Reply to Interactive comment on "Compositional Evolution of Particle Phase Reaction Products and Water in the Heterogeneous OH Oxidation of Aqueous Organic Droplets" by Man Mei Chim et al.

Anonymous Referee #2

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-440, 2017.

The authors present experimental results on the OH oxidation of methyl succinic acid particles, which were generated from solution and maintained as aqueous particles at high humidity (RH=85%). Accompanying measurements of the water content of methyl succinic acid particles under varying humidity conditions are also presented. Experimental results for the oxidation rate of the methyl succinic acid and the hygroscopicity of methyl succinic acid are then used to model the changes in composition and size of methyl succinic acid particles as they are oxidized by OH. The model uses simplified chemistry (only two oxidation products and no secondary oxidation) with a sophisticated thermodynamic model (AIOMFAC) that predicts water content/particle size taking into account the changing activity coefficients of the methyl succinic acid, the two oxidation products, and water activity. The major conclusions are that oxidized methyl succinic acid particles increase in hygroscopicity and lose a notable amount of organic mass due to formation of volatile fragmentation products. The work presented is clearly described and presented fairly well. Understanding the oxidation of water soluble organic material, such as the di-acid presented here, is important in understanding the effects of water on particle oxidation processes. I recommend publication pending minor revisions.

We would like to sincerely thank the reviewer for his/her thoughtful comments and suggestions. Please see our responses to reviewer's comments and suggestions below.

General Comments

The authors must clarify the range of oxidation conditions. The high levels of oxidation are equivalent to a week in the atmosphere even for a moderate to high level of OH (2E6 mol/cmˆ3). A time axis for a given atmospheric OH level should be added to Figure 3.

Author Response:
We have clarified that the high levels of oxidation used in this work are equivalent to 8.5 days in the atmosphere for a moderate to high level of OH concentration (2×10^6 molecule cm^{-3}). This information is added to **Fig. 3** and the manuscript.

Page 5 Line 19, "The high levels of oxidation used in this work are equivalent to 8.5 days in the atmosphere for a moderate to high level of OH concentration (2×10^6 molecule cm^{-3})."

A better sense of the mass balance during the experiments is needed, particularly for the volatilization. Some analysis of the amount of organic material lost to the gas phase must be presented. Using a simple mass balance and the assumed (or known) product hygroscopicities, how much fragmentation/volatilization is suggested given your experimental results? The simplified chemical mechanism is hard to reconcile with the results in Figure 3, because it would appear that the ratio of the products should always be (0.57/0.37). It seems like the predicted decrease in particle size would require a greater extent of fragmentation/volatilization. In any case the results in Figure 3 should be more clearly discussed in terms of the simplified chemical mechanism.

Author Response:
We have analyzed the amount of organic material (i.e. fragmentation products) lost to the gas phase from our model simulations. The simulated particle-phase carbon mass normalized to its initial mass as a function of OH exposure is plotted in **Fig. 6** to investigate the extent of fragmentation and volatilization during oxidation. As shown in **Fig. 6**, about 7 % of the particle-phase carbon mass is lost at the maximum OH exposure. The relative abundance of major fragmentation product remaining in the particle phase is estimated to be 5 % as shown in **Fig. 3**. Volatilization and gas-phase oxidation of the fragmentation product is predicted to be significant as a greater fraction of the fragmentation products formed from oxidation is volatilized to the gas phase under our experimental conditions. This information is added in the revised manuscript.

Page 15 Line 15, "To quantify the amount of fragmentation products volatilized to the gas phase during oxidation, the normalized particle-phase carbon mass is plotted against OH exposure in **Fig. 6**. Model simulations show that about 7 % of the carbon mass is lost at the maximum OH exposure, while the relative abundance of particle-phase fragmentation product is about 5 %. Volatilization and gas-phase oxidation of the fragmentation product is predicted to be significant under the experimental conditions."

