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Interactive Comment

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.

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General Comments

The manuscript presents an interesting and extremely comprehensive study of the fate of a methoxy-phenolic compound, vanillin, in the atmospheric aqueous-phase. Two important cloud processing reactions were studied: oxidation by aqueous OH radicals and direct photolysis. Vanillian was processed in the bulk-aqueous-phase and continuously atomized to produce secondary organic aerosol (SOA). The authors used a variety of on-line and off-line instrumentation to monitor product composition. The results of these exhaustive experiments yield several important conclusions related to the degree of oxygenation, cloud-condensation nuclei activity, and the specific compounds formed in the SOA. They conclude that SOA generation from cloud-processing of methyl-phenolic compounds is significant and should be included in chemical transport models. Both the breadth and depth of this paper are impressive. In addition, the authors do a nice job expanding and supporting the experimental results in the Supporting Information. The paper is also well-written. I recommend publication after the authors address the following comments:

Specific Comments

The authors use a 254 nm lamp to generate OH from H2O2 photolysis and to induce direct photolysis. However, using a 254 nm light to induce photolysis may not be atmospherically relevant. Actinic radiation is only present at wavelengths longer than ~290 nm. There is the potential for this higher energy light to open up additional reaction channels that would not be available in the atmosphere. This should be addressed in the manuscript. I would be somewhat cautious when extrapolating experimental results from the laboratory to the atmosphere.

Certain aqueous reactions may involve dissolved oxygen. Is the experimental setup oxygen limiting? Do the authors have any evidence that the reaction products are oxygen dependent? How does the availability of oxygen within the experiment compare to the availability of oxygen in a typical cloud or fog droplet?

Last paragraph of section 3.6: The authors state that the measured decay rate of 2.3 x 10ˆ-4 sˆ-1 is comparable to the vanillin loss rates from gas phase oxidation by OH and the loss rate of common aqueous organic compounds. However, the measured decay rate in the experiment is a function of the wavelength dependence and power of the UV-lamp. If the lamp intensity (typically quantified with an actinometer) and the wavelength dependence (quantified with a UV-Vis) are determined, one can calculate the corresponding atmospheric loss rate constant after picking a solar zenith angle and

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ozone column depth.

Last paragraph of section 3.6: When comparing rates of atmospheric processes, it is more helpful to compare the rate and not the rate constant. E.g. Even if the rate constant of aqueous photolysis is fast, concentrations in the aqueous phase could be so low that aqueous photolysis is not significant. The concentration of vanilin in the aqueous phase relative to the gas phase should be considered when determining the significance of aqueous photolysis.

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

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