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Interactive comment on “Impacts of mechanistic changes on HO_x formation and recycling in the oxidation of isoprene” by A. T. Archibald et al.

Anonymous Referee #2

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Archibald et al. present a modelling study examining the impact of a number of changes to isoprene oxidation mechanisms on simulated radical concentrations and isoprene oxidation products. This work is of current interest due to several recent studies showing model-measurement discrepancies in simulated radical budgets in remote regions characterised by high emissions of isoprene (eg. Lelieveld et al., 2008; Pugh et al., 2010). In particular, current-generation models of isoprene oxidation appear to severely underestimate the concentration of the hydroxyl radical (OH). Archibald et al. find that chemistry recently proposed by Peeters et al. (2009) (isomerisation of isoprene-derived peroxy radicals, followed by rapid photolysis of a subsequently formed unsaturated hydroperoxy-aldehyde) is capable of significantly increasing model simulated OH concentrations in conditions similar to those encountered in remote forested regions. The results presented here highlight the urgent need for experimental investigation of what

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are still theoretical predictions.

The manuscript is well structured and clearly written. Methods are described in sufficient detail and conclusions are well argued. Careful attention is given to the previously published literature. The present manuscript is not the first study to have implemented the chemistry proposed by Peeters et al. (2009) into a model of atmospheric chemistry; Karl et al. (2009) have also done this. In the opinion of this referee, the scope of Archibald et al. is however substantially different than that of Karl et al. (2009).

- Karl et al. (2009) focus their analysis of the Peeters et al. (2009) chemistry on its impact on OVOC, not on HO_x budgets.
- Karl et al. (2009) do not include the very important subsequent chemistry of the unsaturated hydroperoxy aldehyde.
- Archibald et al. do a thorough systematic evaluation of various changes to a near-explicit chemical mechanism under a wide range of atmospherically-relevant conditions. Karl et al. (2009) report results relevant to a single field study using a set of inherently simplified representations of isoprene chemistry.
- Both studies employ box models, but only Archibald et al. go on to explore the implications of their box modelling studies in a global model.

The manuscript represents an important contribution to this rapidly evolving area of atmospheric chemistry, and I recommend that it be published in ACP with the following minor revisions.

- R8 and R9 (on page 5869) would be better following on from R2 in the introduction (page 5865), especially given the discussion of ozone formation in the introduction.

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- Page 5872, line 16: this reads as if the “simplified treatment” is actually being applied in the present study. You should make it clearer that this is a feature of the MCM itself.
- R13b on page 5872 is missing its reactants.
- Page 5879, line 23: this reads as if the Peeters chemistry has been incorporated into the MCM itself, rather than just the version used in this study.
- Page 5880, line 5: “was calculated to be significant”. Calculated by whom?
- Page 5887, line 18: it would improve clarity here if you also list the reactions for RU14O₂ which are already present in the CRLv2 mechanism, and then go on to explain what you have added to the mechanism.
- Page 5888, line 10: so do k_{24} and k_{25} vary in your model with NO concentration or not?
- Section 5: Butler et al. (2008) also present the results of global modelling studies performed with a parameterised source of OH in high-isoprene low-NO_x environments based on model-measurement comparisons from the GABRIEL campaign. How do your simulations compare with theirs?

References

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