We would first like to thank both referees for valuable comments on the manuscript. Our responses to comments by each referee and a summary of additional changes made to the revised manuscript are given below.

Responses to Anonymous Referee #1 (Referee comments are indicated by italics.)

1.) Recently there has been evidence that oxidant-limited conditions influence the amount of SOA formed in aqueous phase experiments, both in laboratory (Nguyen et al., ACP, 2014) and modeling (Ervens et al, JGR, 2014) work. Can the authors describe their findings in this context? How is oxidant availability different in the smog chamber vs. bulk experiments? In which are they more/less limited? Could oxidant availability account for some of the differences observed in the work described here?

Thank you for this suggestion. We have added estimated OH concentrations and OH exposures in both the bulk and chamber experiments. We have also added a supplementary figure (S5) showing estimated OH exposures as a function of reaction time.

Specific text changes:

Page 13658 line 16-18 (from the ACPD version) replaced with: "Using a k_{OH} of 1.9 x 10^9 $M^{-1} s^{-1}$ (Herrmann et al., 2010), this decay is consistent with an initial aqueous OH concentration of 4.8 x 10^{-12} M, which is within an order of magnitude of the average OH concentrations estimated for ambient deliquesced particles (Herrmann et al., 2010). The OH concentration, estimated from the time dependence of the polyol concentration (see Supporting Information), drops over the course of the experiment, reaching a final OH exposure of 2.7 x 10^{-9} M s."

Page 13660 line 17 added: "A maximum OH concentration of 3.5 x 10^{-12} M is reached between 30 and 40 min, and subsequently decreases to give a final OH exposure of 4 x 10^9 M s; these values are similar (within a factor of two) to those of the bulk experiments."

Page 13661 line 26 added: Estimated OH concentrations and exposures were also similar between the bulk and chamber cases (see Fig. S5 in the Supplement).

Page 13663 line 7 added: "The final OH exposures for the oxidation of erythritol in the bulk solution (4.7 x 10^{-12} M s) and in the submicron particles (2.7 x 10^{-9} M s) agree to within a factor of two. This is true for the larger polyols (C5-C7) as well (Fig. S5), suggesting that differences in oxidant availability are not likely to account for the observed differences between the bulk and chamber results."
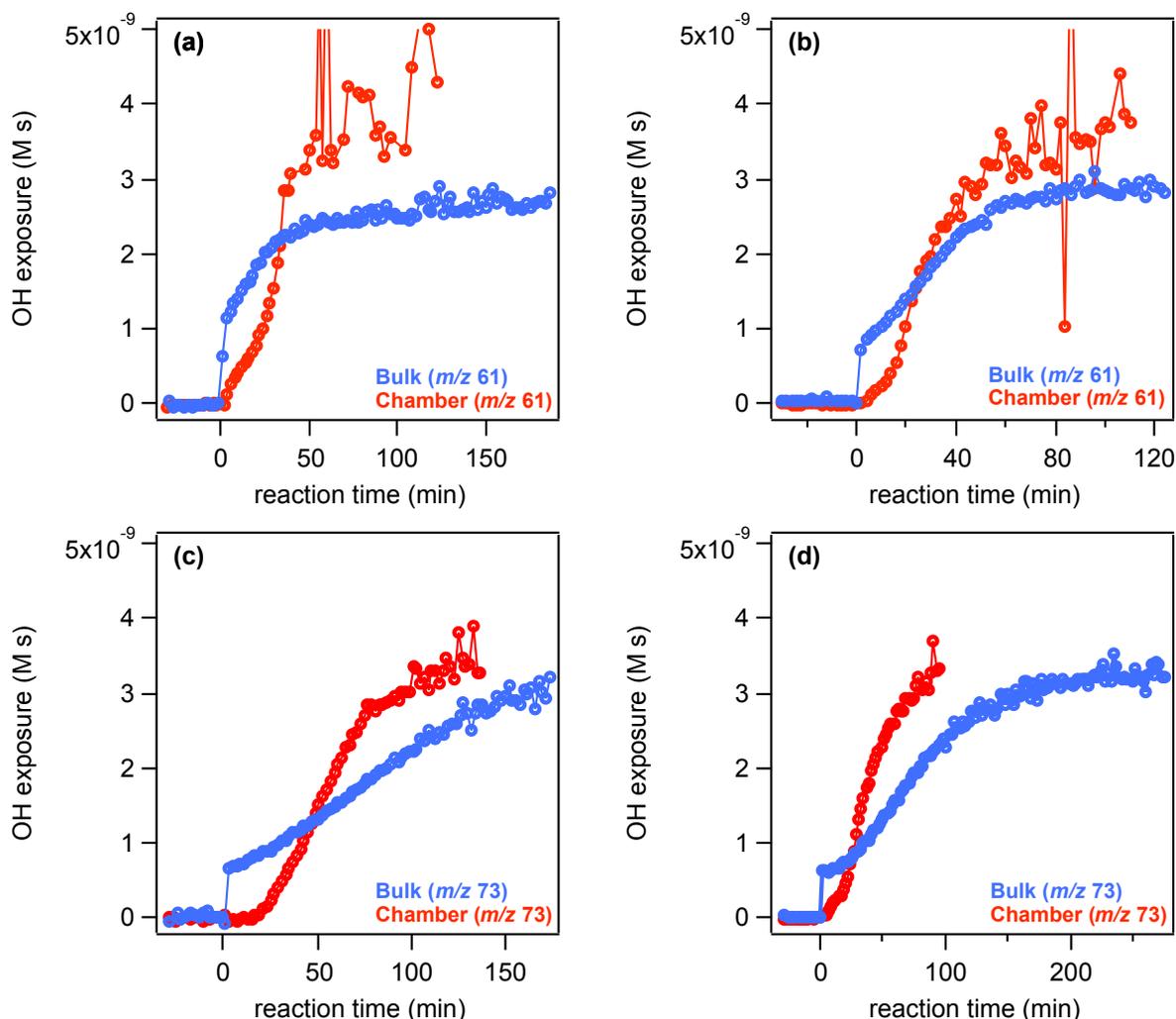
Added to Supplement:

