

***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 detailed review.

**Specific points**

1)The manuscript misunderstands the results of Lei, et al (2001). 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 The Lei, et al., 2000 paper is superseded by the much more rigorous work of Greenwald, et al., (J. Phys.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

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numbers represent a 20% change in Y1 and Y4 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.

After personal communication with the referee, we have confirmed that no error was made in the use of the Lei et al. results. Rather, an error in the citation led to a misunderstanding of our approach. Even though the data we used were reported in their 2001 work (Fig 1), as the referee mentioned, the constraints were originally derived in their 2000 work, which is now properly cited.

Nevertheless, we were not aware of the new theoretical determination of the isoprene peroxy radical branching ratios by Greenwald et al. (2007). This study does raise concern regarding the uncertainty of the initialization of our mechanism and has lead us to reevaluate how sensitive we are to the initialization of the branching ratios. In particular, we cannot find a solution that is consistent with both the most recent experimental determinations of MVK/MACR yield from isoprene (Sprengnether 2001; Karl 2006) and the Greenwald et al. (2007) theoretical yields. Sprengnether et al. reports a MACR yield of 28% while Greenwald et al. calculate a branching ratio  $Y_4 = Y_{4,3} + Y_{4,1}$  of 29%. Assuming channel 3,4 entirely yields MACR with a nitrate yield of 5%. We are left with 1.5% of the carbon following channel 4,1, which is in disagreement with the early formation of HACET and the detection of PROPNN (yield of 1%) observed in our study.

We have added a more detailed discussion of the branching ratio issue in the revised version of the manuscript emphasizing the difficulty in accommodating, in a consistent way, the theoretical and experimental results. We chose to weigh the experimental results more heavily, and thus chose the Lei et al. (2000) branching ratios as additional constraints as they are consistent with Sprengnether's study. We discuss the implications of this choice explicitly in the appendix.

**Greenwald, report Y2 and Y3 as highly uncertain. Moreover, Park et al, (PCCP**

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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.

Despite their theoretical interest, the admittedly uncertain fate of the channel 3,4 and 2,1 represent a relatively small uncertainty in our mechanism compared to the uncertainty on the major branching ratio  $Y_1$  and  $Y_4$  and the yields of MVK and MACR. Unfortunately, the yield of the nitrate which would originate from the compound proposed by Park et al. is too small to provide conclusive evidence in favor or against its formation. Since our data do not enable to constrain this branch, the added complexity of adding these channels to the mechanism is not warranted at this time. Nevertheless, we now point out this issue explicitly and hope for further experiments to resolve the yield of these channels.

**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).**

We have modified the structure of the manuscript to include a result section, which briefly describes the different compounds measured by CIMS. The details of the mechanism are now in the Appendix.

**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.**

Since the model attempts to be nearly explicit, MVK and MACR are being treated in the mechanism. This treatment is not emphasized in the manuscript, however, since no direct data enables to constrain their fate (with the exception of the organic nitrate

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yield).

**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 being detected as the F or CF<sub>3</sub>O 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 .**

As mentioned previously, we have added a short result section which introduces the more detailed discussion on the derivation of the different branching ratios and rate coefficients. As suggested by the reviewer, we have added a table which includes the different ions monitored, their nature (cluster/transfer) as well as their likely attribution.

**The manuscript and its appendix indicated that isoprene, CO, and CO<sub>2</sub> were detected, but the method is not specified.**

Isoprene was monitored by GC. More details will be given in the section 2.1. CO and CO<sub>2</sub> were not monitored in this experiment.

**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.**

J(HOOH) was calculated following the approach presented in section 3.2.5. No heterogeneous chemistry of HONO is assumed, since HONO profile can be correctly captured using only homogeneous processes. This reaction is unlikely to be very important in the first hours of the experiment where NO<sub>x</sub> levels are very elevated. We have added the value of J(HOOH) in the photolysis Section.

**The detailed mechanism is presented via many Figures, but does not include rate constants and branching ratios which the authors must have calculated. Without**

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**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.**

Rate constants and branching ratio which do not obey the schemes presented in the model description section are given explicitly throughout the manuscript. To facilitate the reading, we have added to the mechanism figures the different branching ratios used. The full mechanism will also be available upon request.

