

Interactive comment on “Isoprene oxidation mechanisms: measurements and modelling of OH and HO₂ over a South-East Asian tropical rainforest during the OP3 field campaign” by D. Stone et al.

Anonymous Referee #2

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This paper presents an analysis of several recently proposed mechanisms for HOx radical recycling in the oxidation of isoprene through a comparison of the model predictions with OH and HO₂ concentrations measured during the OP3 campaign in Borneo. The authors perform several statistical analyses of the results in order to determine the ability of these mechanisms to reproduce the observed concentrations. The main conclusion of the paper is that while many of these proposed radical recycling reactions improve the agreement between measurements and models for the OH radical, they tend to worsen the agreement between measured and modeled HO₂. The paper

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is well written and appropriate for publication in ACP. I have a few comments that the authors should consider in their revision of the manuscript.

1) As discussed by the authors, Fuchs et al. (2011) have reported a potential interference in FAGE HO₂ measurements from alkene-based peroxy radicals, including isoprene-based peroxy radicals. As pointed out in the paper, this interference will depend on the instrument configuration, including the concentration of added NO and the reaction time before OH detection. The authors claim that because the observed to modeled ratio for HO₂ is independent of the concentration of isoprene (as shown in Figure 6b) it is possible that their instrument is insensitive to isoprene peroxy radicals. However, if the measured HO₂ does include an interference from peroxy radicals, then this could have a more significant impact on the model/measurement agreement for HO₂ and the ability of the proposed recycling mechanisms to reproduce both OH and HO₂. Although this may not change the overall conclusions of the paper, the authors should include a brief discussion of the potential impact of an interference on their conclusions.

2) I am confused with the author's treatment of the photolysis of the PACALDs produced from HPALD photolysis in Table 7, which has been updated in Peeters and Müller, 2010 (not Müller and Peeters as indicated in the Table). The updated reaction PACALD photolysis mechanism in Peeters and Müller leads to the formation of 2 OH radicals rather than 1 OH and 1 HO₂ radical as listed in Table 7. It is not clear how this change would affect their model results, but it could bring the modeled HO₂ into better agreement with the observations. It appears that the sensitivity study described in Table 8 removed HO₂ as a product of PACALD2 photolysis (indicated by the “i.e. no HO₂” statement), however this is not clear as the reaction shown in Column 1 for PACALD2 photolysis is the same as the base mechanism in Table 7.

3) The radical budget in Figure 7 suggests that NO is a major propagator of HOx radicals, although it is not clear what NO mixing ratio was used for this particular calculation. It is also unclear why the radical budget is not balanced (the production of

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OH from the HO₂ + NO reaction in Figure 7a is much less than the loss of HO₂ due to HO₂ + NO in Fig. 7b). Unfortunately the model/measurement comparisons are not binned according to different NO concentrations as they are for isoprene, as it appears that there was some variability in NO concentrations during the campaign (52.6 ± 109.0 ppt, range of 0.02 to 1240 pptv from Table 2). Was the model/measurement agreement better at higher NO concentrations than lower NO concentrations?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 10343, 2011.