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Interactive comment on “Aqueous-phase photooxidation of levoglucosan – a mechanistic study using Aerosol Time of Flight Chemical Ionization Mass Spectrometry (Aerosol-ToF-CIMS)” by R. Zhao et al.

Anonymous Referee #2

Received and published: 18 May 2014

General Comments:

In this manuscript the authors describe results of lab experiments in which they investigated the products and mechanisms of the OH radical-initiated reaction of levoglucosan in an aqueous solution. Levoglucosan is a widely used tracer for biomass burning aerosol. The experiments were conducted in a glass photoreactor in which OH radicals were formed by the photolysis of hydrogen peroxide, yielding oxidation conditions similar to those found in clouds. The reaction products were analyzed con-

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tinuously online by atomizing the reaction solution and then evaporating the drops in a heated tube prior to analysis with an aerosol time of flight chemical ionization mass spectrometer. The instrument allowed for time resolved measurements of the elemental composition of reaction products. The reaction products are consistent with mechanisms developed previously for this and other OH reactions. It is shown that the ratio of double bond equivalence/carbon number follows a smoothly increasing curve to a value of 1 with increased reaction time, which represents a new and interesting relationship for following the oxidation of organic compounds to multifunctional carbonyls and carboxylic acids. Measurements of the fractions of (m/z 44) and (m/z 60) in the mass spectra vs time made using an Aerodyne Aerosol Mass Spectrometer also overlapped well on a plot of similar measurements made in the field for the evolution of biomass burning aerosol, indicating that aqueous phase oxidation may play a significant role in the atmospheric aging of this class of aerosol.

The experiments, data analysis, and interpretation are very well done, and yield interesting and important results. The manuscript is also clearly and concisely written. The paper should certainly be published in ACP, after the following minor comments are addressed.

Specific Comments:

1. Page 8823, lines 21–23: Have any tests been conducted to evaluate compound losses in the tubing? The TAG instrument is just one example of an instrument that uses heated coated tubing to transport oxidized compounds and is known to suffer significant losses. What effect might such losses have on the results?
2. Page 8823, lines 25–26: Thorsten Hoffmann was the first to use a heated tube with an API/MS for organic aerosol particle analysis [JGR, 103, D19, 25,569-25,578 (1998)].
3. Page 8826, lines 15–23: Could wall losses during transport also be a cause for the absence of oligomers? Have you ever detected oligomers using this instrument?

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4. Page 8831, lines 3–14: How accurately can you quantify H, O, and C with the CIMS? Are there any selectivity issues with regards to ionization of compounds with different combinations of functional groups that might lead to significant uncertainties?

5. Page 8833, lines 1–23: Presumably the DMSO reaction with OH leads to formation of sulfuric acid (similar to DMS). Could the sulfuric acid catalyze other reactions of levoglucosan, since the timescale for this experiment is relatively long (~ 1 hr)?

6. Page 8833, lines 13–15: How does the measured rate constant compare with the diffusion-limited value?

7. Throughout the manuscript when proposed reactions lead to the addition a hydroxyl group, shouldn't there also be a carbonyl co-product formed by the Russell mechanism? Such a reaction is indicated once in the SI, but you seem to focus only on the alcohol formation pathway elsewhere. In cases where you see an alcohol product, it seems that the time dependence of that product should be similar to that of the carbonyl co-product. Formation of this same carbonyl from OH reaction with the alcohol should occur more slowly and thus be shifted in time. What do you see with regards to time profiles of potential carbonyl co-products?

8. I think the only mechanism proposed here for the formation of carboxylic acids is hydration of aldehydes followed by OH/O₂ reaction. How fast do these aldehydes hydrate and react with OH? What about other possible pathways such as dehydration of α -hydroxyhydroperoxides formed from the reaction of H₂O₂ with aldehydes?

9. Might photolysis play any role in the reaction mechanisms other than to form OH radicals?

Technical Comments:

1. Page 8824, line 15: I believe this compound is called acetic anhydride not anhydrate.

2. Page 8826, line 15: It should probably be noted whether the m/z values observed between 173 and 351 are with or without attached I⁻.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 8819, 2014.

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