

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.

T. Stavrakou et al.

jenny@oma.be

Received and published: 28 September 2010

We thank the reviewer for his/her comments to our manuscript. In the following, we address the concerns raised. Reviewer's comments are *italicized*.

The introduction makes it very clear which mechanism the authors favor (the formation of HPALDs). I strongly recommend the whole section be rewritten using much more neutral language. For example, it is stated that this mechanism is "An even more promising explanation for the gap between modeled and measured HO_x abundances",

C8081

though (prior to this work) it is completely unclear why one might be more promising than the other. Secondly, the regeneration of OH by RO₂+HO₂ reactions, suggested by Lelieveld and others, is repeatedly referred to as "artificial". This rather pejorative term probably should be avoided, unless the authors want to explicitly define what they mean by "artificial", and explain why the other mechanisms are "real". Finally, a lack of experimental evidence is cited as a problem in the Lelieveld scheme; however, the HPALD-formation channel is purely theoretical at present, with even less laboratory evidence to support it. This needs to be explicitly mentioned as a potential weakness in the mechanism.

We cannot agree with the reviewer, since the production of several OH radicals in the reaction of first-generation isoprene peroxy radicals with HO₂ was clearly conceived and termed as artificial by Lelieveld et al. (2008) and Butler et al. (2008). As noted by Lelieveld et al. (2008), "HO₂ + RO₂ reactions are unlikely to recycle more OH than 60% directly, and some of the artificial OH production assumed here may actually be due to other sources." Note that the reaction ISOPO₂ + HO₂ → ISOPOOH + *n* OH is not stoichiometrically balanced, and that the natural co-product of OH should be the oxy radical RO, as in the OH-forming channel of other RO₂ + HO₂ reactions (e.g. Dillon and Crowley, 2008). In contrast, the reactions proposed by Peeters et al. (2009) are confirmed and quantified by high-level theoretical calculations. Furthermore, a consistent body of experimental evidence has been presented by Peeters and Müller (2010) in support of all new pathways in the proposed mechanism, although we agree (and insist on the fact) that further laboratory evidence is needed to confirm and refine the theoretical predictions. Nevertheless, in accordance with the reviewer's comment, we modify the introduction by using more neutral language, e.g. "An even more promising explanation" is replaced by "A promising explanation".

p. 16559: it is argued that the HPALD species photolyze extremely rapidly, generating a lot of additional HO_x radicals beyond those that are initially formed. This is a reasonable argument given the structure of the molecule. However, very little is known about

C8082

the photolysis rates of any organic hydroperoxides (with more than 2 carbon atoms); these - even without the conjugation found in the HPALDs - might be extremely facile as well, as first pointed out by Thornton et al. 2002 [JGR-Atmospheres 107:4146]. Such photolysis processes might even happen in the near-IR, as has been observed for molecules such as HOONO₂. Allowing only one mechanism (LIM0) to form HOx via rapid hydroperoxide photolysis might bias the results somewhat. Thus an additional sensitivity study is necessary, in which the rapid photolysis of ALL hydroperoxide species from the different mechanisms can occur; this would provide an important point of comparison to HPALD photolysis. This upper limit to HOx formation by the other mechanisms will allow for a strong test of the relative importance of the LIM0 mechanism as an additional source of HOx.

The hypothesis that enhanced ROOH (and RO₂) photolysis can account for the missing OH source determined from the GABRIEL campaign measurements has been ruled out by Kubistin et al. (2008) in a box model study. Fast ROOH photolysis was indeed proposed by Thornton et al. (2002) as one among several possible explanations for their overestimated modelled HOx sink through ROOH formation, but a large part of the discrepancy might be due to the unimolecular reactions of the isoprene hydroxyperoxy radicals, generating (instead of consuming) HOx radicals, and of course not considered in their study. There is no physico-chemical reason why organic hydroperoxides with more than 2 C's would photolyse two orders of magnitude faster than CH₃OOH does. The few available data for C₂ hydroperoxides (ethylhydroperoxide and peroxyacetic acid) actually suggest lower absorption cross sections compared to CH₃OOH (Monod et al., 2007; Keller et al., 2008). Hydroxy substitution (as frequently found in hydroperoxides from isoprene oxidation) has very little effect on the cross sections, as shown by the case of hydroxymethyl hydroperoxide HOCH₂OOH (Bauerle and Moortgat, 1999).

Fast photolysis of specifically the first-generation hydroxy hydroperoxides from isoprene oxidation is contradicted by the observation by Paulot et al. (2009) that almost

C8083

all ISOPOOH form epoxides (see their Fig. 1), which can be explained only by reaction with OH. Moreover, based on the observed temporal evolution of ISOPOOH and epoxide concentrations, Paulot et al. (2008) derived a total rate constant of $7.9 \cdot 10^{-11}$ molec.⁻¹ cm³ s⁻¹ for the reaction ISOPOOH+OH, assuming it to be the only sink for ISOPOOH; this value corresponds very well to the SAR-based value $(8.5 \pm 1.5) \cdot 10^{-11}$ molec.⁻¹ cm³ s⁻¹, providing further evidence that photolysis of ISOPOOH is minor at best. Fast photolysis would have also resulted in a much higher yield of MVK+MACR than the 12% value measured by Paulot et al. (2009).

