

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

Received and published: 7 July 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,

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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.

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 ($2E6 \text{ mol/cm}^3$). A time axis for a given atmospheric OH level should be added to Figure 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.

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 10^9 , should be shown.

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.

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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.

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)." 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.

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