Reply to Interactive comment on "Effects of Inorganic Salts on the Heterogeneous OH oxidation of Organic Compounds: Insights from Methylglutaric Acid-Ammonium Sulfate" by Hoi Ki Lam et al.

Anonymous Referee #2

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-218-RC1, 2019.

This study reports differences in the heterogeneous OH oxidation kinetics and particle-phase products of representative pure-component organic aerosol and mixed organic-inorganic aerosol under conditions of particle deliquescence. The authors report the reactive uptake coefficients between OH + methylglutaric acid and OH + methylglutaric acid/ammonium sulfate aerosol measured using an oxidation flow cell coupled with a direct analysis in real time (DART) mass spectrometer and conclude that while oxidation products are similar between the two aerosol systems, the uptake kinetics are significantly slower in the case of the methylglutaric acid/ammonium sulfate aerosol mixture. Overall, the manuscript is well written, the topic is of interest, and the study appears to be sound/not overstated. I recommend publication in ACP after the authors respond to the following comments.

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.

Comment #1

Page 2, line 4: Be careful not to understate the role of dissolved salts – this study was performed on deliquesced particles at 85% relative humidity. Because of the hygroscopicity of AS, 3-MGA–AS will deliquesce at a lower relative humidity than pure 3-MGA particles. This may not significantly affect the reaction mechanism itself, but diffusion of reactants from the particle bulk to the surface may be quite different at a different relative humidity, thus the extent of reaction I would expect depends also on the diffusivity of the reactants, which may be more important under more relevant daytime relative humidity (when [OH] peaks in the real environment). Written like this suggests the inorganic component has no influence on the reaction.

Author Response:

Thanks for the comment. We did experiments to show that the water activity of saturated 3-MGA solution is 0.935 (i.e. DRH = 93.5%). The effloresced 3-MGA–AS particles absorbed water gradually upon moistening, with the AS rich phase dissolved at ≤ 80% RH and the remaining fully deliquesced at ~85 % RH. These observations agree with the reviewer's comment that 3-MGA–AS particles deliquesce at a lower RH than pure 3-MGA particles. We acknowledge that this work only investigates the role of dissolved salts in the heterogeneous reactivity of well-mixed aqueous organic–inorganic droplets at a sufficiently high relative humidity (85%). The effects of inorganic salts on the heterogeneous reactivity could vary greatly, depending on the particle composition and environmental conditions (e.g. RH and temperature). For instance, as pointed out by the reviewer, the diffusivity of species from bulk to the surface plays an important role in the extent of heterogeneous reaction. For aqueous 3-MGA–AS particles at 85 % RH in our work, we are not certain about the effect of AS on the particle viscosity, but the viscosity is expected to be in the liquid-like regime due to the substantial water content. We postulate that the particle viscosity may decrease due to the increase in water uptake by the addition of hygroscopic, dissolved AS, which allows for faster bulk diffusion of species. Therefore, 3-MGA–AS particles are likely well-mixed during oxidation and no substantial bulk diffusion limitation is expected in our case. On the other hand, at lower RH, aqueous 3-MGA–AS droplets likely become more concentrated and more viscous before efflorescence, possibly giving rise to diffusion limitation during oxidation. To our best knowledge, the effect of inorganic salts on the particle viscosity of organic–inorganic mixed phases remains largely unexplored. Further studies on the effect of inorganic salts on diffusivity of the reactants within organic–inorganic particles are warranted. We have revised the manuscript and added the information above.

Page 2, Line 13, "Our results suggest that inorganic salts likely alter the overall heterogeneous reactivity of organic compounds with gas-phase OH radicals rather than reaction mechanisms in well-mixed aqueous organic–inorganic droplets at a high humidity (i.e. 85% RH). It also acknowledges that the effects of inorganic salts on the heterogeneous reactivity could vary greatly, depending on the particle composition and environmental conditions (e.g. RH and temperature). For instance, at lower relative humidities, aqueous 3-MGA–AS droplets likely become more concentrated and more viscous before efflorescence, possibly giving rise to diffusion limitation during oxidation under relatively dry or cold conditions. Further studies on the effects of inorganic salts on the diffusivity of the species under different relative humidities within the organic–inorganic particles are also desirable to better understand the role of inorganic salts in the heterogeneous reactivity of organic compounds."

