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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.

Anonymous Referee #2

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The work described in this manuscript involves the model implementation of various recently-proposed schemes for the regeneration of HO_x radicals in isoprene oxidation. Results indicate that one scheme in general - the formation and photolysis of hydroperoxy-aldehydes (HPALDs), advanced previously by two of the authors - leads to a large increase in calculated HO_x abundances, and vastly improved model-measurement agreement. Given the importance and timeliness of the topic, this is a useful study, and certainly warrants publication in ACP. However, I have a few major concerns that need to be addressed prior to publication.

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- 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 HOx abundances”, 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.

- p. 16559: it is argued that the HPALD species photolyze extremely rapidly, generating a lot of additional HOx radicals beyond those that are initially formed. This is a reasonable argument given the structure of the molecule. However, very little is known about 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 array of structure-related acronyms used (LISOPACOOH, ISOPBO₂, ISOPDO₂,

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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.

- 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.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 16551, 2010.

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