Response to Reviews

We thank the editor and the reviewers for their comments and suggestions. We herein provide a list of major modifications made in the manuscript, followed by point-by-point responses to each specific comment.

Referee #1:

General: This is a very good contribution on the aqueous phase degradation of levoglucosan which has been identified to possibly be degraded in the atmosphere including its aqueous phase. The study re-determines the rate constant for the OH reaction and confirms published kinetic data within a factor of about two. Further to the kinetics study, the paper contain a wealth of very valuable mechanistic information, which, however, could be more comprehensively summarized (see below). This contribution surely merits publication in ACP subject to a couple of issues listed below which should be addressed prior to publication.

Details:

Comment: Page 3, line 96: When competition kinetics are used, the reference rate constant should always be given.

Response: The reference rate constant was indeed provided in the Results and Discussion (Sect. 3.2). In the revised manuscript, we have added a clause in Page 3 to guide the readers to where the rate constant is provided.

Comment:
Page 3, line 215: As it is nice to know that the LG concentration range might be similar to cloudwater concentrations, this is not a prerequisite for the determination of a correct rate constant. The concentration levels of both the oxidant (OH) and the substrate (LG), however, are of course important for the mechanistic studies. Maybe this could be remarked in that second paragraph, right column on page 3.

Response: Thanks for this excellent suggestion. The following sentence has been added to the revised manuscript Line 144:
"We believe that the reaction mechanism investigated in the current study is representative for cloud processing given that similar reactant concentrations are used as those in cloudwater."

Page 4, line 264: The mechanistic studies are described in sections 3.1.1., 3.1.2. and 3.1.3 discriminating between functionalisation, bond scission and information from the ToF-CIMS instrument which make sense in view of the methods applied. However, for summarising the information obtained as a whole it would be very good for the manuscript to have another, following section, maybe 3.1.4, where all mechanistic information should be integrated into an LG degradation scheme which does not need to be complete but should reflect at least the main findings leading to the identified products - 'a mechanism in line with the identified products'. Such summary is currently missing and would be a strong improvement of the manuscript.

Response: This is a good suggestion. We have added a new section (Sect. 3.1.4.), alone with a summary diagram (Figure 8) in the revised manuscript for the proposed reaction mechanisms.

Referee #2

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 photoysis of hydrogen peroxide, yielding oxidation conditions similar to those found in clouds. The reaction products were analyzed continuously 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?

Response: The Aerosol-CIMS and TAG instrument are indeed both utilizing thermo-desorption of aerosol for organic compound detection. A major difference between the two techniques is that organic compounds are injected to a TAG instrument in pulses, while the Aerosol-CIMS is a continuous flow system. In the Aerosol-CIMS, as the solution is continuously atomized, and the line is conditioned, most of the organic compound signals reach a steady state. The time required to achieve the steady state depends on the chemical nature of each specific compound, with less volatile compounds generally exhibiting longer partitioning time. Inversely, when the atomization is stopped or the solution is removed, the signals exhibit a first-order decay, presumably arising from desorption from the wall. Here is what we propose as potential effects of wall conditioning on the results.

Mechanistic study: We cannot exclude the possibility that highly oxygenated products are lost to the wall and are not observed, if there are cold spots in the system. However, the wall losses will not change our current conclusions which are qualitative and based on only the observed compounds. This point is now made in the revised manuscript line 166 (also see response to Comment 3).

Kinetic Study: Since the steady state signal is not instantly achieved, we did consider the effects of wall partitioning to the kinetics observed. Prior to the initiation of each kinetic experiment, the LG solution was atomized until the steady state of the LG signal was achieved. However, the desorption of LG from the wall may affect the observed decay rate of LG. This may potentially explain why the rate constant

obtained in our study is smaller than previous values. This point has been newly added to the revised manuscript line 365, alone with a comparison with the estimated diffusion limited rate constant of this reaction (see response to Comment 6).

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)].

Response: Thanks for this information. We have added this reference in Sect. 2.2 of the revised manuscript.

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?

Response: In our previous work (Aljawhary et al. 2013), dimers of α-pinene SOA components were observed from aqueous abstract using the same instrument . This study demonstrates that dimers can be detected using our system if their concentrations are sufficiently high. We have added this point to the revised manuscript Line 164.

That being said, condensational loss of oligomers to the wall could be a cause of their absence on the mass spectra, if there are cold spots in the line. The current Aerosol-CIMS system is carefully designed to eliminate cold spots by wrapping the heated line thoroughly and evenly. We believe that a cold spot on the line is unlikely, but the Ion Molecular Region (IMR) of the CIMS system can potentially be a cold spot because the IMR temperature is lower than the heated line. Nevertheless, we now mention this in the revised manuscript Line 166 as below:

"Oligomers can be potentially lost to the wall of the volatilization line, if there are cold spots. Although the volatilization line is carefully wrapped by a heating tape thoroughly and evenly to minimize cold spot, the inner wall of the CIMS's ion molecular region can potentially be a cold spot because its temperature is lower."

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?

Response: We do not have a standard method to assess the accuracy of elemental assignment at the moment.

The O/C and H/C at the beginning of the photooxidation can be used as a check because the solution contains only LG at this point. The observed O/C at the beginning of photooxidation is 0.82 while the theoretical O/C of LG is 0.83. The measured H/C at the beginning of photooxidation was 1.82 while the theoretical H/C of LG is 1.67. These initial values of O/C and H/C are highly reproducible among replicates. We take this as an indication that the uncertainty of elemental assignment is within 10%. This comparison is now briefly mentioned in Line 103.

