

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

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General Comments: The use of chemical ionization mass spectrometry (CIMS) with CF₃O anion as the reagent is novel and offers interesting possibilities to constrain product yields and gain new insights into the mechanisms of isoprene chemistry. The material is certainly relevant to ACP. The present manuscript misinterprets the Lei, et al., (2001) theoretical paper, and important related theoretical work is not cited; this grossly changes branching ratios Y₁₄, Y₂₁, Y₃₄, and Y₄₁. For this reasons, this manuscript will need to be extensively reworked before being suitable for publication

Specific Comments: 1) The manuscript misunderstands the results of Lei, et al (2001).

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That paper calculated the branching ratios $Y_{1,2}/(Y_{1,2} + Y_{1,4})$, $Y_{1,4}/(Y_{1,2} + Y_{1,4})$, $Y_{4,3}/(Y_{4,3} + Y_{4,1})$, and $Y_{4,1}/(Y_{4,3} + Y_{4,1})$ as 0.60, 0.40, 0.78, and 0.22, respectively. Their previous work (Lei, et al., Chem. Phys. Lett. 326 (2000) 109-114) computed Y_1 , Y_2 , Y_3 , and Y_4 .

The Lei, et al., 2000 paper is superseded by the much more rigorous work of Greenwald, et al., (J. Phys. Chem. A 2007, 111, 5582-5592), which gives Y_1 , Y_2 , Y_3 , and Y_4 as 0.67, 0.02, 0.02, and 0.29, respectively. These numbers represent a 20% change in Y_1 and Y_4 from Lei, et al., 2000. I suggest that a similar uncertainty be assumed in the Lei et al., 2001 results, which used a very similar approach as their 2000 paper.

Greenwald, report Y_2 and Y_3 as highly uncertain. Moreover, Park et al, (PCCP 2003, 5, 3638-3642) indicate that the isoprene-OH adduct resulting from OH addition to C2 of isoprene is quantitatively converted to pent-4-en-2-one, so that $Y_{21} = 0$. The analogous adduct from OH addition to C3 only yields the corresponding peroxy radical in ca. 50% yield, the balance being 3-methyl-but-3-enal. Subsequent experimental work with 1,3-butadiene (J. Phys. Chem. A, 109, 7915-22, 2005) provides support for the theoretical work of Park, et al.

The theoretical results described above indicate a maximum molar yield of MVK of 0.24 (if no ISOPN is formed), which is slightly lower than the experimental molar MVK yield of 0.27. This is reasonable agreement considering the uncertainties in theory, alone.

2) The structure of the manuscript was difficult for me. I would suggest discussing the basic isoprene mechanism (Figure 3, etc.) before the Section 3 (Photooxidation Mechanism). It would have helped me to have known, before reading Section 3, which compounds were or were not being treated by the mechanism described there. I am still not sure if this section describes the chemistry of MVK and MACR.

There is no Results section of this manuscript, rather, results are entangled with interpretation. It might help to provide a Table that identifies all the relevant masses along with the identification of the analyte (or analytes) being detected and whether they are

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being detected as the F or CF₃O adduct. It might also help to organize Table B1 by mass, so that masses and collision rate constants can be easily compared with signals in the Figures that present the experimental and model results.

The manuscript and its appendix indicated that isoprene, CO, and CO₂ were detected, but the method is not specified.

3) Important details of the kinetic model were not provided (J values for HOOH, assumptions about heterogenous HONO formation). Without this sort of data, the model is not reproducible by the reader.

The detailed mechanism is presented via many Figures, but does not include rate constants and branching ratios which the authors must have calculated. Without this sort of data, the model is not reproducible by the reader. Supplementary information may be advisable to provide this information but avoid lengthening the paper.

Branching ratios may be important points of uncertainty. Most significantly for the present manuscript, the model of Peeters, et al, is used to get branching ratio for the formation of PROP_N from ISOPN(4,1). I do not believe the Peeters model can be used for the alkoxy radical from ISOPN(4,1), because the model does not include the effects of nitrate group (which should be significant in this case).

4) The source and extent of uncertainties in the reported branching ratios of the detailed mechanism are not provided.

The manuscript presents errors in peak concentration and peak time for several analytes, and does a good job presenting the uncertainties in the rate constants for collisions of CF₃O anion with analytes. I am concerned that uncertainties the branching ratios which are the RESULTS of this paper are not presented. Many of the sources of uncertainty may not be quantifiable, and many parameters may have to be assumed exact, but some effort should be made at addressing the magnitude and sources of uncertainties in the branching ratios.

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5) 3-methyl furan: The mechanism cited the manuscript for formation of 3-methylfuran is plausible, but not well-supported.

Note that 1,4-hydroxycarbonyls from alkanes are converted heterogeneously in the absence of reactive species to hydrofurans (Atkinson, et al, Atmos Env 42 (2008) 5859-71). I showed (Chem Phys Lett (2007) 447, 5-9) that the analogous formation of 3-methylfuran from C₅H₈O₂ compounds is more thermodynamically favorable while no less kinetically disfavored (as a homogeneous gas phase reaction). For this reason, I suggested that formation of 3-methylfuran from isoprene is, at least in part, heterogeneous. If correct, this limits one's ability to use 3-methylfuran production as a constraint on the isoprene mechanism, as on page 14662.

6) Resonance: The authors appear to misunderstand resonance. Resonance is not a process. For example, allyl radical (CH₂CHCH₂) is described simultaneously as CH₂=CH-CH₂ AND CH₂-CH=CH₂, connected by a double-headed arrow to represent resonance. Neither one of those two Lewis electron dot structures conveys the equal sharing of three electrons in two pi orbitals which is resonance.

