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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxy radical" *by* D. Huang et al.

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To Reviewer 2

Thanks for your effort and constructive comments. Here are our responses to your comments:

(Q1) The manuscript describes an experimental study of aqueous isoprene oxidation together with a box model study. Although aqueous aerosol chemistry is of much current interest, the manuscript suffers from substantial shortcomings with respect to its atmospheric relevance. From a fundamental kinetics point of view the work is quite interesting (for example the ratio of MVK/MACR and formation of glyoxal and methylglyoxal), however, a very important aspect missing in the manuscript is the fact that it does not show that the aqueous oxidation of isoprene is of atmospheric relevance and I believe that this is also not the case: Even with a cloud liquid water content of 1 g/m^3 the Henry's law constant determines that many orders of magnitude more isoprene are in the gas-phase and are also oxidized in the gas-phase compared to the aqueous phase. Unless the authors demonstrate that aqueous isoprene oxidation is of relevance in the atmosphere, which I believe it is not, the manuscript is not suitable for publication in ACP. I believe the publication should be submitted to a more specialized journal.

(A1) We have discussed the importance of aqueous phase oxidation of isoprene in the former reply and have added relative discussion in our revised manuscript.

Seinfeld and Pandis have pointed out in their book that "The above analysis suggests that species with a Henry's law coefficient lower than about 1000 M atm^{-1} will partition strongly toward the gas phase and are considered relatively insoluble for atmospheric applications. Species with Henry's law coefficients between 1000 and 10000 M atm^{-1} are moderately soluble, and species will even higher Henry's law coefficients are considered very soluble. As can be seen from Table 7.2, remarkably few gases fall into the very soluble category. This does not imply, however, that only very soluble gases are important in atmospheric aqueous-phase chemistry." (Seinfeld and Pandis, page 290, 2006). For example, SO_2 has a Henry's law coefficient of 1.23 M atm^{-1} at 298 K, however, its aqueous oxidation is considered to be an important pathway for its transformation in the atmosphere. The Henry's law of OH at 298 K is 25 M atm^{-1}, for gas-phase mixing ratio of OH of 0.3 ppt (7.4*10^6 molecule cm^{-3}), the corresponding equilibrium concentration in the aqueous phase is 7.5*10^{-12} M (Seinfeld and Pandis, page 306, 2006). Considering the available rate constants for isoprene reaction with OH radical, which are 1.0*10^{-10} $molecule^{-1}$ cm^3 s^{-1} in the gas phase at 298 K (Atkinson and Arey, 2003) and 1.2*10^{10} M^{-1} s^{-1} in the aqueous phase at 283 K (this work), we can estimate the lifetimes of isoprene as follows: 23 min for the gas phase and 11 s for the aqueous phase. This means that the lifetime of isoprene in the gas phase is

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122 times that in the aqueous phase. Recently, the aqueous phase oxidation of VOCs is considered to be a potential contributor to the SOA formation (e.g., Yu et al., 2008; Enami et al., 2010).

Reference: Seinfeld, J. H. and Pandis, S. N.: From Air Pollution to Climate Change, Atmospheric Chemistry and Physics, second edition, Wiley, New York, pages 290 and 306, 2006. Atkinson, R. and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev. 2003, 103, 4605–4638 Yu, Y., Ezell, M. J., Zelenyuk, A., Imre, D., Alexander, L., Ortega, J., Thomas, J. L., Gogna, K., Tobias, D. J., D'Anna, B., Harmon, C. W., Johnson, S. N., and Finlayson-Pitts, B. J.: Nitrate ion photochemistry at interfaces: a new mechanism for oxidation of a-pinene, Phys. Chem. Chem. Phys., 10, 3063–3071, 2008. Enami, S., Hoffmann, M. R., and Colussi, A. J.: Prompt formation of organic acids in pulse ozonation of terpenes on aqueous surfaces, J. Phys. Chem. Lett., 1, 2374–2379, 2010.

(Q2) P1a and P1b should be shown

(A2) We have shown them in our revised manuscript.

