

Interactive
Comment

Interactive comment on “HO_x observations over West Africa during AMMA: impact of isoprene and NO_x” by D. Stone et al.

Anonymous Referee #2

Received and published: 1 September 2010

General comment

The manuscript shows an attempt to assess the impact of isoprene oxidation and NO_x on HO_x concentrations during the field campaign AMMA. The topic is within the scope of ACP. The methods and tools in the analysis are clearly described and appropriate. The manuscript is a good contribution to the ongoing discussions on how terpene oxidation control HO_x concentrations in the troposphere. However, I would like the authors to clarify and improve one aspect of the discussion. Once this issue is clarified, I recommend the publication of the manuscript.

Major comment

Despite the recent advancements in isoprene oxidation mechanisms and problems in

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reproducing many HO_x measurements, it seems that a fortunate combination of conditions make possible that the isoprene mechanism in MCM, nearly unchanged for 12 years (Jenkin et al., J. Atmos. Chem. 1998), could reproduce HO₂. The new mechanism proposed by Peeters et al., PCCP (2009) still awaits experimental confirmations. In the meanwhile, what is shown in Fig. 8, the reaction ISOPOOH + OH → ISOPO, does not correspond to neither what standard VOC oxidation knowledge would suggest nor to what is in the MCM. In the latter the isomer ISOPBOOH reacts with OH giving solely ISOPBO₂ at a rate that is about 10 times higher than the actual H-abstraction from the -OOH group. ISOPBO₂ is the major RO₂ isomer from isoprene. The other three ROOH isomers recycle OH entirely upon reaction with OH and produce long-lived carbonyl species and not alkoxy radicals. None of the ISOPOOH isomers produce HO₂ upon reaction with OH. Overall, this may lead to misunderstandings and confusion for the reader that is not familiar with MCM. In Fig. 7b the third and the fourth most important loss for HO_x are the ISOPO₂ + HO₂ and ISOPBOOH + OH reactions. However, the latter reaction produces additional ISOPBO₂ radicals that will artificially enhance the loss of HO₂ due to ISOPO₂ radicals. This aspect of the model should be mentioned as it may have an effect opposite to the calibration issues for $J(O^1D)$. For further clarification Fig. 8 could be changed but I don't know how this could be possible for such a simplified diagram. Probably, either in the captions or in the text it could be specified that the MCM chemistry of the hydroperoxides from isoprene does not consider OH-addition to the double bonds and this is a source of uncertainty for the present assessment.

Minor comments

p 17041 | 2: 24 -> 24h

Caption Fig. 10: instead of "forest" it should be "Sahel"

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17029, 2010.

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