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 #1

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

This study examines the impact of the presence of hygroscopic ammonium sulfate (AS) on the heterogeneous OH oxidation of 3-methylglutaric acid (3-MGA) particles at 85% relative humidity (RH). Complementary microscopy measurements show that 3-MGA–AS particles are in a single liquid phase prior to oxidation at high RH. The effective OH uptake coefficient for 3-MGA–AS particles is determined to be smaller than that for 3- MGA particles by about a factor of ~2.4. The OH oxidation products are found to be the same for both particle systems investigated using Direct Analysis in Real Time (DART). The observation of smaller reactivity for 3-MGA–AS particles is explained by a higher surface concentration of water molecules and ammonium and sulfate ions, which are chemically inert to OH radicals. This may lower the collision probability between the 3-MGA and OH radicals, resulting in a smaller overall reaction rate but similar reaction products. The topic of this study fits well within the scope of Atmospheric Chemistry and Physics. Indeed, the impact of salts on the heterogeneous oxidation kinetics of organic particulate mass involving OH radicals has not been much studied. This manuscript reads well and I have only minor revisions to suggest before publication of this study.

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

For making interpretation of the data easier, it would be beneficial to mention some experimental parameters regarding the flow reactor OH exposure studies. For example, after atomization, the particles are likely in a solid/crystalline phase state. How long was the particle residence time in the flow reactor? Is it assumed that the particles were completely deliquesced for the entire OH exposure time (residence time)? In other words, did the particles have sufficient time to adjust to RH? How was RH controlled and maintained in the flow reactor? RH and water uptake may impact OH concentration? How water soluble is 3-MGA? Comparison to similar soluble species and corresponding hygroscopicity factor (and growth) should be mentioned to support the case that the particles are homogeneously mixed under the conditions in the flow reactor experiment.

Author Response:

Thanks for the comments. In our experiments, aqueous droplets generated by the atomizer did not pass through a diffusion dryer and were directly mixed with gases such as humidified nitrogen, oxygen, ozone and hexane before entering the flow tube reactor. The aqueous droplets would have sufficient time to adjust to RH (i.e. 85%) after mixing and before entering the reactor. Since the particles were always exposed to high humidity in our system, 3-MGA and 3-MGA–AS particles were always aqueous droplets for the entire OH exposure. The particle residence time in the flow tube reactor is experimentally determined to be 1.3 min.

The RH was controlled and maintained by the ratio of dry to humidified nitrogen stream being introduced into the reactor. A water jacket around the flow tube reactor was used to maintain temperature inside the reactor. In this study, gas-phase OH radicals were generated through the photolysis of ozone in the presence of water vapor. The concentration of OH radicals would be higher when RH (and the amount of water vapor) increases. Since the particles had achieved their equilibrium states before entering the reactor, we expect the water uptake of particles would not significantly alter the amount of water vapor inside the reactor and the generation of gas-phase OH radicals. Furthermore, in this study, the OH exposure was determined by the in situ measurement of the decay of 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 would have been taken into account.

We have measured a solubility of 45.3 wt% in water for 3-MGA at 298K, which is highly soluble. The hygroscopicity data of 3-MGA has been shown in the work of Marsh et al. (2017) with a growth factor of ~1.2 at 85 % RH. As shown by the hygroscopicity curve measured, 3-MGA particles absorb and desorb water reversibly as the RH increases or decreases, indicating that they are likely aqueous droplets prior to oxidation. With the addition of AS, the morphology of 3-MGA–AS particles (OIR = 2) upon dehumidification also demonstrate a homogeneous single liquid phase (see the supplementary material), suggesting that 3-MGA–AS particles are likely well-mixed at high humidity (i.e. 85%). We have added the above information in the revised manuscript.

Page 5, Line 12, "In brief, the particle stream did not pass through a diffusion dryer and was directly mixed with O_3, oxygen (O_2), dry nitrogen (N_2), humidified N_2 and hexane before being introduced into the reactor. 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. A water jacket around the reactor was used to maintain a constant temperature of 20 °C inside the reactor."