(Q3) P2a suggest a RO_2+OH reaction, which appears very unlikely and I do not believe exists in MIM2. The text following the equation also discusses reaction of a peroxy radical with OH.

(A3) You point out our mistake about this reaction. We have checked the P2 pathway in MIM2. There, this pathway is described as: $C_5H_8O_2$ + OH => 0.52* $C_5H_9O_5$ => 0.5*MG + 0.5*GL + . . . We misread the lumped formula $C_5H_8O_2$ as the peroxy radical. The actual one represents the C_5 carbonyls with internal double bonds, and $C_5H_9O_5$ is a peroxy radical from C_5-hydroxy aldehydes. We have corrected this in our revised manuscript.

(Q4) Although it is mentioned that control experiments were undertaken they need to be discussed more.

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(A4) Yes, we have detailed this in our revised version.

(Q5) The discussion of determination of uncertainties in the experimental concentrations should be extended as should the discussion of uncertainties in determined rate constants.

(A5) The uncertainties of experimental concentrations determination arise from the deviation between the parallel experiments. The major uncertainties in determined rate constants originate from the modeled concentration of OH radical and the determined concentration of isoprene. There are certainly uncertainties in determining the aqueous phase concentration of isoprene. The chemical titration method needs to be compared with other reasonable method to further confirm its reliability.

(Q6) What is the uncertainty in modeled OH concentrations, which is central to the main point of the paper.

(A6) The major uncertainty in modeled OH concentrations is the photolysis rate constant of H_2O_2 and the rate constant of isoprene react with OH radical. Because the photolysis of H_2O_2 is the main source of OH radical, and the rate constant of isoprene-OH reaction is the largest in the whole mechanism and the concentration of isoprene is prevail in the first 20 min irradiation. To validate our modeled result, we have estimated the rate constant of aqueous phase OH-oxidation of isoprene using salicylic acid as a reference compound. We have added a section about these in our revised manuscript.

(Q7) How is acetic acid produced?

(A7) We have mentioned in the manuscript (section3.1.2, page8526, line 12 to 14) that the acetic acid fate is the same as described in our previous work (Zhang et al., 2010). The sources of acetic acid may include three pathways: (1) the rapid transformation of pyruvic acid to acetic acid in H_2O_2 solution, which is consistent with the previous study (Carlton et al., 2006); (2) the decomposition of R1R2CHOâĂć radical which formed via the reaction of “R_1R_2CHOO-OOCHR_1R_2 => 2 R_1R_2CHO.+ O_2” as described in the

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OH-initiated mechanism scheme for MAC and MVK (Zhang et al., 2010, Fig 4 and 5.).

Reference: Zhang, X., Chen, Z. M., and Zhao, Y.: Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: Significance to the in-cloud SOA production, Atmos. Chem. Phys., 10, 9551–9561, doi: 10.5194/acp-10-9551-2010, 2010. Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, Geophys. Res. Lett., 33, L06822, doi: 06810.01029/02005GL025374, 2006.

(Q8) In the supplement a table with reactions is given but it is not shown how MVKOOA etc. are formed.

(A8) MVKOOA etc. are formed in the OH radical and O_2 addition to MVK/MACR. The reactions initiated by MVK/MACR are the same as shown in our previous work (Zhang et al., 2010), and we have added these reactions into our present model mechanism in the revised manuscript.

Reference: Zhang, X., Chen, Z. M., and Zhao, Y.: Laboratory simulation for the aqueous OH-oxidation of methyl vinyl ketone and methacrolein: Significance to the in-cloud SOA production, Atmos. Chem. Phys., 10, 9551–9561, doi: 10.5194/acp-10-9551-2010, 2010.

In addition, We have added a kinetic experiment. A competition kinetics method was employed to determine the rate constants of OH oxidation of isoprene, MACR, and MVK, using salicylic acid as a reference compound. Accordingly, we have replaced the Figure. S2 in the supplementary material by the competition kinetics curves. We have used the newly determined three rate constants in the box model, and renewed the corresponding modeled data and figures. We have added the aqueous OH oxidation mechanism of MACR and MVK into Table. S1 in the supplementary material according to the reviewer's suggestion.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8515, 2011.

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