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Atmospheric Chemistry and Physics Discussions

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 #3

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This is an interesting paper that has lots of interesting aspects to it. Two different experimental approaches are used: laser tweezers for aerosol hygroscopicity measurements and DART MS for aerosol oxidation. The experimental results are understood using extensive chemical mechanism prediction and a kinetic model which uses thermodynamic input from the AIOMFAC model. However, the paper has a number of deficiencies that need to be tackled before it can be published. There are lots of details missing that are required for subsequent researchers to replicate the experiments. And the methodology makes some big assumptions that need to further explored.

Major Comments Since this paper is in an atmospheric journal, it needs to acknowl-

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edge that the oxidation experiments were run under non-atmospheric conditions. In particular, the OH concentrations were very far from being atmospherically relevant, even if the exposures are reasonable. What possible consequences are there of using the very high OH concentrations?

What is the size distribution of the aerosols in the flow tube experiments? An average size is stated (P7 L 19, 237.2 nm diameter) but no details of the size of the distribution is given. This is important since size has been shown to be important for aerosol reactivity as shown in Al Kindi et al. (2016). The work of Marcoli et al. (2004) suggests that the deliquescence point of methyl succinic acid is 95%, which is significantly higher than the RH used in the heterogeneous oxidation experiments. How did you ensure the particles were aqueous? Do you disagree with the results of Marcoli et al.?

The ionization efficiency of all oxidation products is assumed to be the same as methyl succinic acid (P7 line 3). This is a big assumption. Previous MS work has shown that ionization efficiencies vary massively. For example, in Al Kindi et al. (2016) there is approximately a factor of 20 between difference dicarboxylic acids and mono-carboxylic acids, albeit whilst using a different type of MS. The Orbitrap approach has also shown big differences in ionization efficiency as well – see the work and references of Markus Kalberer in Cambridge including Gallimore et al. (2011). Since the simplified reaction scheme uses products with 3 and 1 carboxylic acid groups, I really worry how the experimental results with the huge uncertainties in ionization efficiency can be fed into this model. This point has potential repercussions throughout the paper especially with respect to the modelling and reaction mechanism sections. For example, on P8 L26 “The low abundance of smaller products is presumably due to their higher volatility. . .” or it could be that their ionization efficiency is much smaller because of a lack of carboxylic acid and other functional groups. Another example is on P13 L10, the fitted yields will be very different if the ionization efficiencies are significantly different to each other. These repercussions need to be made very clear and more justification of the approach is required. I understand that standards might not be available but if the relative concentrations cannot be known then it makes for very weak foundations for the rest of the paper.

In the conclusion it needs to be emphasized that a highly idealized system was investigated. This system can potentially provide insights into atmospheric chemistry but it does not mimic real atmospheric chemistry due to the atmospherically unrealistic single component system, high OH concentrations, etc.

Minor comments Title – should acknowledge that the paper investigates the OH oxidation of methyl succinic acid not organic species in general. Suggested title "Composition evolution of particle phase reaction products and water in the heterogeneous OH oxidation of aqueous methyl succinic acid droplets"

Abstract – line 16 change "at/near" to "at or near"

Intro – somewhere in the intro it should be noted that methyl succinic acid is a deliquescent compound, see Marcolli et al. (2004)

Intro – line 4 "This radical initiated heterogeneous oxidation. . ." Previous sentence talks about ozone as well as OH. Ozone is not a radical species.

Intro P2 – line 5 ". . .change the aerosol composition and, therefore, alters the properties of aerosols.." This statement is too strong. I think the jury is still out about how important organic oxidation is for general aerosol properties.

Intro P2 – lines 15-20 – there is a nice description of the roles of water in organic aerosol chemistry in Gallimore et al. (2011). The water can modify the viscosity/diffusion. It can also act as a reactant, this is in comparison to the reference given in the text Chim et al. (2017). The Gallimore reference is for ozonolysis of organic species but the water could still potentially interact with the radical chemistry.

Intro P3 – line 2 – changing composition can also change the deliquescence and efflorescence points of aerosol.

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P4 – lines 4-5 – need to make clear that methyl succinic acid whilst one of the most abundant components in aerosol, its concentration is still low compared to all the other species. i.e. understanding the reactivity of one species does not give you a good understanding of the total aerosol composition reactivity.

P4 Line 17 what concentration of ozone was used? Note at high concentrations, ozone can react with moieties other than double bonds.

P4 L27 – how do you know that all particles are vaporized at 250 ïĆřC? What is the evidence? Or if appropriate, provide a reference.

P5 Line 3 – this seems like an excessive number of references for one technique. What do the different papers add? Which one is the key reference?

P5 Line 5 – How good was the mass calibration, how accurately can you define the different reaction products?

P5 hygroscopicity measurements – how many particles were measured? It sounds like only one particle was measured? If this is the case, then that is a little cavalier but the agreement with Marsh et al. gives confidence. What do the error bars in Figure 1 represent?

P6 L4-4 the assumption that AIOMFAC is good predictor of oxidation produce hygroscopicity because it correctly predicts the hygroscopicity of methyl succinic acid seems quite big. It would be good to reference papers that look at the general performance of AIOMFAC. Does AIOMFAC make good predictions of species with similar functional groups as the oxidation products measured in this paper?

P6 L15-23 a long justification is given for possible differences between the CK-EDB and laser tweezer experiment. Since the two measurements agree with each other, within experimental errors, I'm not sure the justification is required?

P7 Line 22. The error bars on the gamma value need to be acknowledged. I think the large error bars preclude a discussion of the gamma likely being greater than 1. For

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OH, a gamma of 1 is expected.

P11 Line 3 When the error in the gamma measurement is propagated through the model what is the outcome?

References

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