Figure S5. Estimated OH exposures for all experiments. These are determined from OH exposure = $\ln([polyol]_0/[polyol]_t)/k_{OH}$, where $[polyol]_0$ and $[polyol]_t$ are the sulfate-normalized mass concentrations of the fastest decaying tracer ion at times 0 and t, respectively, and k_{OH} is the rate constant for aqueous reaction with OH (Herrmann et al., 2010). OH exposures for both bulk and chamber oxidation are shown as a function of time from 30 min prior to adding H_2O_2 until exposure to UV lights for (a) erythritol using m/z 61 as a tracer and k_{OH} = 1.9 x 10^9 $M^{-1}s^{-1}$, (b) adonitol using m/z 61 as a tracer and k_{OH} = 1.6 x 10^9 $M^{-1}s^{-1}$, (c) mannitol using m/z 73 as a tracer and k_{OH} = 1.6 x 10^9 $M^{-1}s^{-1}$, and (d) volemitol using m/z 73 as a tracer and k_{OH} = 1.6 x 10^9 $M^{-1}s^{-1}$. (Because no k_{OH} has been reported for volemitol, it was assumed to be equal to the k_{OH} for mannitol.)

2.) The authors make this comment: compounds with 1 M atm-1 < H* < 10^9 M atm-1 will be primarily in the aqueous phase for the bulk LWC, but primarily in the gas phase at aqueous LWC.

My understanding of Figure 1 is that all of the material within this range will be in the condensed phase for bulk LWC. From figure 1, it appears that range for when the fraction is >.5 (material is predominantly in the condensed phase) is for 10^-2 M atm-1 to 10^9.

Thank you for this correction. At 10^{-2} M atm^{-1}, the fraction in the condensed phase for bulk LWC is actually <0.5 (f_{aq} = 0.2). It reaches 0.5 at 4 x 10^{-2} M atm^{-1}, so rounding to the nearest order of magnitude within the range would be 0.1 M atm^{-1} < H* < 10^9 M atm^{-1}. We have corrected this in the manuscript on page 13664 line 17, and on page 13675 line 3 of the figure caption.