The effect of weak absorption features in the range 365-640 nm (including the vibrational overtone-induced dissociation which was found to be significant for HOONO₂) on the photolysis of CH₃OOH has been determined by Matthews et al. (2010). The enhancement of the photolysis rate due to these features is found to be only about 10%, in sharp contrast with the case of HOONO₂, for which near-IR dissociation has been found to be a dominant sink (Roehl et al., 2002).

The array of structure-related acronyms used (LISOPACOOH, ISOPBO₂, ISOPDO₂, etc.) makes the mechanisms extremely hard to follow for those not intimately familiar with the Mainz Isoprene Mechanism. A figure or legend that shows the (general) structure of each acronym would be very helpful.

We follow this helpful suggestion, and include a table providing the chemical formulae (Lewis structures) of the compounds discussed in the manuscript.

p. 16566: it should be mentioned that the substantial decrease in epoxide formation will have large consequences for modeled secondary organic aerosol from isoprene. SOA modeling is obviously beyond the scope of this work, but this is an important potential consequence of the LIM0 mechanism.

Agreed. A sentence has been added in this section: "The decreased epoxide formation might have a large consequence on the modelled secondary organic aerosol (SOA)

C8084

formation through this pathway (Paulot et al., 2009)"

References:

Bauerle, S., and G. K. Moortgat: Absorption cross-sections of HOCH₂OOH vapor between 205 and 360 nm at 298 K, *Chem. Phys. Lett.*, 309, 43-48, 1999.

Butler, T. M., D. Taraborrelli, C. Brühl, H. Fischer, H. Harder, M. Martinez, J. Williams, M. G. Lawrence, and J. Lelieveld : Improved simulation of isoprene oxidation chemistry with the ECHAM5/MESy chemistry-climate model: lessons from the GABRIEL airborne field campaign, *Atmos. Chem. Phys.*, 8, 4529-4546, 2008.

Dillon, T. J. and J. N. Crowley: Direct detection of OH formation in the reactions of HO₂ with CH₃C(O)O₂ and other substituted peroxy radicals, *Atmos. Chem. Phys.*, 8, 4877-4889, 2008, <http://www.atmos-chem-phys.net/8/4877/2008/>.

Keller, B. K., M. D. Wojcik, T. R. Fletcher: A directly-dissociative stepwise reaction mechanism for gas phase peroxyacetic acid, *J. Photochem. Photobiol. A*, 195, 10-22, 2008.

Kubistin, D., H. Harder, M. Martinez, M. Rudolf, R. Sander, H. Bozem, G. Eerdeken, H. Fischer, C. Gurk, T. Klüpfel, R. Königstedt, U. Parchatka, C. L. Schiller, A. Stickler, D. Taraborrelli, J. Williams, and J. Lelieveld : Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, *Atmos. Chem. Phys. Discuss.*, 8, 15239-15289, doi:10.5194/acpd-8-15239-2008, 2008.

Lelieveld, J., T. M. Butler, J. N. Crowley, T. J. Dillon, H. Fischer, L. Ganzeveld, H. Harder, M. G. Lawrence, M. Martinez, D. Taraborrelli, and J. Williams: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737-740, 2008.

Matthews, J., A. Sinha, and J. S. Francisco: The importance of weak absorption fea-

C8085

tures in promoting tropospheric radical production, *Proc. Nat. Acad. Sci.*, 102, 7449-7452, 2005.

Monod, A., E. Chevallier, R. Durand Jolibois, J. F. Doussin, B. Picquet-Varrault, and P. Carlier: Photooxidation of methylhydroperoxide and ethylhydroperoxide in the aqueous phase under simulated cloud droplet conditions, *Atmos. Environ.*, 41, 2412-2426, 2007.

Paulot, F., J. D. Crouse, H. G. Kjaergaard, J. H. Kroll, J. H. Seinfeld, and P. O. Wennberg: Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, 9, 1479-1501, 2009a, www.atmos-chem-phys.net/9/1479/2009/.

Peeters, J., T. L. Nguyen and L. Vereecken: HO_x radical regeneration in the oxidation of isoprene, *Phys. Chem. Chem. Phys.*, 11, 5935-5939, doi: 10.1039/b908511d, 2009.

Peeters, J., and J.-F. Müller: HO_x radical regeneration in isoprene oxidation via peroxy radical isomerisations, II: Experimental evidence and global impact, *Phys. Chem. Chem. Phys.*, accepted, doi:10.1039/C0CP00811G, 2010.

Roehl, C. M., S. A. Nizkorodov, H. Zhang, G. A. Blake, and P. O. Wennberg: Photodissociation of peroxyxynitric acid in the near-IR, *J. Phys. Chem. A*, 106, 3766-3772.

Thornton, J. A., P. J. Woolridge, R. C. Cohen, et al.: Ozone production rates as a function of NO_x abundances and HO_x production rates in the Nashville urban plume, *J. Geophys. Res.*, 107, 4146, doi:10.1029/2001JD000932, 2002.

C8086