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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding the impact of recent advances in isoprene photooxidation on simulations of regional air quality" *by* Y. Xie et al.

Anonymous Referee #2

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General Comment

The present manuscript describes the update of isoprene oxidation in the SAPRC-07 mechanism whithin the CMAQ model. The performance of the model relative to 3 field campaingns over the US is shown to lead to significant improvements. The results are thorougly analized. Finally, a series of sensitivity simulations aimed at evaluating the uncertainty expecially with respect to alky nitrates chemistry are shown. The manuscript is of great interest and falls well within the scope of ACP. It is clear and well structured. I recommend publication after the major comments below are taken into

consideration.

Major Comments

1) In the IS mechanism the reactions of OH with glycoladehyde and hydroxyacetone are updates according to the studies of Butkovskaya et al. These study reported significant yields of organic acids and OH reformation. However, the oxidation mechanism proposed looks unlikely and contrast with other studies finding little or no formic acid (Magneron et al. (2005), Orlando et al. (2012)). Moreover, the proposed Butkovskaya's mechanism is responsible for the overestimation of HCOOH in the UT/LS, where only production from HCHO + HO_2 chemistry can easily explain the measurements. The Butkovskaya's mechanism is also implicitly considered in the oxidation of IEPOXOO. Therefore, I would like to see the results of a sensitivity simulation in which the OH-reformation and acid production related to glycolaldehyde and hydroxyacetone chemistry are shut down. I expect significant differences.

2) Instead of evaluating the impact of new rate constants for the $RO_2 + HO_2$ reactions, which are updated anyway, I find more useful to test the impact of the radical-propagating channel of the $RO_2 + HO_2$ reactions. Curiously, the authors introduced a 12% OH-yield for the $ISOPO_2 + HO_2$ reaction, which was only attributed by Paulot et al.(2009). However, starting from 2004 direct and indirect measurements have been showing a 44-75% yield for the specific $CH_3CO_3 + HO_2$ reaction (Hasson et al.(2004), Jenkin et al.(2007), Dillon and Crowley (2008), Taraborrelli et al.(2012)). β-keto-RO_2 show a much lower yield (10-15%). These robust experimental results are not implemented in the IS mechanism. Since this OH-channel has a significant effect on HO_x and likely indirectly on PNs, the need for at least a sensitivity simulation is compelling. The OH-channel for the reaction of HO_2 with CH_3CO_3, MACO3, MACROO, MVKOO, HC5OO, $HOCH_2CO_3$ could be implemented and

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tested.

3) In my opinion 1) and 2) should be part of the IS mechanism. However, this would imply a major revision of the manuscript. Nonetheless, points 1) and 2) should be considered for the next update of the SAPRC-07 mechanism.

Addtional References

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