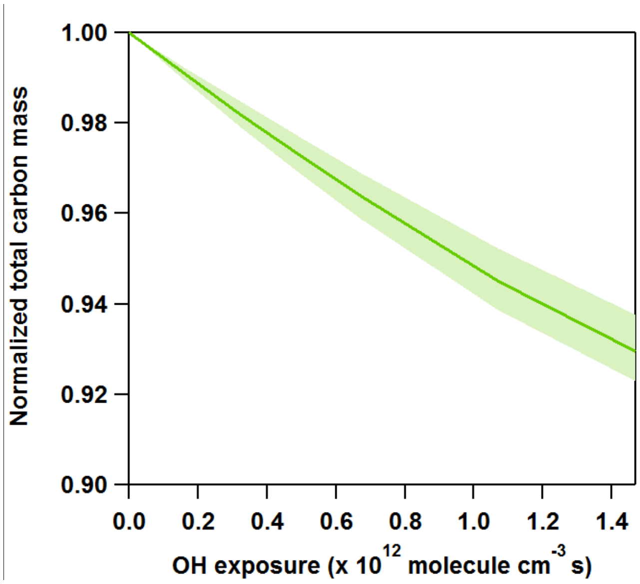
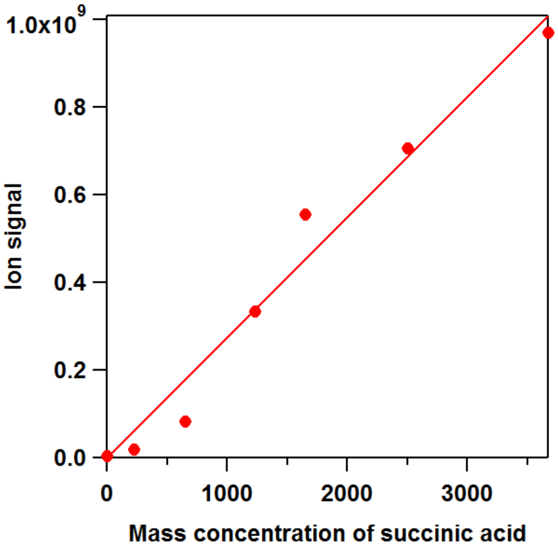


Figure 6. Simulated normalized total carbon mass during heterogeneous OH oxidation of aqueous methylsuccinic acid droplets at 85 % RH.

The linearity of your mass spectrometry measurements should be shown. All the analysis presented assumes that the response of your mass spectrometer is linear over the wide range of MSA and product concentrations. A calibration using known amounts of MSA, and the linearity of response up to signal levels of 10ˆ9, should be shown.

Author Response:

We agree with the reviewer's comment. However, the linearity of the methylsuccinic acid mass spectrometry measurement has not been tested when we performed the experiments about three years ago. In a separate study performed at the same time, we have measured the response of the mass spectrometer at different mass concentration of succinic acid particles using the same experimental setup. A quasi-linear response was observed over a range of aerosol mass concentration (see the graph below). As the methylsuccinic acid is structurally similar to succinic acid and very similar experimental conditions were applied in these two measurements, we assume that the response of the mass spectrometer is also linear for methylsuccinic acid.



Specific Comments

Page 7 Line (10) It should be directly stated that this rate constant is an effective rate constant for OH radicals with aqueous methyl succinic acid particles.

Author Response:

We have revised the sentence in the manuscript.

Page 8 Line 28, "the decay of methylsuccinic acid due to oxidation by OH exhibits an exponential behavior and can be fit with an exponential function to obtain an effective rate constant (*k*) for OH radicals with aqueous methylsuccinic acid particles:"

It needs to be clear that the rate constant for OH + MSA was not directly measured in a single phase. 14 (5) "As the oxidation proceeds further (i.e. to the higher OH exposures), the formation of the fragmentation product becomes more significant " It is not clear how the model accounts for this. Do the alpha values change during the course of the oxidation? Is secondary oxidation of the functionalization and fragmentation products taken into account? It seemed that the model description specifically does not include the secondary oxidation.

Author Response:
In the model, we assume that alpha values did not change during oxidation. Secondary oxidation of the functionalization and fragmentation products is not considered since the determined abundance of the second or higher generation reaction products is not significant. With the original sentence, we intended to mention that more fragmentation products are formed (in absolute, cumulative terms) as more methylsuccinic acid is oxidized; we did not intend to state that the fragmentation process become more favorable than the functionalization processes at higher oxidation stages. We have clarified this point and revised the sentence in the manuscript.

Page 15 Line 28, "As the oxidation proceeds further (i.e. to the higher OH exposures), more fragmentation product is formed in accumulative amount since more methylsuccinic acid is oxidized."

14(12) "The largest deviation is observed at the maximum OH exposure. This could be explained by that for the particle composition (Fig. 3), the model-experiment discrepancy increases with increasing OH exposure, as discussed in the preceding section." This point is nearly lost in the awkward sentence construction. Please re-word such as: "The large deviation in particle size observed at the maximum OH exposure can be explained by the poorly predicted particle composition at high OH exposure (Fig. 3)."

Author Response:
We have revised the sentence in the manuscript.

Page 16 Line 5, "The larger deviation in particle size observed at the maximum OH exposure can be explained by the poorly predicted particle composition at high OH exposure (**Fig. 3**)."

14(30) "net hygroscopicity of the aerosols is slightly enhanced due to the formation of more oxidized functionalization products." Hygroscopicity is an intensive property, so the term "net" hygroscopicity lacks a clear meaning. In fact you present that the hygroscopicity of the particle organic content increases. In other words, the activity of water is further suppressed. The particles lose water due to loss of mass of soluble material. Please remove the term "net hygroscopicity" and re-word this sentence more similarly to Page 1 line 33.

Author Response:
We have revised the sentence in the manuscript.

Page 16 Line 21, "Although the oxidized droplets can uptake more water than unreacted ones (relative to the organic content), the hygroscopicity of the aerosols is reduced as the number of water molecules is found to decrease at the entire OH exposure."