

Interactive comment on “Identifying precursors and aqueous organic aerosol formation pathways during the SOAS campaign” by N. Sareen et al.

Anonymous Referee #2

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1 General Comments:

The authors of this manuscript collected gas phase compounds during the SOAS measurement campaign and measured their reaction progress in the presence of OH to understand the aqueous phase chemistry that occurs as a result of gas-to-particle partitioning of these compounds. They measured loss rates of several oxidized compounds and formation rates of four organic acids as a result of reaction of these ambient compounds with OH and monitored the formation of highly oxidized oxalate, pyruvate, acetate, and glycolate over time. This indicates that the aqueous phase oxidation of water soluble organic compounds may be very important for the formation of these compounds, possibly followed by repartitioning back to the gas phase after oxidation. This study is important for the atmospheric chemistry because it uses ambient com-

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pounds as precursors for oxidation, instead of single “proxy” compounds or simple mixtures of such. The authors were able to track both precursor and product compounds, which could lead to mechanistic conclusions about the formation of organic acids in atmospheric waters. However, more details are needed about both the sampling method (e.g., recovery of compounds through the mist chambers and instrumental precision, see comments below) and about other compounds besides those discussed here. This will give the reader a better sense of the significance organic acid formation from the compounds discussed here.

The five masses that exhibited “reactant-like trends” are discussed in detail. Are these the only compounds observed in the initial mixtures? If not, were there others that reacted with OH or that stayed constant over the course of the experiment? It seems unlikely that these are the only compounds detected, and more detail would be appreciated to give the reader a sense of the concentrations of these compounds as compared to others. How significant were these five compounds in terms of the percentage of organic matter? Why wouldn't other compounds react with OH? How likely is it that compounds that are not detected contribute to organic acid formation? If these are the only compounds that displayed “reactant-like trends,” then this will allow for the conclusion that oxalate, pyruvate, acetate, and glycolate are directly produced from these compounds and not from others. Otherwise, this argument is hard to make. A similar comment can be made for the oxidized species formed from the OH reaction. Only four organic acid products are mentioned in the manuscript. Were others observed? If not, is this expected? The reaction of OH with organics is likely to produce these small organic acids eventually, but I would expect to see other acids formed as intermediates in this process as well.

Discussion of the significance of these compounds in WSOC would strengthen this manuscript. As is, the authors make some interesting conclusions about the formation of aqueous SOA formation, but it is difficult to determine the magnitude of their contributions to aqueous phase chemistry. An upper bound estimate of this contribution

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might also be interesting to see.

2 Specific Comments:

The authors state in the methods section that intensive days were chosen because of high concentration predictions by NCAR and that during those days, they observed higher than usual TOC content in general. However, in examining Supplementary Table S1, it seems that the days marked "intensive" are not much higher than others, if at all. The range given in the text (92-179 $\mu\text{M-C}$) does not match the range of TOC on intensive days. Can this be clarified? Does this range only represent the days that were used in further measurements?

Line 208: Why is glyoxal the only standard compared across all analysis days? Were the variabilities of the other standards on a similar scale? If so, this should be stated here.

Line 215-219: Limit of detection and precision information is given here for oxalate, but this is not the only organic acid measured by IC. Can all the acids studied be considered to be similar to this or do they vary significantly?

In Figure 2, m/z 187 is actually the sodium cluster, which is not shown in the figure. However, Figure 4 makes it clear that this is the case. These should be changed to be consistent with each other.

A predicted structure for m/z 187 is shown in Figure 2, along with the predicted gas- and aqueous- phase structures. However, the observed mass contains an extra methoxy group. From previous comments on the methodology and the discussion that follows about the compound at m/z 173, I assume this is a result of hydration by methanol in the FT-ICR-MS. However, this is not stated until after the discussion of m/z 187, and should be explained the first time it is seen.

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In line 319 and again in lines 360-364, the authors state that they expect IEPOX, ISOPOOH, and glyoxal were lost in their experiments during sampling or storage. Have any tests been done to quantify losses of other compounds during sampling or storage? If these compounds were lost, it seems likely that there are others that are either lost or not fully recovered. Were any recovery studies done with known amounts of standards instead of spiking the samples just before analysis?

In Figure 5, for m/z 125, how likely is it that the first structure shown (the aldehyde) is detected as such and not hydrated in the aqueous mixture? Is this a likely structure? The authors also state in the discussion of this figure that gas phase compounds are seen at m/z 129 and 143. However, it seems unlikely that these compounds are the polyols found in Figure 5. Are there any compounds with those masses that may be found in the same form in both the gas- and aqueous- phase?

In the Figure 6 caption, special mention is made of the fact that oxalate is present in all samples. Is this not true for pyruvate as well?

I'm not really sure why Supplementary Figure S3 is not included in the main portion of the manuscript. It is discussed in the main text and seems to be important to the overall conclusions of the paper. It is also hard to follow, mainly because there are so many points. It would be easier to see the trends if a general trend line was added as in Figure 6.

Acetate and glycolate are found in some samples, but in varying concentrations. Did the authors see any trends that might explain their formation on some days and not others? Also related, if acetate and glycolate co-elute on the IC, how can the statement be made that "Acetate formation is seen on some but not all days" when any signal seen is due to the combination of both? Was acetate also measured via another method? There seems to be a lack of discussion about the glycolate present. In the discussion of these results (lines 375-380), acetate is mentioned but not glycolate. Is this because it is expected that most of this combined signal is acetate or because glycolate is not

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expected to be an important oxalate precursor in these ambient mixtures?

Were any measurements of oxalate in the particle phase taken at SOAS? in lines 421-423, the authors state that based on their conclusions, it is unlikely that oxalate will be present in the particle phase, but it would be interesting to test this.

3 Technical Corrections:

Page 6, line 140: "ml" should be "mL"

Page 7, line 159: "Henry's law" should be "Henry's Law"

Page 12, line 270: Should this refer to Figures 2 and 4 instead of 2 and 3?

Page 13, line 288: Figure 3 does not show a mechanism, but only initial and final structures.

Page 14, line 327: It is unclear to me why the word "*these*" is italicized.

Page 16, line 363: There is an extra parenthesis at the end of the paragraph.

Supplementary Figure S2: This figure is missing axes labels.

Supplementary Figure S3 caption, line 2: "co-elude" should be "co-elute"