All references to resonance as a process (e.g., "followed by resonance" or the "r" notation in many of the Figures) should be deleted. Use of the phrases "resonance channels", "resonance peroxy radicals", etc., to describe the 1,4 and 4,1 but not the 1,2 or 4,3 channels/species reflects the idea of resonance as a process, and really ought to be changed; I would suggest "delta-hydroxy channels" instead.

7) The Dibble mechanism: On page 1458, line 21, the key reaction is described as a delta(1,5) hydrogen shift, but it is actually a double hydrogen atom transfer. Dibble's prediction the chemistry of the 1,4 branch is mostly accurately reflected in the manuscript; however, the 4,1 branch was predicted to be largely different. Dibble (2004b) indicated that the alkenoxy radical produced in the 4,1 branch would mostly undergo chemically activated decomposition to CH₂OH and 3-hydroxy-but-2-enal (an isomer of OBL) radical rather than be thermalized and react with O₂.

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It is interesting to see evidence in support of this mechanism, especially since Simon North pointed out to me a good argument against it. Miyoshi et al (J. Phys. Chem. 1990, 94, 3016-3019) found that O₂ reaction with alkyl and hydroxyalkyl radicals proceeded with a rate constant that was inversely proportional to the ionization potential of the radical. One might extend this idea to determine the preferred site of O₂ reaction in the allylic radical precursor of the peroxy radical shown at the top of page 14659: this would suggest that formation of the peroxy radical shown is significantly disfavored as compared to O₂ addition to C1 (leading to formation of a C₅H₈O₂ 1,4 hydroxycarbonyl). The Lei, et al, (2001) results are consistent with the extension of the Miyoshi's work to competition between two sites in an allylic radical.

7) Page 14649, line 15. The use of an averaged calibration factor is sometimes necessary. It also means that the model affects the reported "experimental" concentrations. Some comment on the magnitude of the resulting uncertainties in concentration would be appropriate.

Uncertainties in concentrations do not seem to be addressed, in general!

8) Page 14650, line 9. It states that in the absence of data or SAR, OH is assumed to add to alkenes only at the most favored site. There is an SAR due to Vereecken (J. Phys. Chem. A, 111, 1618-31, 2007) that may provide guidance here. In addition, the affect of the assumption on the model results should be discussed.

9) Alkyl nitrate yields (Page 14651). Carter's parameterization is used. The experimental results of Espada and Shepson (2005) and Cassanelli et al. (PCCP 2007, 9, 4332-37) differ from Carter's parameterization, particularly in the effect of primary vs. secondary vs. tertiary peroxy radicals. Comments?

Espada and Shepson (2005) is cited in the manuscript in relationship to isoprene nitrates, but does not mention isoprene.

10) Page 14662, lines 2 ff. The results favor the Z over the E pathways in the 1,4 chan-

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nel, which, the authors note, disagrees with theoretical results of Dibble (2002). The authors point out that O₂ reaction with activated radicals is likely. They suggest that the distribution of E and Z isomers of the chemically activated alkyl radicals (isoprene-OH adducts) might favor the Z isomers at high energy. If true, O₂ reaction with activated alkyl radicals would produce more Z isomer of the peroxy radicals than E isomer, resolving the discrepancy. The issue of reactions of O₂ with chemically activated radicals is important and of general interest, but has been mostly neglected in studies to date.

Some data in Dibble (2002) contradicts the authors' suggestion. For this adduct, the initially formed E configuration is extensively converted to Z in < 0.1 ns, far faster than the time scale for collision with O₂ in experiment. The ratio of the density of states of the E and Z isomers changes little with energy, so the predicted distribution of E and Z isomers does not change during the process of thermalization. So the theoretical results do not support the explanation offered in the manuscript. The most obvious deficiency of the theory is the failure to treat low frequency modes as hindered torsions, which might significantly affect the results.

Technical Points 1) Page 14649, lines 4 and 20. Are these points due to Crouse, et al.?

2) Page 14650, line 8 (and many other places). "hydrogen in alpha to" more usually is presented as "hydrogen in the alpha position" or "hydrogen alpha to"

3) Page 14650, line 8. In line 2 the criterion of a factor of 10 was used to justify neglect of ozonolysis reactions. Does a factor of 10 also apply to the neglect of NO₃ reactions with alkenes?

4) Page 14655, line 18. "PAN" should be "PNA"

5) Page 14655, line 22. Should "methylperoxide" be "methylhydroperoxide"?

6) Page 14656, line 19. What are the experimental uncertainties in the MVK and MACR yields? As these are important mechanistic constraints, they should be stated.

7) Page 14657, line 8: PROP_N and DHB are produced competitively, this should be made clear, along with the branching ratio indicated by Peeter's SAR.

8) Page 14657, line 23: The higher nitrate yields for the delta-hydroxy versus the beta-hydroxy channels is also consistent with the suggestion (J. Phys. Chem. A (1998) 102, 8903-8908) that hydrogen bonding in beta-hydroxy substituted ROONO intermediate weakens the RO-ONO bond, enhancing RO + NO₂ production.

9) Page 14658, line 15: clarification is needed as it is not true that "the peroxy radical undergoes a delta(1,5) isomerization"

10) Page 14660, line 25: While the configuration of the radical (E rather than Z) prevents the isomerization, its structure prevents decomposition (which would produce a vinyl type radical with a large endothermicity: Dibble, J. Phys. Chem. A 1999, 103, 8559-8565).

11) Page 14661, line 6: Since HOPL concentrations in Figure 9 are model results, it might be better to point the reader to Figure 4, which shows that HOPL production requires OH reaction with a stable product of the chemistry along the E1,4 channel.

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

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