Comment #2

Page 5, lines 10-12: Presumably, quantification of [OH] was done prior to addition of the aerosol particles to the flow cell? The reported second-order rate coefficients for heterogeneous OH oxidation of 3-MGA and 3-MGA–AS (2.72-3.26×10^{-12} *cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$*) are competitive with that for hexane (5.21×*10^{-12} *cm*^{3} *molecule*$^{-1}$ *s*$^{-1}$*) (Atkinson, 2003). Please specify. If mixed, how would this affect the determination of [OH]?*

Author Response:

In this study, the OH exposure was determined by the in-situ measurement of the decay of gas-phase hexane in the presence of particles inside the reactor using a gas chromatograph coupled with a flame ionization detector (GC-FID). Hence, the impacts of competitions between the heterogeneous oxidation and the gas-phase oxidation on the quantification of OH concentration have been taken into account. We have revised the manuscript to clarify the point.

Page 6, Line 8, "Since the OH exposure (and OH concentration) was determined by the in situ measurement of the decay of gas-phase hexane inside the reactor, the impacts of RH and water uptake by particles inside the reactor on the generation and concentration of gas-phase OH radicals have been taken into account. The competitions between the heterogeneous oxidation and the gas-phase oxidation have also been considered when quantifying OH concentration."

Comment #3

Page 5, lines 21-23: Please indicate where the relative humidity measurement was made in the setup. Do you expect the particles that get sampled through the inlet of the DART instrument to be at a different relative humidity than when they were oxidized? From personal experience, Carulite catalyst can decrease the relative humidity. Please comment on potential variations in the relative humidity as part of the experimental setup and whether it has an effect on the products analyzed.

Author Response:

The relative humidity (RH) was measured at the inlet of the reactor. We have not measured the RH of the particle stream before and after the Carulite catalyst denuder and do not know to what extent the humidity of the particle stream dropped. We agree with the reviewer that the RH inside the reactor was slightly higher than RH after passing through the Carulite catalyst denuder. Although the particles got sampled at a different RH during the DART analysis, this would not have significant effect on the reaction products analyzed because the decrease in RH after oxidation would not significantly affect the formation of reaction products which primarily occurred inside the reactor. We have revised the manuscript and added the information above.

Page 5, Line 14, “The RH within the reactor was controlled by varying the dry N_2 to humidified N_2 ratio and was measured at the inlet of the reactor.”

Page 6, Line 15, “It acknowledges that Carulite catalyst denuder can slightly decrease the RH of the particle stream. However, this would not have significant effect on the reaction products analyzed, because the decrease in RH after oxidation would not significantly affect the formation of reaction products, which primarily occurred inside the reactor.”

Comment #4

Page 6, lines 1-4: It is known that thermal desorption methods lead to inaccurate estimates of particle volatility, e.g., Stark et al. (2017) demonstrate that many organic acids and alcohols, common constituents of secondary organic aerosol, can decompose at temperatures as low as 200 ◦C. In that study, a significant fraction of detected compounds resulted from thermal decomposition, suggesting the detected fragments were not actually present in the atmosphere, but rather formed during decomposition in the inlet of the instrument. Please discuss potential caveats of the thermal desorption technique used here and its impact on the observed product distribution.

Author Response:

Thanks for the comments. The thermal composition of particle-phase products could possibly occur during the thermal desorption processes in our chemical analysis. The mass spectra of some organic acids and alcohols (e.g. succinic acid, ketosuccinic acid and tartaric acid) are available in the work of Chan et al. (2014), showing insignificant thermal decomposition during the DART analysis. In this study, the thermal decomposition of 3-MGA was found to be insignificant before oxidation as the deprotonated molecular ion of 3-MGA is the dominant peak in the mass spectra (Figure 1). We acknowledge that the reactions between peroxy radicals may yield organic peroxides and oligomers, which may decompose thermally. We cannot completely rule out the possibility of that, but there was no indication of any fragment ions expected from the thermal decomposition in the mass spectra. Together, these results suggest that the impact of thermal decomposition on the observed product distribution is likely insignificant. This information is added in the revised manuscript

Page 7, Line 17, “It acknowledges that thermal composition of reaction products could possibly occur during the thermal desorption process (Stark et al. 2017). The mass spectra of some organic acids and alcohols (e.g. succinic acid, ketosuccinic acid and tartaric acid) are available in the work of Chan et al. (2014), showing insignificant thermal decomposition during the DART analysis. In this study, the thermal decomposition of 3-MGA was found to be insignificant as the deprotonated molecular ion of 3-MGA is the dominant peak before oxidation in the mass spectra (**Figure 1**). We acknowledge that reactions between peroxy radicals may yield organic peroxides and oligomers, which may decompose thermally. We cannot completely rule out the possibility of such reactions, but there was no indication of any fragment ions expected from the thermal decomposition in the mass spectra. Together, these results suggest that the impact of thermal decomposition on the observed product distribution is likely insignificant.”

