

We thank the reviewer for the detailed and helpful comments. We have provided our response below, together with specific comments of the reviewers in italics.

*1) In the IS mechanism the reactions of OH with glycolaldehyde and hydroxyacetone are updated 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<sub>2</sub> 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.*

As the reviewer pointed out, the reactions of OH with glycolaldehyde and hydroxyacetone in the IS scheme lead to formation of formic acid, acetic acid, and OH reformation (Butkovskaya et al., 2006a, b). Currently, global models generally underpredict these organic acids (Paulot et al., 2011; Stavrou et al., 2012). Recent work by Orlando et al. (2012) suggests limited acid formation from glycolaldehyde and hydroxyacetone oxidation under atmospheric conditions. Therefore, our study likely represents an upper limit for the amount of organic acids originated from isoprene oxidation. This, however, should have only a minor impact on the focus of our study (i.e. uncertainties in isoprene nitrate chemistry). We have analyzed our results and find that the reactions glycolaldehyde + OH and hydroxyacetone + OH account for only 3% of all OH reactions. Therefore, OH reformation from these reactions has a small impact on the OH budget.

To ensure that other readers are aware of this issue, we augmented the Supplementary Information and (i) have included a footnote on the relevant reactions and (ii) have included a note on Page 7, Line 7: “[20]: Butkovskaya et al. (2006a, b) (Recent work by Orlando et al. (2012) suggests limited acid formation from glycolaldehyde and hydroxyacetone oxidation under atmospheric conditions. Therefore, our study likely represents an upper limit for the amount of formic and acetic acid originated from isoprene oxidation.)”

In future versions of SAPRC in CMAQ we will investigate these updates as suggested by the reviewer.

*2) Instead of evaluating the impact of new rate constants for the RO<sub>2</sub> + HO<sub>2</sub> reactions, which are updated anyway, I find more useful to test the impact of the radical-propagating channel of the RO<sub>2</sub> + HO<sub>2</sub> reactions. Curiously, the authors introduced a 12% OH-yield for the ISOP<sub>2</sub>+HO<sub>2</sub> 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<sub>3</sub>CO<sub>3</sub> + HO<sub>2</sub> reaction (Hasson et al.(2004), Jenkin et al.(2007), Dillon and Crowley (2008), Taraborrelli et al.(2012)). β-keto-RO<sub>2</sub> 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<sub>x</sub> and likely indirectly on PNs, the need for at least a sensitivity simulation is compelling. The OH-channel for the reaction of HO<sub>2</sub> with CH<sub>3</sub>CO<sub>3</sub>,MACO<sub>3</sub>,MACROO,MVKOO,HC5OO,HOCH<sub>2</sub>CO<sub>3</sub> could be implemented and tested.*

Laboratory studies have observed OH reformation from RO<sub>2</sub>+HO<sub>2</sub> reactions, with differing yields depending on the source of peroxy radicals (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008; Taraborrelli et al., 2012). In this work we have considered OH reformation from isoprene peroxy radicals (Paulot et al., 2009b, Taraborrelli et al., 2012; Liu et al., 2012), but not from acyl peroxy radicals and β-oxo peroxy radicals. We have now analyzed the likely impact of these pathways on the IS scheme. Assuming OH yields of 0.5, these reactions could be a source of OH that is equal to about 50% of the sum of the HO<sub>x</sub> recycled from ISOP<sub>2</sub>+HO<sub>2</sub> pathway and the OH formed from the ISOP<sub>2</sub> isomerization pathway.

Recent studies have looked at the impact of including OH recycling from RO<sub>2</sub>+HO<sub>2</sub> reactions. Assuming OH yield up to 50%, modeling work in the tropics have shown that these reactions increase OH concentrations by 5–40% (Pugh et al., 2010; Kubistin et al., 2010; Stone et al., 2011). For the Southeast US, smaller impact (~4%) was reported (Stavrakou et al., 2010). Studies also found including these reactions with reported yields are not able to close the gap between observed and measured OH levels, and recycling of 200-400% OH was required (Lelieveld et al., 2008; Butler et al., 2008; Stone et al., 2011). Our calculations above suggest that if these reactions were included in our modeling system, we would expect a larger increase than reported by Stavrakou et al. (2010) but the increase likely would not be sufficient to match the INTEX observations of OH.

We have added the following sentences to Page 27197, Line 7: “Laboratory studies have observed OH reformation from RO<sub>2</sub>+HO<sub>2</sub> reactions, with differing yields depending on the source of peroxy radicals (Hasson et al., 2004; Jenkin et al., 2007; Dillon and Crowley, 2008; Taraborrelli et al., 2012). In this work we have considered OH reformation from isoprene peroxy radicals (Paulot et al., 2009b, Taraborrelli et al., 2012; Liu et al., 2012), but not from acyl peroxy radicals and β-oxo peroxy radicals. Assuming OH yield of up to 50%, recent modeling work have shown that these reactions increase OH concentrations by 5–40% (Pugh et al., 2010; Kubistin et al., 2010; Stavrakou et al., 2010; Stone et al., 2011). We would expect an additional increase in OH if this source of OH were included in the IS mechanism.”

