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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Unexpected high yields of carbonyl and peroxide products of aqueous isoprene ozonolysis and implications" *by* H. L. Wang et al.

H. L. Wang et al.

zmchen@pku.edu.cn

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There is a ever growing interest in atmospheric aqueous phase chemistry in recent years, and this paper gives interesting insights in aqueous ozone chemistry. I think this paper would be more robust if the authors put more caution in extrapolating experimental findings.

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

(Q1) This paper conclude that "unsaturated VOCs ... may potentially contribute significantly to aqueous SOA in the atmosphere" (pg 6435, line 9). However, as the authors acknowledged, such reactions could happen (and I think they would only happen) "on the atmospheric surfaces of wet particles and plants". This limitation might make current conclusions questionable. Can the authors determine if such reactions are significant atmospheric sinks for unsaturated VOCs compared to gas phase reactions? Are these reactions as important as aqueous oxidation of other studied species (e.g. glyoxal, phenols)? I agree these reactions could happen in the atmosphere, but the current conclusion is too bold before some critical questions are answered.

(A1) We are not sure about the significance of the interface oxidation of isoprene according to the current knowledge. We have discussed this in our previous study (Huang et al., 2011). We suggest that the aqueous oxidation might be a potential sink of unsaturated VOCs in cloud/fog/wet aerosol, or inversely, the aqueous VOCs oxidation would modify (age) the aerosols, although currently we have not quantified this sink or modification yet. There are two main reasons. For one thing, it is likely that the aqueous interface concentration of hydrophobic gas (like ozone and isoprene) would be much higher than the calculated concentrations based on the Henry's law constant (please see the evidence and references listed in Huang et al. (2011)). For another, the aqueous surface rate constant of isoprene ozonolysis may be higher or at least comparative compare to that in the gas phase. There are great uncertainties about the surface concentration of ozone and isoprene and the surface rate constant. Unfortunately, there are no measured data for these parameters.

We have not made a comparison between the reactions of VOC and glyoxal/phenols in the aqueous phase. More measured parameters like the aqueous surface concentrations of hydrophobic gas and surface rate constants are needed to give a reliable evaluation. We have removed “significantly” in pg 6435, line 9.

Huang, D., Zhang, X., Chen, Z. M., Zhao, Y., and Shen, X. L.: The kinetics and mechanism of an aqueous phase isoprene reaction with hydroxyl radical, Atmos. Chem. Phys., 11, 7399–7415, doi:10.5194/acp-11-7399-2011, 2011.

(Q2) This paper also suggest that ozonolysis of poorly water soluble VOCs could "give an implication for partly explaining the “missing” OH radical source over the tropical rain forest" (pg 6435, line 10). The observed OH radical discrepancy was in the gas phase. If this chemistry happens on plant surfaces, the mechanism for produced OH radicals to enter free troposphere is quite uncertain; if this chemistry happens on wet aerosols, the significance of such chemistry would be highly dependent on uptake efficiency and reaction time scale compared to other sinks. As the paper did not discuss these questions in depth, it is unsafe to make such strong statements.

(A2) Thanks for your suggestion. We have deleted this sentence in the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6419, 2012.