

Interactive comment on “Isoprene photooxidation mechanism: resonance channels and implications for the production of nitrates and acids” by F. Paulot et al.

F. Paulot et al.

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We thank the reviewer for his/her helpful comments.

1) particular attention should be drawn to quantitative uncertainty

As mentioned in our reply to the first reviewer, we now address, in a specific Section, uncertainty (see reply to comment 1 in the response to Dibble’s comments)

The experimental section is very short and appears to be dispersed throughout the manuscript. I think it should be made clear early on (in the experimental section or an experimental results section) what the most important observations are so the reader can have these in mind when looking later at the arguments in

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favour of one pathway or another. We have expanded the experimental section and added a Result section which summarizes the most important observations.

My comments on this first step are (a) the MACR and MVK yields reported by Karl et al., and referenced in the manuscript are 0.27 and 0.41, respectively. This appears to be the other way around in the manuscript (eqns (6) and (7)).

This was a typographical error and is now corrected in the revised text.

2)there is no way for the reader to appreciate the magnitude of the uncertainties in the non-linear fit results given. Lei et al. states that an uncertainty of +/- 1 kcal mol⁻¹ is expected on the energies of the initial adducts in the isoprene mechanism (this is probably a slight underestimation given the size of the basis sets they used). If one can rely on the quoted +/- 1 kcal mol⁻¹ uncertainty of Lei et al., how does this translate into the uncertainty in your fit coefficients? One also has to include the uncertainties in the experimental MACR and MVK yields.

As pointed out by the reviewer, the uncertainty in the study of Lei et al. is probably greater than the one reported in the paper. The more recent determination of the branching ratio brought to our attention by the first reviewer (Greenwald et al 2007) is indeed very different from Lei et al.'s results. As pointed out in the answer to Dr Dibble, it seems that experiment and theory disagree at this point. As described in detail in the revised manuscript, we cannot reconcile the Greenwald result with the reported MVK/MKRN yields.

3)the authors then make some slight adjustments to these fit coefficients based on the experimental isoprene nitrates concentration profiles in the early stages of the reaction. Could the authors give also an indication as to the expected uncertainty of the concentrations of the various species? Section 2.3 describes the absolute calibration for the species monitored but there are several steps (i.e. estimation of the collision rate via estimated dipole moments and estimated polarizabilities and modification of sensitivities due to the presence of ligands)

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each of which could introduce significant uncertainties.

We agree with the reviewer that deriving a calibration from QM is an important source of error. Nevertheless, we note that computed calibration do not differ from the nitric acid experimental calibration by more than 40%. We believe that reflects our maximum uncertainty. Furthermore experimental calibrations for glycolaldehyde and measurement of the yield of isoprene nitrates in a NO₃ + isoprene experiment (Ng et al 2008) showed a very good agreement between experimental and theoretical calibrations. A conservative estimate lies between 20 and 30 %. The uncertainty is now reported with our results.

Other comments

1)Section 3.1.1

Are there not now site-specific SARs (e.g. such a those developed by Peeters et. al.) that will help refine these estimates?

cf. reply to comment 9 in reply to Dibble's comments

2)Page 14647 The authors mentioned that the zero scans "gave insight" into the strength of the interaction of the measured compound with the equipment walls. Could the authors be a bit more clear on this. Were the corrections large in the case of some of the important compounds measured?

What was done for all signals was to use the average value of the data collected prior to the lights turning on as the combined instrument/bag background. The background scans collected after the lights were turned on were not used except for qualitative evaluation of the 'stickiness' of various compounds. Note the instrumental background signals for most all of the large MW products produced in isoprene oxidation are 0 (after the instrument has been sampling clean zero air for an extended period of time), so variation in instrumental background over the course of the experiment is not important for these signals. The smaller MW compounds (eg. formic and acetic acids) do have

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instrumental backgrounds, but the level of the instrumental background is small (more than 10x smaller) relative to the signal generated in the isoprene oxidation experiment, so ignoring instrumental background changes over the course of the experiment for these species should not introduce a large error.

3)Page 14646 change "slpm" to "slm" to be consistent with "sccm" Corrected

4)Page 14655 change "0.7 ppC/min" to "0.7 ppv(C)/min"

Corrected

5)Page 14662 Change "15 kcals/mol" to "15 kcal/mol" change "collisions-1" to "per collision"

Corrected

6)Page 14665 The authors mention that ETHL_N was monitored in a similar experiment featuring a lower HO concentration and its lifetime was slightly longer suggesting that this discrepancy originates from a faster HO sink rather than an error in the photolysis rate.

We agree with the reviewer that we should be more conservative in our statement regarding ETHL_N. At this point we will probably suggest that HO reaction with ETHL_N may be underevaluated by SAR.

7)Page 14667 the statement "the first few dozen" should be re-written.

Corrected

8)Page 14654 How critical to the mechanism is the accurate assignment of photolysis cross-sections to those compounds whose cross-sections have not be determined?

This is an excellent question as is clearly a weakness of this study. We have attempted to use the photolysis of similar compounds to tackle the photolysis of important inter-

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mediates which photolysis cross sections and quantum yields. Photolysis appears to be negligible compared to HO reactions for the compounds of interest.

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