Atmos. Chem. Phys. Discuss., 13, C8771–C8773, 2013
www.atmos-chem-phys-discuss.net/13/C8771/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aqueous-phase photochemical oxidation and direct photolysis of vanillin – a model compound of methoxy-phenols from biomass burning" *by* Y. J. Li et al.

Anonymous Referee #1

Received and published: 4 November 2013

General impressions: This is a nice paper that will be valuable to the community and should be accepted after a few relatively minor modifications. The paper very nicely highlights the importance of particle phase chemistry on aerosol mass yields / composition. Results suggest that a "one size fits all" approach falls short, and detailed understanding of cloud/fog water composition and photochemistry is important to predict the atmospheric fate and lifetime of molecules produced in biomass burning events.

The paper could be improved by additional experiments on other model compounds within the same class, and additional efforts to oxidatively age aerosol produced under condition "B." My suspicion is this experiment would result in a very similar pattern to

“A.” In addition, the concentration of H2O2 in condition "A" appears to be far too high to really be interesting. The chosen conditions really represent "all" or "nothing" - that is the H2O2 concentration is so high that all of the organic will quickly decompose, or the concentration is so low that the other processes will be favored. In addition, the authors atomize an aqueous phase reaction mixture. While this is interesting, to a certain degree it eliminates the need for a AMS. Why not probe the chemistry of particles when they react in the aerosol phase and use the AMS to measure the particles? Heterogeneous phase chemistry may yield very different results. This is speculative, however, the authors have been provided with this fine measurement instrument to answer such questions.

top of page 27646 – concentration of H2O2 – It lists 34.5 – 36.5 wt %. Is this correct? It seems this experiment is then somewhat dangerous, so I encourage the authors to include a section on safety measures. In addition, this is much, much higher than relevant atmospheric conditions. At such a high concentration of H2O2 it is not surprising most of the organic is quickly degraded - treatment with high conc. of H2O2 is a known wastewater treatment strategy and the literature on kinetics / mechanisms of organic degradation is very large. I feel that experiments at much lower concentration of H2O2 are warranted to better understand the chemistry of this system.

page 27650, line 5-10. The authors discuss conditions A and B and draw conclusions regarding the OH mediated mechanisms vs direct photolysis of vanillin. Can the authors present a justification for this assumption? It seems the reality may be more complicated. For instance, is the ’branching ratio’ H2O2 conc. dependent? Is OH generated during photolysis rxns? The authors later seem to allude to the fact that the conc. ratio may be important (bottom of 27659), so it seems this is important issue to clear up. Again, additional experiments in which the H2O2 conc. is varied could be quite valuable.

general comment – it would be nice if authors could pursue measurements on other phenolic compounds produced in biomass burning. With only one model compound, it

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is not clear if results should serve as guidance for the entire class of materials or just vanillin.

general comment: the authors consider cases A (with H2O2) and B (without H2O2). Several times, they refer to the “final” product or the “final” condition of the experiment when comparing cases. Is it possible that data shown in figure 3B or 2 for that matter would begin to appear very similar to case “A” if sufficient oxidative aging occurred? As a general theme, it seems to be important how we define “final” condition with regards to aerosols in Earth’s atmosphere. Are the results here simply suggesting the aerosol of case “B” simply has not experienced the oxidative aging case “A” has? It seems to me this is the case.

page 27659 line 21 – the work cited (Chang and Thompson) would clearly be of relevance to this study, however they did not report observations of brown carbon in ambient samples. Their conditions seem to be somewhere between case A and B reported here.

FIgure 2 - a major point of this paper is that differences exist between case A and B. Can you enlarge the mass spectra of figure 2 in an attempt to really make this point? Addition discussion in the text is also warranted.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27641, 2013.