Comment #5

Page 9, lines 4-5: Please specify whether these studies were performed using mono or polydisperse aerosol. Are the reported diameters a median value or geometric mean? Also, are the reported diameters number- or surface area-weighted? Please comment on the effect of particle size, e.g., regarding evaporation (Vaden et al., 2011) and mixing timescales of volatile/semi-volatile components (Meng and Seinfeld, 1996).

Author Response:

Thanks for the comment. Polydisperse particles were used in this work. The diameter reported is the surface area-weighted mean diameter of these particles. Upon oxidation, fragmentation products evaporate and partition back to the gas phase. Vaden et al. (2011) have discussed that evaporation of highly viscous particles is likely independent of particle size distribution and is unlikely to be significantly influence the overall evaporation behavior. As the study of Vaden et al. (2011) focused on highly viscous particles while the focus of this study is more liquid-like particles, their results may not be applicable in our study. Since 3-MGA-AS particles are more liquid-like particles, the evaporate rate would scale with the total surface area of the polydisperse particle population. Since the spread of the polydisperse particle population is small in this work, the size change is not likely substantial with regard to determining γ_{eff} as the total particle surface area did not change dramatically. In the work of Meng and Seinfeld (1996), the mixing timescales of volatile/semi-volatile species are evaluated. Although it was suggested by the study that the timescales may increase with increasing particle size, the difference may not be that significant in our study as the span of the polydisperse particles is much smaller than the difference between coarse particles and fine particles used in their studies. We thus postulate that the spread of particle size and the mixing timescale would not play a role in the evaporation of fragmentation products during oxidation. We have revised the manuscript.

Page 10, Line 16, “The surface-weighted mean diameters prior to OH oxidation (203.0 nm for 3-MGA and 200.8 nm for 3-MGA–AS, respectively) are used in the calculation of γ_{eff}. Upon oxidation, the surface-weighted mean diameters decreases from 203.0 nm to 170.7 nm for 3-MGA particles and decreases from 200.8 nm to 187.8 nm for 3-MGA–AS particles (**Figure S5**, *supplementary material*). The decrease in the particle diameter upon oxidation is likely attributed to the formation and volatilization of fragmentation products and the associated evaporative loss of water molecules. Vaden et al. (2011) have discussed that evaporation of highly viscous particles is likely independent of particle size distribution and is unlikely to be significantly influence the overall evaporation behavior. As the study of Vaden et al. (2011) focused on highly viscous particles while the focus of this study is more liquid-like particles, their results may not be applicable in our study. Since 3-MGA-AS particles are more liquid-like particles, the evaporate rate would scale with the total surface area of the polydisperse particle population. Since the spread of the polydisperse particle population is small in this work, the size change is not likely substantial with regard to determining γ_{eff} as the total particle surface area did not change dramatically. In the work of Meng and Seinfeld (1996), the mixing timescales of volatile/semi-volatile species are evaluated. Although it was suggested by the study that the timescales may increase with increasing particle size, the difference may not be that significant in our study as the span of the polydisperse particles is much smaller than the difference between coarse particles and fine particles used in their studies. We thus postulate that the spread of particle size and the mixing timescale would not play a role in the evaporation of fragmentation products during oxidation."

Comment #6

Page 9, lines 11-12: Isn't γeff for 3-MGA–AS more than twice as small as that for 3- MGA, rather than 59%? The relative percent difference is 59%. This is a bit confusing as written. Please consider rephrasing. Did the authors measure the aerosol size distribution after OH oxidation? If so, is there evidence of particle mass growth (functionalization) or volatilization (fragmentation)? This can be assessed simply by plotting the ratio of initial aerosol volume to final aerosol volume as a function of OH exposure. Such an analysis would be a valuable addition to the paper. The authors provide a reasonable argument for the difference in γeff between 3-MGA and 3-MGA–AS particles, but I would caution extension (i.e., overall applicability) of Eq. S1 to other aerosol systems at different relative humidity. Equation S1 is an oversimplification of the likely complex interactions and concentration gradients present in atmospheric aerosol. In this study, Eq. 1 simply indicates there is less 3-MGA in the 3-MGA–AS mixture to react with OH compared to the pure 3-MGA particles. However, if the particles were phase-separated or exhibited core-shell structure, e.g., at low relative humidity, does Eq. S1 indicate what is at the surface?