Page 5, Line 23, "The OH exposure, a quantity defined as the product of OH concentration and particle residence time (~1.3 min), can be determined by the following equation (Smith et al., 2009):"

Page 6, Line 8, "Since the OH exposure (and OH concentration) was determined by the in situ measurement of the decay of hexane, 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."

Page 8, Line 7, "The hygroscopicity data of 3-MGA has been reported in the work of Marsh et al. (2017) with a growth factor of ~1.2 at 85 % RH. As shown by the hygroscopicity curve measured, 3-MGA particles absorb and desorb water reversibly as the RH increases or decreases, indicating that they are likely aqueous droplets prior to oxidation. Optical microscopy measurements have been carried out (**Figure S1**, *supplementary material*) and show that 3-MGA–AS particles are in a single-liquid phase prior to oxidation at 85.0 % RH as the particles become phase-separated when the RH is below the separation RH (SRH = 72.7–73.6 %) (**Figure S2**, *supplementary material*). Details of the optical microscopy measurements have been given in the Supplementary Material."

Comment #2

The size of the particles is a crucial input parameter when deriving the uptake coefficient. It is not clear if the particle size distribution was measured under dry or humidified conditions? It is also not clear if the size distribution was determined before or after OH oxidation? If acquired after oxidation, one would need to show that the particle sizes did not change upon oxidation. Lastly, which particle diameter was chosen to calculate the uptake coefficient? Does the spread and uncertainty in the size distribution contribute significantly to the uncertainty in the reactive uptake coefficient?

Author Response:

The particle size distribution was measured under humidified conditions after leaving the reactor at each OH exposure recorded. From the particle size measurements, the surface-weighted mean diameter 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 upon oxidation (please see the figure below). 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. We have added the change in particle diameter as a function of OH exposure (**Figure S5**, *supplementary material*) in the supporting material.

The particle size used in the calculation of the uptake coefficient (i.e. γ_{eff}) is the mean surface-weighted diameter prior to OH oxidation. As the change in particle size upon oxidation is not very significant, the initial mean surface-weighted diameter was used. We did not account for the change in particle diameter in our calculation of uptake coefficient. The uptake coefficient in this work may thus be considered as an initial uptake coefficient.

We agree with the reviewer that the spread of particle size could potentially affect the determination and uncertainty of uptake coefficient but we could not quantify it since the particles are polydisperse in this study. To address this comment, we would like to suggest that future investigations can be carried out to measure the uptake coefficients for both monodispersed (size-selected) particles and polydispered particles for the same reaction system upon oxidation. The uptake coefficients assembled from different monodisperse particle populations can be compared with that obtained from polydisperse particle populations using the mean surface-weighted diameter in order to assess how the spread and uncertainty in the size distribution of polydisperse particle affect the determination of the uptake coefficient. We have revised the manuscript to clarify these issues.

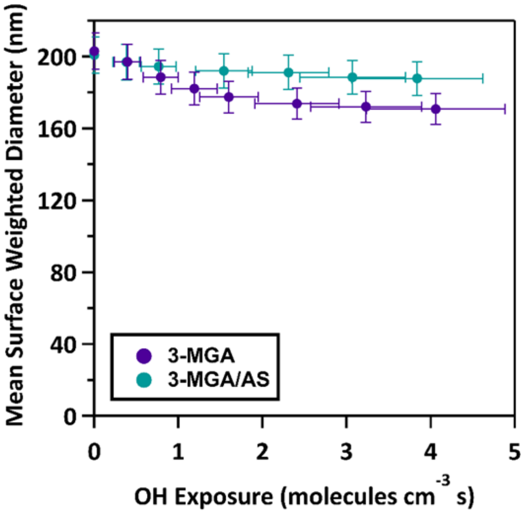

Figure S5. The change in surface-weighted mean diameter as a function of OH exposure for 3-MGA particles and 3-MGA–AS particles, respectively.