Responses to Anonymous Referee #2

While I fully agree with the point being made by the authors that LWC will affect the partitioning of partially soluble species, I do wonder why they don't address more the possibility that oxidant levels are difference between the two conditions? i.e. Could it be that higher OH levels are present in the particles due to the very high dissolved H2O2, and different production conditions involving iron, and/or from different light levels? Why not estimate the OH concentrations int eh particles from the polyol decay rate as they did in the bulk work? This would address my main criticism of this paper, i.e. that it is an interesting qualitative study but that it is really very difficult to get anything qualitative out of the work. It is not surprising that if you have an OH source in the particles that they will get oxidized. What is really needed is an estimate of how fast that chemistry occurs. When re-writing the paper for ACP, I suggest the authors be more clear about these issues, stressing uncertainties associated with such statements as "substantially less carbon loss". For example, in the Conclusions I do not think that the authors can claim that this "is an efficient pathway for the rapid formation of highly oxidized material". My problem is with the word "efficient". Without OH concentration measurements in the particles, this study remains qualitative.

This is an excellent suggestion. As discussed in our response to Referee #1, we have added estimated OH concentrations and OH exposures in both the bulk and chamber experiments, and a supplementary figure showing estimated OH exposures as a function of reaction time. (See above for specific changes to text and supplement.) As noted in the text, aqueous OH concentrations in these experiments reasonably match (best estimates of) concentrations in ambient particles (Herrmann et al., 2010). Therefore we believe the statement that this chemistry *"is an efficient pathway for the rapid formation of highly oxidized material"* is reasonably supported by the available evidence.

Is the AMS spectrum of oxalate sufficiently unique that it can be uniquely identified? Or, is the spectrum instead indicating small di-acids are present?

We have compared the AMS spectrum of oxalate to those for other diacids (malonic acid, succinic acid, adipic acid, and glutaric acid) and found it to be sufficiently unique. See

Why state that 3.7e10(-12) M is an upper limit to the OH concentration in the bulk experiments? Is it not a good measure of the concentration itself?

Thank you for suggesting this clarification. It is a good measure of the OH concentration when the concentration is at its highest level (i.e. when the polyol decay is most rapid), so as a measure of the average OH concentration over the course of the experiment, it is an upper limit. We have modified this statement to say "initial" OH concentration instead of "maximum".

I realize there are huge uncertainties, but even a conceptual mechanism showing how you can go from these polyols to oxalate might be valuable, with OH as the oxidant.

We have added the following sentence to page 13659 line 19 citing similar mechanisms proposed by other studies:

"A pathway for the formation of oxalic acid from the aqueous oxidation of ethylene glycol (a C2 diol) has been shown by Tilgner & Herrmann (2010) and mechanisms for the formation of oxalic acid from larger diacids have been described by Ervens et al. (2004)."

Additional Changes to Manuscript

For consistency, we have chosen to report only V mode data for all AMS measurements. (In the ACPD version of the paper, all high-resolution data was reported in W mode and all unit-mass resolution data in V mode.) We also found and corrected an error in the NH_4^+ and CO_2^+ time traces. These changes affect Figures 3-5 and Supplementary Figures 1-4, but do not affect the paper's conclusion in any way. The only required changes to the text are minor edits to notify the reader that all data is from V mode, and to indicate which traces are UMR vs. HR:

page 13657 line 11: added "All data reported here was taken with the instrument operated in V mode."

Page 13662 line 8: changed "[Org] is the average sulfate-normalized mass concentration of total organic" to "[Org] is the average high-resolution sulfate-normalized mass concentration of total organic"

Page 13662 lines 12-14: updated the percentages to match the new V mode version of Figure 5

Page 13677: added to the end of Fig 3 caption: "Results in panels a, c, and d are from high-resolution mass spectrometric analysis. All traces in panel b are from unit mass resolution, except NH_4^+ and CO_2^+, which are high-resolution traces."

Page 13679: changed first sentence to "… from Eq. 2, using high-resolution V mode data."

Supplement, page 1 line 7: added "All data is shown in unit mass resolution, except for NH_4^+ and CO_2^+, which are high-resolution traces."

References:

Ervens, B., Feingold, G., Frost, G. J., and Kreidenweis, S. M.: A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, J. Geophys. Res., 109(D15205), doi:10.1029/2003JD004387, 2004.

Tilgner, A. and Herrmann, H.: Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM, Atmos. Environ., 44(40), 5415–5422, doi:10.1016/j.atmosenv.2010.07.050, 2010.