

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

### **Anonymous Referee #2**

Received and published: 25 September 2008

These authors attempt to shed further light on the complex isoprene oxidation mechanism using time-resolved observations of gas-phase products, over a period of about 12 hours, in a 28 m<sup>3</sup> atmospheric chamber in which the isoprene mechanism was initiated in the presence of 500 ppbv NO by steady photolysis of H<sub>2</sub>O<sub>2</sub> (initially at 2.1 ppmv).

The authors arrive at the various conclusions in the paper using arguments based on both their experimental work - mainly as a guide and constraint to the construction of the isoprene mechanism - and earlier experimental and theoretical work of others.

The results are potentially important and could have a major impact. The novel de-

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tection method used certainly adds significantly to the array tools applied to crack the hard nut of the isoprene mechanism.

I believe that work presented is suitable for publication in ACP as the subject matter is of great interest to the readers of this journal and a number of important mechanistic points are thoroughly discussed. But I recommend publication only after the following points have been considered and addressed.

The manuscript as it stands is complex. In my view, the authors probably try to achieve a little too much in creating a whole mechanism. It would be rather better to break the study down and focus on the most important aspects and those that are most certain. I do not require that this be done, but the readability should certainly be improved. Perhaps this can be done by putting some of the details in supporting information. Particular attention should be drawn to quantitative uncertainties as there are very many estimates and assumptions throughout the manuscript and it is not clear to me how these estimates impact of the various conclusions made. This really begins to occur from section 4.

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 favour of one pathway or another.

The major focus of the study is the determination of the yields and production routes of organic nitrates arising from subsequent reactions of the two peroxy radical channels (each giving two rotamers) formed by initial addition of OH to carbon 1 or carbon 4 of isoprene followed by O<sub>2</sub> addition to carbon 4 or carbon 1, respectively. These are termed "resonance" channels.

The authors focus initially on the branching to these channels (Y<sub>1,4</sub> and Y<sub>4,1</sub>) and their overall organic nitrate yield. For this they use two sources of information.

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(1) the experimental MACR and MVK yields by Sprengnether et al and Karl et al (summarised in Eqn (6) and Eqn (7)), and

(2) the branching ratios for the initial addition of OH to isoprene estimated in the computational study of Lie et al. (summarised in eqns (8) to (11))

Following this, the authors solve a non-linear equation to arrive at values for the branching ratio the six possible peroxy radicals (rotamers being lumped together) and the total nitrate yield for the resonance channels (Y<sub>1,4</sub> and Y<sub>4,1</sub>) and the non-resonance channels (the other four).

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)).

(b) 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<sup>-1</sup> 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<sup>-1</sup> 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.

(c) 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) each of which could introduce significant uncertainties.

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## Other comments

Section 3.1.1 "For the addition of HO onto double bonds, in the absence of data or previous information enabling differentiation between two carbons, we assume that the reaction occurs only on the most favourable location based on steric considerations". The authors used the SAR method of Kwok and Atkinson, 1995 to estimate the unknown reaction rates.

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

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?

Page 14646 change "slpm" to "slm" to be consistent with "sccm"

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

Page 14662 Change "15 kcals/mol" to "15 kcal/mol"

change "collisions-1" to " per collision"

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.

This is rather a qualitative argument and unconvincing. The authors should give values to support it.

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

Page 14654 How critical to the mechanism is the accurate assignment of photolysis

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cross-sections to those compounds whose cross-sections have not be determined?

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14643, 2008.

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