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 diameter 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 Meng and Seinfeld (1996). We thus postulate that the spread of particle size and the mixing timescale would not play a substantial role in the evaporation of fragmentation products during oxidation. As the change in particle size upon oxidation is not very significant, the change in particle diameter was not accounted for in the γ_{eff} calculation. The γ_{eff} may thus be considered as an initial uptake coefficient (Chim et al., 2018). We acknowledge that the spread of particle size could potentially affect the uncertainty and determination of γ_{eff}, but we could not quantify it since the particles are polydisperse in our study. Future investigations can be carried out to measure the γ_{eff} for both monodisperse (size-selected) and polydisperse particle populations. The γ_{eff} assembled from different monodisperse particle sizes can be compared with that obtained from polydisperse populations using the surface-weighted mean diameter in order to assess how the spread and uncertainty in the particle size distribution of polydisperse particle populations affect the determination of γ_{eff}."

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.

Comment #3

The reactivity between 3-MGA and 3-MGA–AS particles varies by a factor of 2.4. The authors suggest that this is due a different surface concentration of 3-MGA and corresponding difference in collision flux among these particle systems. I am wondering why the authors do not show this using, e.g., the resistor model? In the derivation of the reactive uptake coefficient, one normalizes with the collision flux. Assuming a surface reaction, one may be able to verify, if indeed the change in collision flux can explain the difference in the determined uptake coefficients. If added to the manuscript, this would significantly elevate the results of this manuscript.

Author Responses

Thanks for the suggestion. We agree with the reviewer that a quantitative analysis could provide more insight into how change in collision flux or particle surface composition would affect the oxidative kinetics. As suggested by the reviewer, we have attempted to analyze the uptake coefficient ($\gamma_{\text{meas}} = \gamma_{\text{eff}}$) using a resistor model developed by Worsnop et al. (2002)

$$\frac{1}{\gamma_{meas}} = \frac{1}{\Gamma_{diff}} + \frac{1}{S} + \frac{1}{\Gamma_s + \frac{1}{\frac{S-\alpha}{S\alpha} + \frac{1}{\Gamma_{rxn}}}} + \frac{1}{\Gamma_{diff}^{p}} \qquad (\text{Eq. }1)$$

where Γ_{diff} represents gas-phase diffusion, Γ_s represents surface reaction, S is the adsorption accommodation coefficient, α is the mass accommodation coefficient, Γ_{rxn} represents chemical reaction in the particle bulk and Γ_{diff}^{p} represents a diffusion-limited gradient of the reactant concentration (i.e. 3-MGA) within the particle. For heterogeneous oxidation, the gas-phase species (i.e. OH radical) are likely reacting with particle-phase species (i.e. 3-MGA) at or near the surface via a mechanism that is kinetically separable from reaction within the particle bulk or from other processes. If we assume an efficient surface reactivity, we could simplify the resistor model into (Eq. 2), which represents for the surface reaction (Worsnop et al., 2002):

$$\gamma_{\text{meas}} = \Gamma_s = \frac{4k_2^s H_s RT K_s [Y]}{\bar{c}} \qquad (\text{Eq. }2)$$