The variable sensitivity of different compounds using the iodide water cluster reagent ion is indeed something we considered when using signal intensity as an indicator for the amount of product formation. As a general rule, the iodide water cluster reagent ion is not sensitive to mono-alcohols, acids and aldehydes, but exhibits high sensitivity to more oxygenated compound with multiple functional groups. Our previous study showed that the detection sensitivity of iodide cluster is constant to within a factor of two for a number of oxygenated compounds with a carbon number of 3 or more (Aljawhary et al. 2013).

Since we did not intend to make quantification of each specific product but focused instead on a semi-quantitative assessment of the overall trends, we do not expect the difference in detection sensitivity significantly alters our conclusions. This point has now been made in the revised manuscript line 197.

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)?

Response: H$^+$ from H$_2$SO$_4$ may affect the reaction. We did not perform pH measurement for the kinetic experiment and do not know how much pH change was accompanied by the DMSO photooxidation. If the 5 uM DMSO used as reference is stoichiometrically converted into H2SO4, the pH of solution can be acidified a neutral solution to pH 5. This is likely an upper limit case, because the time scale of the kinetic experiment probably did not allow the completion of DMSO photooxidation.
That being said, we do not think change of acidity would affect the kinetic of LG photooxidation. To our best knowledge, the only reaction that might be of concern is the acid-catalyzed hydration of LG, leading to formation of D-glucose. D-glucose should be able to be detected by our CIMS, but was absent throughout the kinetic experiment. This is consistent with a previous study (Fraser and Lakshmanan 2000), where LG hydration was observed to be slow.

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

Response: We calculated the diffusion limited rate constant to be 1.9×10^9 M^{-1}s^{-1}, in reasonable agreement with, but larger than the obtained value from the current study ($1.08 \pm 0.16 \times 10^9$ M^{-1}s^{-1}). We have added this comparison in Sect. 3.2. Line 369 in the revised manuscript, together with a potential reason (wall effect) leading to a slower rate observed in the current study. We have also added Appendix SI for a detailed calculation of the diffusion limited rate constant.

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 protential carbonyl co-products?

Response: This is a good point. Yes, a carbonyl should indeed form along with an alcohol in the Russell mechanism. As can be seen from Fig.2, the time profiles of the carbonyls (i.e. the -2H products) seems to be delayed compared to those of the alcohols (i.e. the +O products). This observation indicates that OH oxidation of alcohols seems to be the major formation pathway for the carbonyls, giving rise to the -2H trend. This is consistent with the mass defect plot in Fig. 3a, showing that the amount of +O products seem to be much smaller than the -2H product (note that the area of data points represents signal intensity in log scale).

In summary, we think the Russell mechanism is indeed occurring in the system and is the major mechanism giving rise to the alcohols (the +O trends). However, the Russell mechanism seems to be a minor formation mechanism for the carbonyls (the -2H trends), compared to the OH reaction with the alcohols. This has likely caused a delay in the time profile of the -2H products compared to the +O

products. We agree with the referee that the Russell mechanism, as a formation pathway for carbonyls, should not be overlooked.

We have added the following sentence in Sect. 3.1.1. as part of discussion for the mechanism leading to formation of the -2H trend.
"We note that carbonyls can be also formed via the same mechanism leading to the formation of the hydroxyl functional group (i.e. R1 in Figure 4). However, formation via this pathway would not lead to the observed -2H trend and is likely a minor formation pathway of carbonyls compared to R5."

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 a-hydroxyhydroperoxides formed from the reaction of H2O2 with aldehydes?

Response: Hydration of small aldehydes is rapid. For example, the first-order hydration rate constant of glyoxal is estimated to be 7 s^{-1} (Ervens et al. 2011), while that of methylglyoxal is measured to be 11 s^{-1} (Creighton et al. 1988). However, hydration of larger aldehydes can be expected to be slower due to stearic effects. Although the potential importance of α-hydroxyhydroperoxide formation in atmospheric aqueous-phase chemistry has been elaborated in a few recent studies (Zhao et al. 2013, Schone and Herrmann 2013), the fate of this class of organic peroxide is largely unknown. Dehydration of α-hydroxyhydroperoxides is definitely something that should be addressed in future studies as a potential source of carboxylic acids. We have added a sentence in the revised manuscript Sect. 3.1.1 Line 225, elaborating the importance of investigating hydroperoxide formation in future studies.

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

Response: As mentioned in the original manuscript, we performed a control experiment and confirmed that LG was not directly photolyzed by the light used. However, what is difficult to determine is whether the proposed poly-carbonyl compounds may exhibit light absorption and photolyse due to conjugation in their structures. We measured the light absorption of the reaction solution during the photooxidation experiments using a waveguide capillary UV-Vis spectrometer (Ocean Optics). However, the solution did not exhibit observable absorption in the wavelength range of the lamp used in the current study. This is perhaps because the concentrations of the poly-carbonyl compounds are too low, and their absorption is below the detection limit of the spectrometer.

Technical Comments:

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

Thanks for pointing this out. Acetic anhydride is the correct term.

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–.

Thanks for the suggestion. It is now clarified that the m/z range is for I$^-$ clusters.

References

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