

**Review of “Importance of isomerization reactions for the OH radical regeneration from the photo-oxidation of isoprene investigated in the atmospheric simulation chamber SAPHIR” by Novelli et al.**

This publication presents a set of chamber studies carried out under representative ambient atmospheric conditions in the outdoor SAPHIR chamber on the photooxidation of isoprene. A comprehensive set of measurements (including radicals HO<sub>x</sub> and RO<sub>x</sub>) were made over a range of VOC/NO<sub>x</sub> conditions, so that the sensitivity of “low-NO” peroxy radical isomerisation reactions and subsequent radical regeneration chemistry can be mapped out in order to evaluate the detailed isoprene degradation chemistry described in the detailed MCMv3.3.1 and Caltech isoprene mechanisms. The chamber measurements and modelling were supported by detailed theoretical calculations focusing on the chemistry of the di-HCARP-RO<sub>2</sub> species. The experimental and theoretical work here have been used to recommend updates to the chemistry in both mechanisms and highlight where further research into the low NO isoprene chemical mechanism (i.e. HPALD vs. diHCARP yields and further chemistry) needs to be focused.

This is an interesting and valuable detailed study into the sensitivity of isoprene photooxidation chemistry over a range of NO<sub>x</sub> conditions, under atmospherically relevant conditions, providing an important dataset with which to evaluate and optimise our current mechanistic understanding of the atmospheric chemistry, providing future focus in which the chemical uncertainties lie. The manuscript is generally written well, with a few spelling and grammatical errors which need to be fixed. I recommend publication in ACP after the following points are addressed.

I agree with the anonymous Referee #2 that more detail on the development of the MCMv3.3.1 and Caltech isoprene chemical mechanisms need to be brought out in the introduction and place into context of how the developments of these schemes stem from the original LIM1 mechanism, with the further developments of the chemistry applied so that they fit a range of atmospheric conditions. For example, the development of the MCMv3.3 to MCMv3.3.1 comes from detailed discussions between the MCM and LIM1 development teams, using the latest experimental data at the time to scale various rate constants that are very pertinent to the current study (i.e. why the equilibrium rate constants between the isoprene - RO<sub>2</sub> species are increased by a factor of 5 (Line 57) and why the 1,6-H shift RO<sub>2</sub> isomerisation rates are reduced by a factor of 5 (Line 67)). Much of this developmental discussions is given in the ACPD responses section (<https://www.atmos-chem-phys.net/15/11433/2015/acp-15-11433-2015-discussion.html>), and should be referenced appropriately. One more thing to note is that the MCMv3.3.1 and the main updates to the Caltech isoprene mechanism (including evaluated in the kinetics and products of 1,6 H-shift reactions of Z- $\delta$ -hydroxy peroxy isomers and of first-generation  $\beta$ -hydroxy peroxy isomer + HO<sub>2</sub> reactions) have been evaluated over a range of NO<sub>x</sub> conditions in Jenkin et al., (2019) (<https://doi.org/10.1016/j.atmosenv.2019.05.055>), showing some differences in the HPALD and di-HCARP-RO<sub>2</sub> formation, as well as RONO<sub>2</sub> formation, with general agreement over the different NO ranges looked at deemed acceptable.

In the **Model Calculations** section, add at line 182 that “... with newly updated isoprene chemistry in line with LIM1 chemistry, updated/optimised to recent experimental results, as described in Jenkin et al., (2015)”

Line 330. The statement about an overprediction of ISOPOOH is not backed up by the measurements here, unless you can estimate the relative fractions of MACR, MVK and ISOPOOH that make up the mass signal in the PTR.

Line 379. Consider putting the additional model run described here in the Supplimentary

Line 455. So the additional global model run includes M3 chemistry?

Figure 5. Consider adding the MCMv3.3.1 model simulation to Figure 5, for a direct comparison with Figure 4.

The **Supplementary Material** pdf consists of 1074 pages!! The majority of this consists of the raw quantum chemical and theoretical kinetic database. Please place this information into an online data store (github) or a supplementary zip files as this data (all though important) is only really relevant/useful to specialist QM chemists.

### Minor Comments

- Abstract – is “disregarded” the right word here? I would use “unrecognised” or “undiscovered” here, or re-write the sentence to say that they were previously not thought to be important under atmospheric conditions...
- Define “parts per billion” earlier, when first used
- Line 27 - “aldehydic hydrogen”
- Throughout the main text and supplementary, please refer to “**MCMv3.3.1**” and not “**MCM 331**”.
- Line 165 – define “ROx”
- Line 210 – “{10 % methyl peroxy radical and 30% RO<sub>2</sub> radicals from isoprene}”- give a reference for these numbers
- Line 216 – Link bullet points to Table 2 or expand into a better version of Table 2
- Line 235 -Link changes to the isoprene chemistry to Table S7
- Should “DHP-MVK” be “DHP-MEK” throughout the manuscript (Figures 2 and 3)?
- Line 557. Define OH additions on C4 and C1 – “radical formed from initial OH attack at the C4 and C1 positions...”