**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).**

As stated by the reviewer, Peeter's SAR cannot be used in the absence of parameterization of the ONO2 group. This applies not only to ISOPN (4,1) but to all nitrates in general. Therefore we did not use Peeter's SAR to tackle nitrates fate but rather the experimental data. This point is emphasized in the revised version of the manuscript.

**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.**

As pointed out by the referee, there are important uncertainties in our approach. Uncertainties in the calibration of course but also in the development of the mechanism,

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which has to heavily rely on various SAR in the absence of experimental data for numerous intermediates. Nevertheless, the CIMS data provide measurements of a large variety of compounds, thus providing constraints for the mechanism. As a result, we believe most of the uncertainty affecting our estimates resides in the initial computation of Y<sub>1,2</sub>; Y<sub>1,4</sub>, Y<sub>4,3</sub>, Y<sub>4,1</sub>. In the revised manuscript, we address directly the different uncertainties affecting our estimates in a dedicated Section.

**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 C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> 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.**

This is an important point. We did not take into account the potential heterogeneous processes leading to 3-MF from HC<sub>5</sub> because of the lack of firm experimental data on this topic.

Using the measured surface area, we derive a collision rate of HC<sub>5</sub> with the aerosol of about 0.06 s<sup>-1</sup>, about two orders of magnitude faster than the reaction with HO. If no 3-MF originates from the alkoxy radical Z<sub>1,4</sub> and Z<sub>4,1</sub>, then the yield of HC<sub>5</sub> would increase by about 50%. In order to match the measured temporal profile, the rate of the heterogeneous processes would have to equal about half of the reaction rate due to HO. This would correspond to an accommodation coefficient of 0.005. Even though this accommodation coefficient is very large considering the dry conditions under which the chamber was operated, we cannot rule out this hypothesis. With the heterogeneous process included, the HC<sub>5</sub> yield would be closer to the one recently reported by Baker

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et al 2005 (15%). . We explicitly address this issue in the corrected manuscript.

**6)Resonance:** The authors appear to misunderstand resonance. Resonance is not a process. For example, allyl radical ( $\text{CH}_2\text{CHCH}_2$ ) is described simultaneously as  $\text{CH}_2=\text{CH}-\text{CH}_2$  AND  $\text{CH}_2-\text{CH}=\text{CH}_2$ , 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 .

We agree with the reviewer that we used resonance imprecisely and have altered the text as suggested.

**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  $\text{CH}_2\text{OH}$  and 3-hydroxy-but-2-enal (an isomer of OBL) radical rather than be thermalized and react with  $\text{O}_2$ . 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  $\text{O}_2$  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  $\text{O}_2$  reaction in the allylic radical precursor of the peroxy radical shown at the top of page 14659: this would suggest that for-

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mation of the peroxy radical shown is significantly disfavored as compared to O<sub>2</sub> addition to C1 (leading to formation of a C<sub>5</sub>H<sub>8</sub>O<sub>2</sub> 1,4 hydroxycarbonyl). The Lei, et al, (2001) results are consistent with the extension of the Miyoshi8217;s work to competition between two sites in an allylic radical.

The experimental data exhibits a clear early source of HACET. The mechanism proposed by the reviewer is, to our knowledge, the only mechanism prompt enough to capture such a phenomenon. In the revised manuscript, we discuss the difference between the theoretical measurements and the data on this specific point.

Furthermore, we point out that if our hypothesis is correct, the Dibble mechanism provides additional evidence for a relatively large amount of carbon going through Y<sub>4,1</sub> consistent with our observation of large amounts of PROP<sub>N,N</sub> and DHBN, both produced in the photooxidation of ISOPN(4,1).

The ratio of Dibble mechanism to HC<sub>5</sub> is set to the ratio of Y<sub>4,1</sub> to Y<sub>4,3</sub> so that HC<sub>5</sub> is favored over the Dibble's mechanism in agreement to the referee comments. If heterogeneous processes are indeed relevant for the formation of 3-MF, the branching ratio would be even more biased toward HC<sub>5</sub>.

**8)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!**

We believe that the use of an 8220;average calibration8221; has been misunderstood. We make use of an average calibration in order to be able to compare a signal encompassing several compounds with model results. The model is multiplied by the ratio of this average calibration to the calibration computed using QM, allowing for a rigorous comparison between the mechanism and the data. We used an 8220;average8221; calibration on the different figures to conserve the proper order of magnitude. We have

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added some text to the revised manuscript to provide better guidance to the readers. As mentioned earlier, uncertainties are now addressed in a dedicated section.

