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Comment

Interactive comment on “Improved global modelling of HO_x recycling in isoprene oxidation: evaluation against the GABRIEL and INTEX-A aircraft campaign measurements” by T. Stavrakou et al.

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Received and published: 21 August 2010

This paper presents an evaluation of the impacts of several recently reported or proposed mechanisms which consider revisions to conventional understanding of isoprene degradation. The main aim of the work is to quantify the effects of these revisions on simulated concentrations of HO_x radicals and to compare the effects with recently reported field observations of HO_x and other species using a global chemistry-transport model. The work shows that a combination of the mechanisms can address the previously reported model-measurement discrepancies for HO_x, with mechanistic changes

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recently proposed by the authors and co-workers (referred to as "LIM0"), based on a theoretical assessment of the system, making the dominant contribution.

The paper is clearly written and contains a valuable discussion of mechanistic detail, and an evaluation of its impacts under atmospheric conditions. The work should therefore be published subject to consideration of the following points.

1) The results show that LIM0 has the potential to close the model-measurement discrepancy gap for HO_x, but does not provide absolute proof that the mechanism is correct. It is possible that there may be other currently unidentified and unrepresented contributors to HO_x formation and recycling, such that getting good model-measurement agreement for HO_x does not in itself constitute validation (even if the result is informative and encouraging). In a final statement on page 16571, the authors are careful to indicate that there are uncertainties in the mechanism and that further experimental work is essential to validate it. This crucial requirement should probably be given even more emphasis, including mention in the Abstract.

2) In the final sensitivity test, S8, a case is made for changes in the isoprene emission rate which result in a final impressive agreement between modelled and observed concentrations for the series of species presented in Table 3. If these changes in emission rate are considered justifiable, should they be implemented at the start of the process so that the results of each mechanistic sensitivity test can be compared more directly with the observations?

3) The large flux predicted for formation of the HPALD species by operation of LIM0 logically results in a corresponding reduction in the formation of conventional isoprene products (hydroperoxides, nitrates, MVK and MACR), as presented in Tables 2 and 3. Implementation of LIM0 therefore generally seems to worsen model-measurement agreement for MVK+MACR during GABRIEL (Table 3), although the final comparison in S8 with the elevated isoprene emission rate and a reduced rate for $k(1,6)$ (0.64 ppb simulated vs. about 1 ppb observed) is considered acceptable by the authors.

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My concern here is that this underestimation is despite the fact that MVK+MACR formation from LIM0 may already be artificially too high. My reasoning for this relates to the use of the yield of MVK+MACR reported in the chamber study of Paulot et al. (2009) to optimise $k(1,5)$ on page 16559, with the clear assumption that there are no other sources of MVK+MACR under the chamber conditions employed. The resultant optimised value is substantially higher than that originally reported by Peeters et al. (2009), and some two orders of magnitude greater than reported recently in another theoretical study (da Silva et al., 2010), which should really be cited and discussed in the present paper.

Given that the initial relative formation rate of RO₂ and HO₂ in the Paulot study is about 3:1, it is highly likely that a major contribution to MVK+MACR formation comes from the self- and cross- reactions of the RO₂ species, which are able to compete partially with RO₂+HO₂. The RO₂ self- and cross- reactions are stated to be represented in the global calculations (page 16561), but are not apparently considered in appraisal of a chamber experiment, where they are likely to be more important. In my opinion, the high rate applied to $k(1,5)$ is therefore probably not justified, and the formation of MVK+MACR simulated with LIM0 may be artificially elevated. A reduction in the yield would clearly worsen the model-measurement agreement for MVK+MACR in Table 3, suggesting that this aspect of performance may not be validated by the present comparison. Please can the authors comment.

4) As discussed by Peeters et al. (2009), the formation of the HPALD species (and HO₂) following the 1,6 H-shift isomerisation of the d-hydroxy RO₂ radicals requires reaction of a hydroxy-allyl radical with O₂. Peeters et al. (2009) reasonably argue that the necessary alpha- O₂ addition dominates over gamma O₂ addition. However, in view of the experimental observation of formation of epoxy compounds from similar structures by Paulot et al. (2009), I would be interested to know the authors' view on whether direct elimination of OH in conjunction with formation of an epoxy compound (see Fig.1 below) could compete with alpha- O₂ addition. This would provide a direct

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route to OH recycling (although the HOx chain-branching aspect of the mechanism would be lost).

Minor comments

Abstract, line 6: I would suggest replacing "validated" by "evaluated" (as in the paper title).

Page 16564, line 28: The comment about the yields of HPALDs being lower in polluted regions seems to be presented as if it is a surprising result, whereas it is surely as expected. Perhaps "interestingly" could be replaced by something like "logically".

References

Da Silva, G., Graham, C. and Wang, Z-F.: Unimolecular b-hydroxyperoxy radical decomposition with OH recycling in the photochemical oxidation of isoprene. *Environ. Sci. Technol.*, 44, 250–256, 2010.

Paulot, F., Crouse, J. D., Kjaergaard, H. G., Kürten, A., St. Clair, J. M., Seinfeld, J. H. and Wennberg, P. O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science*, 325, 730-733, 2009.

Peeters, J., Nguyen, T. L. and Vereecken, L.: HOx radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 28, 5935-5939, 2009.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 10, 16551, 2010.

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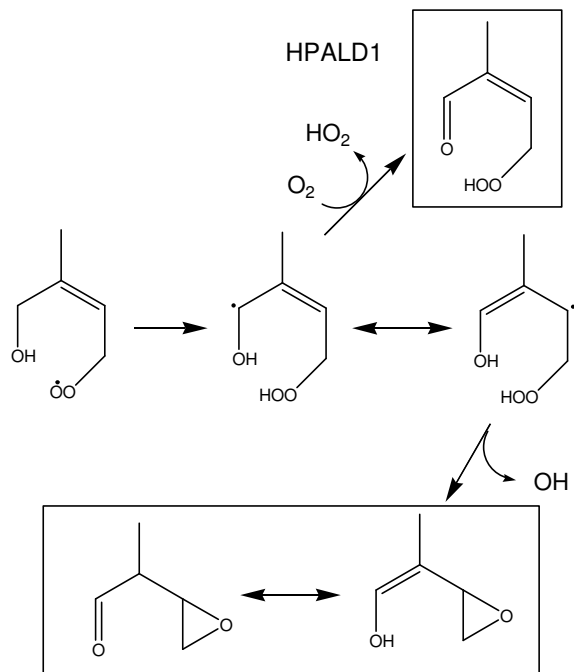


Fig. 1. Possible chemistry competing with HPALD formation