Author Response:

Thanks for the comments. We have rephrased the sentence in the revised manuscript that the values of γ_{eff} for 3-MGA particles is larger than that of 3-MGA–AS particles by about 2.4 times.

The size distribution was measured after OH oxidation using the SMPS. The size decreases upon oxidation from 203 to 171 nm for 3-MGA and from 201 to 188 nm for 3-MGA–AS. This may be an indicator of the possible volatilization (fragmentation) processes. We have added the plot of particle size against OH exposure (**Figure S5**, *supplementary material*) in the supplementary material.

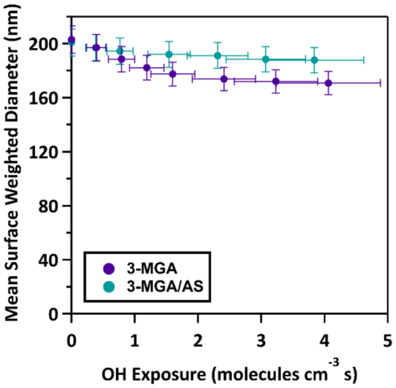

Figure S5. The change in surface-weighted mean diameter as a function of OH exposure for 3-MGA particles and 3-MGA–AS particles, respectively.

We agree with the reviewer that Eqn. S1 may not be applicable to providing explanations for particles with complex interactions and concentration gradients such as phase separation. This equation would fail for predicting the surface composition if the particles were phase-separated or exhibited core-shell structure. Understanding the surface activity of 3-MGA and performing molecular dynamic simulations are desirable to better understand the surface composition of the particles with different phases (e.g. well-mixed homogeneous liquid phase or phase separated). We have added the following information in the revised manuscript.

Page 6, Line 18, "Size distribution of the particles was determined by sampling a small portion of the particle stream using a scanning mobility particle sizer (SMPS, TSI) after oxidation took place."

Page 10, Line 16, "The surface-weighted mean diameters prior to OH oxidation (203.0 nm for 3-MGA and 200.8 nm for 3-MGA–AS, respectively) are used in the calculation of γ_{eff}. Upon oxidation, the surface-weighted mean diameters decreases from 203.0 nm to 170.7 nm for 3-MGA particles and decreases from 200.8 nm to 187.8 nm for 3-MGA–AS particles (**Figure S5**, *supplementary material*). The decrease in the particle diameter upon oxidation is likely attributed to the formation and volatilization of fragmentation products and the associated evaporative loss of water molecules."

Page 11, Line 23, "The value of γ_{eff} for 3-MGA particles is larger than that of 3-MGA–AS particles by about 2.4 times."

Supplementary material, Page 4, Line 15, "However, it acknowledges that the assumption might not be completely correct. In accordance with the work of Jungwirth et al. (2003) and Jungwirth and Tobias (2006), the sulfate ion (SO_4^{2-}) likely exists in the interior of the particle instead of surface. We also cannot rule out the possibility of 3-MGA being a surfactant as literatures on cloud droplet activation indicate possible surface enhancement of dicarboxylic acid such as suberic acid in dilute aqueous droplets (Ruehl et al., 2016; Davies et al., 2019). However, literature on the surficial properties of branched dicarboxylic acid is not yet available. Further investigation on the surface activity of 3-MGA and molecular dynamic simulations are desirable to better understand the surface composition of 3-MGA and 3-MGA–AS particles. It is also noted that Eqn. S1 may not be applicable to providing explanations for particles with complex interactions and concentration gradients such as phase separation. This equation would fail for predicting the surface composition if the particles were phase-separated or exhibited core-shell structure."

Supporting material, we have added the **Figure S5** in the *supporting material* to illustrate the change in particle diameter for 3-MGA particles and 3-MGA–AS particles upon oxidation

References

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4. Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kang, H., Krechmer, J. E., Kimmel, J. R.,Palm, B. B., Hu, W. W., Hayes, P. L., Day, D. A., Campuzano-Jost, P., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Impact of Thermal Decomposition on Thermal Desorption Instruments: Advantage of Thermogram Analysis for Quantifying Volatility Distributions of Organic Species, Environ. Sci. Technol., 51, 8491-8500, 2017.

5. Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proceedings of the National Academy of Sciences of the United States of America, 108, 2190-2195, 10.1073/pnas.1013391108, 2011.