**9) 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.**

Vereecken's most recent alkene SAR tackles the addition of HO on alkenes without functional groups. We do not think the highly substituted alkenes which are formed in the photooxidation of isoprene can be treated using this approach. Furthermore, the minor channel product frequently overlaps with the major channel so that the effect in the model should be minor.

**10) Alkyl nitrate yields (Page 14651). Carter<sup>2017</sup>'s parameterization is used. The experimental results of Espada and Shepson (2005) and Cassanelli et al. (PCCP 2007, 9, 4332-37) differ from Carter<sup>2017</sup>'s parameterization, particularly in the effect of primary vs. secondary vs. tertiary peroxy radicals. Comments?**

Carter's parameterization is only used to constrain the fate of minor nitrates. Conversely experimental constraints are used to derive the fate of the most abundant organic nitrates (isoprene nitrates, mvk/macr nitrates, propanone and ethanal nitrate) . The parameterization would indeed fail to capture their profile correctly. Since only minor nitrates will be affected by a change of parameterization, we believe the differences between the more recent nitrate schemes and the scheme used in the paper will cause minor changes in the conclusions derived from the mechanism.

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

Espada and Shepson (2005) is used by Giacobelli et al. to emphasize that peroxy radical featuring an alcohol located more than one carbon away from the peroxy group

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may increase the nitrate yield. We referred to this paper to highlight that our estimate for the yield of nitrates originating from the channels (1,4) and (4,1) are consistent with Giacomelli's conclusion. In the revised version of the manuscript, we only refer to Giacomelli et al. to avoid confusion.

**11)Page 14662, lines 2 ff. The results favor the Z over the E pathways in the 1,4 channel, which, the authors note, disagrees with theoretical results of Dibble (2002). The authors point out that O<sub>2</sub> reaction with activated radicals is likely. They suggest that the distribution of E and Z isomers of the chemically activated alkyl radicals (isoprene-OH 8, S58918211;S5897, 2008 adducts) might favor the Z isomers at high energy. If true, O<sub>2</sub> 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 O<sub>2</sub> 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 authors8217; 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 O<sub>2</sub> 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.**

Experimental data (MOBA, DHMOB, early formation of glycolaldehyde) suggest that a substantial fraction of isoprene photooxidation proceeds through the Z channel. It is also consistent with the reported formation of 3-methylfuran which requires the Z conformer. Conversely, the very small yield observed for DHPN suggests a small branching ratio toward the E channel.

As pointed out in the manuscript, this conclusion disagrees with theoretical computa-

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tions made by the referee. We provide one hypothesis for this disagreement, namely that the reaction of the Z enantiomer with O<sub>2</sub> is significantly faster than the equivalent reaction of the E enantiomer.

In the revised manuscript, we also propose that the observed large discrepancy between cis and trans channels is related to the formation of the beta allyl peroxy radical.

### Technical points

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

Experiments conducted in our lab show that the clusters formed between CF<sub>3</sub>O<sup>-</sup> and large molecules present a relatively low sensitivity to the water content. We will emphasize that the lack of standards for most of the molecules identified in the present study preclude any direct calibration..

#### 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"

corrected

#### 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 NO<sub>3</sub> reactions with alkenes?

Due to the presence of high concentration of NO at the beginning of the experiment, NO<sub>3</sub> is efficiently scavenged so that its reaction with alkenes is neglected.

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

It's actually PAN which formation is favored in the second regime

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

corrected

#### 6)Page 14656, line 19. What are the experimental uncertainties in the MVK and

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**MACR yields? As these are important mechanistic constraints, they should be stated.**

This point is addressed in the uncertainty section (cf. reply to comment 1)

**7)Page 14657, line 8: PROP\_N and DHB are produced competitively, this should be made clear, along with the branching ratio indicated by Peeter8217;s SAR.**

cf. Comment 3

**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 + NO<sub>2</sub> production.**

we have rephrased this point following the reviewer8217;s suggestion

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

we have rephrased the sentence to make clear that it is the alkoxy radical which undergoes the delta 1-5.

**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.**

Corrected

**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.**

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Figure 9 has been removed due to the large uncertainty on pyruvic acid.

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

**ACPD**

8, S9838–S9850, 2008

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