO as well as O<sub>3</sub> photolysis, illustrating the ability of the model to reproduce the chamber’s OH and HO<sub>2</sub> production during the zero-air experiments would give more confidence in the ability of the model to reproduce the radical concentrations after addition of MBO. This should be clarified in the revised manuscript.

2) Similarly, a significant fraction of the modelled HO<sub>2</sub> radical budget appears to be due to the chamber source, which depends on the concentration of OH in the chamber. The authors state that the source is not “atmospherically relevant” (page 7). While I understand that this source is not relevant in the real atmosphere, do the authors mean that it is not a significant source in these chamber experiments, as it accounts for only 30% of the HO<sub>2</sub> production? This could be clarified. What would the budget (and the modeled HO<sub>2</sub> concentrations) look like if this source is removed?

3) Related to this, the authors assume that the chamber source acts similarly to the OH + CO reaction and propagates OH directly to HO<sub>2</sub>. Have the authors done a sensitivity test where they assume the unknown OH reactivity leads to either RO<sub>2</sub> production or to OH radical termination instead of propagation directly to HO<sub>2</sub>? While the resulting modeled HO<sub>2</sub> concentrations appear relatively insensitive to the uncertainty associated with the OH reactivity measurement, it is not clear whether the modeled HO<sub>2</sub> concentrations and budget are sensitive to the assumption of the nature of the missing OH reactivity in the chamber. A missing reactivity mechanism that does not di-

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rectly convert OH to HO<sub>2</sub> may lead to a model underestimation of the measured HO<sub>2</sub> concentrations, suggesting a missing HO<sub>2</sub> source similar to that found in the ambient measurements discussed in section 3.4. Again, demonstrating that the model can reproduce the observed OH and HO<sub>2</sub> during the zero-air experiments would provide some justification for their assumption of the nature of the missing OH reactivity in the chamber, but a sensitivity study that shows that the modeled HO<sub>2</sub> concentrations were relatively insensitive to the nature of the missing OH reactivity would also give confidence in their conclusion that the chemistry of OH and HO<sub>2</sub> is “well described our current understanding of the MBO OH-initiated degradation processes.”

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