*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.*

We agree that modifications described in comments (1) and (2) are important and are under consideration for the next update of SAPRC mechanism in CMAQ. Carter and Heo (2012) (<http://www.cert.ucr.edu/~carter/SAPRC/saprc11.pdf>) have published an updated mechanism called SAPRC-11 that includes changes to the reactions between acyl peroxy radicals and HO<sub>2</sub> similar to suggestions in comment (2). We are in process of merging these and other updates into the chemical mechanism presented in this work.

## References:

Butkovskaya, N. I., Pouvesle, N., Kukui, A., and Bras, G. L.: Mechanism of the OH-initiated oxidation of glycolaldehyde over the temperature range 233-296 K., *J. Phys. Chem. A.*, 110, 13 492–13 499, 2006a.

Butkovskaya, N. I., Pouvesle, N., Kukui, A., Mu, Y., and Le Bras, G.: Mechanism of the OH-initiated oxidation of hydroxyacetone over the temperature range 236-298 K, *J. Phys. Chem. A.*, 110, 6833–6843, 2006b.

Dillon, T. J. and Crowley, J. N.: Direct detection of OH formation in the reactions of HO<sub>2</sub> with CH<sub>3</sub>C(O)O<sub>2</sub> and other substituted peroxy radicals, *Atmos. Chem. Phys.*, 8, 4877–4889, doi:10.5194/acp-8-4877-2008, 2008.

Hasson, A. S., Tyndall, G. S., and Orlando, J. J.: A product yield study of the reaction of HO<sub>2</sub> radicals with ethyl peroxy (C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>), acetyl peroxy (CH<sub>3</sub>C(O)O<sub>2</sub>), and acetonyl peroxy (CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>) radicals, *J. Phys. Chem. A*, 108, 5979–5989, 2004.

Jenkin, M. E., Hurley, M. D., and Wallington, T. J.: Investigation of the radical product channel of the CH<sub>3</sub>C(O)O<sub>2</sub>+HO<sub>2</sub> reaction in the gas phase, *Phys. Chem. Chem. Phys.*, 9, 3149–3162, 2007.

Kubistin, D., Harder, H., Martinez, M., Rudolf, M., Sander, R., Bozem, H., Eerdeken, G., Fischer, H., Gurk, C., Klpfel, T., Knigstedt, R., Parchatka, U., Schiller, C. L., Stickler, A., Taraborrelli, D., Williams, J., and Lelieveld, J.: Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, *Atmos. Chem. Phys.*, 10, 9705–9728, doi:10.5194/acp-10-9705-2010, 2010.

Liu, Y. J., Herdinger-Blatt, I., McKinney, K. A., and Martin, S. T.: Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation, *Atmos. Chem. Phys. Discuss.*, 12, 33323-33358, doi:10.5194/acpd-12-33323-2012, 2012.

Orlando, J. J. and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chem. Soc. Rev.*, 41, 6294–6317, 2012.

Orlando, J. J., Tyndall, G. S., and Taraborrelli, D.: Atmospheric oxidation of two isoprene by-products, hydroxyacetone and glycolaldehyde, AGU Fall Meeting, San Francisco, USA, 3-7 December 2012, Conference Poster, Abstract A33L-0315, 2012.

Paulot, F., Wunch, D., Crounse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J. W., Warneke, C., de Gouw, J. A., Dunlea, E. J., De Mazière, M., Griffith, D. W. T., Bernath, P., Jimenez, J. L., and Wennberg, P. O.: Importance of secondary sources in the atmospheric budgets of formic and

acetic acids, *Atmos. Chem. Phys.*, 11, 1989–2013, doi:10.5194/acp-11-1989-2011, 2011.

Pugh, T. A. M., MacKenzie, A. R., Hewitt, C. N., Langford, B., Edwards, P. M., Furneaux, K. L., Heard, D. E., Hopkins, J. R., Jones, C. E., Karunaharan, A., Lee, J., Mills, G., Misztal, P., Moller, S., Monks, P. S., and Whalley, L. K.: Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box model, *Atmos. Chem. Phys.*, 10, 279–298, doi:10.5194/acp-10-279-2010, 2010.

Stavrakou, T., Müller, J.-F., Peeters, J., Razavi, A., Clarisse, L., Clerbaux, C., Coheur, P.-F., Hurtmans, D., De Mazière, M., Vigouroux, C., Deutscher, N. M., Griffith, D. W. T., Jones, N., and Paton-Walsh, C.: Satellite evidence for a large source of formic acid from boreal and tropical forests, *Nat. Geosci.*, 5, 26–30, doi:10.1038/ngeo1354, 2012.

Taraborrelli, D., Lawrence, M. G., Crowley, J. N., Dillon, T. J., Gromov, S., Gross, C. B. M., Vereecken, L., and Lelieveld, J.: Hydroxyl radical buffered by isoprene oxidation over tropical forests, *Nat. Geosci.*, 5, 190–193, 2012.