where k_2^s is the second-order rate constant at the surface, H_s is the Henry's law constant (M atm^{-1} L^{-1}), $[Y]$ is the surface concentration of the species (i.e. 3-MGA), K_s is the thermodynamic equilibrium constant linking the surface concentration to the bulk concentration (or activities when non-ideality is considered) and $\bar{c}$ is the average thermal speed of gas-phase OH molecules. We would like to note that this formulation (Eq. 1) has been normalized to the molecular collision rate (Worsnop et al., 2002). If we understand the reviewer's comment correctly, we could not assess how the change in collision flux (equivalent to molecular collision) affects the determination of uptake coefficient ($\gamma_{\mathrm{meas}} = \gamma_{\mathrm{eff}}$). From Eq. 2, the reduced form of the resistor model for surface reaction also suggests that the uptake coefficient would depend on the surface concentration of 3-MGA (i.e. $K_s[Y]$). While some parameters required in this formulation can be obtained in this study (e.g. γ_{meas} and k_2^s), some parameters (e.g. H_s and K_s) are not well understood for 3-MGA and 3-MGA–AS particles. This might limit the use of the model for the analysis. We would also like to acknowledge that the uptake coefficient considered by Worsnop et al. (2002) as well as many other resistor models is reported from the perspective of a colliding gas-phase OH radical, whereas the one measured in this work is reported from the perspective of a 3-MGA molecule at the particle surface. Thus, the results obtained from these two approaches may not be comparable. We thus do not plan to analyze the kinetic data using the resistor model, but agree that dynamic and molecular simulations together with the experimental data would greatly help to understand how the change in collision flux and particle surface composition govern the rate of reactions.

Specific Comments #1

Page 3, line 5: Please add the studies by Petters et al., GRL, 2006, Slade et al., ACP, 2015 and Slade et al., GRL, 2017 who studied the OH oxidation of organic and inorganic/organic particles and its effect on hygroscopicity.

Author Response:

We have cited the studies mentioned in the revised manuscript.

Page 3, Line 12: “These heterogeneous oxidative processes can continuously alter the surface and bulk composition of the particles (Slade and Knopf, 2013; Li et al., 2018), and thus modify particle properties such as light extinction, hygroscopicity and cloud condensation nuclei activity (Petters et al., 2006; George et al., 2007; Lambe et al., 2007, 2009; Cappa et al., 2011; Slade et al., 2015; Slade et al., 2017).”

Specific Comments #2

Page 4, line 24: As mentioned in general comments, more details on SMPS measurements are required.

Author Response:

We have added more details on SMPS measurements and discussed the use of surface-weighted mean diameter prior to OH oxidation for the calculation of the uptake coefficient in the revised manuscript. Please see our response in **Comment #2**.

Specific Comments #3

Page 9, Equation 3: Please discuss particle diameter applied.

Author Response:

We have mentioned that the surface-weighted mean diameter prior to OH oxidation was used in the calculation of the uptake coefficient. Please see our response in **Comment #2**.

Specific Comments #4

Page 9, Line 15–20 and Page 10, Line 1–8: It may be a too simple assumption that the ions are homogeneously distributed in small droplets. Please refer to Jungwirth and Tobias, Chem. Rev., 2006; Jungwirth et al., Chem. Phys. Lett., 2003 and subsequent studies. E.g. SO_4^{2-} *is likely not found at the particle surface but in the interior in contrast to the schematics in Fig. 4. Also, can it be ruled out that 3-MGA may show surfactant behavior? Even slight surfactant behavior could alter the surface concentration drastically.*

Author Response:

Thanks for the comment. We agree that it is too simple to assume the dissolved inorganic ions (e.g. SO_4^{2-}) are homogeneously distributed in the droplets with reference to the work of Jungwirth et al. (2003) and Jungwirth and Tobias (2006). Furthermore, we cannot rule out the possibility of 3-MGA being a surfactant as literatures on cloud droplet activitation 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. These factors could alter the surface concentration drastically and have not been considered. In the revised manuscript, we address that the numbers reported in this study should be considered as a first approximation to demonstrate the possible effects of AS on the surface coverage of 3-MGA. Further investigations on the surfactant properties of 3-MGA and molecular dynamic simulation are desirable to better understand the surface composition of both 3-MGA and 3-MGA–AS particles. We have added the following information in the revised manuscript to address these issues.

Page 12, Line 6, "It should acknowledge that dissolved inorganic ions (e.g. SO_4^{2-}) may not be homogeneously distributed in the droplets with reference to the work of Jungwirth et al. (2003) and Jungwirth and Tobias (2006). Furthermore, the surface activity of 3-MGA is not known and slight surfactant behavior could drastically alter the surface concentration. Thus the numbers presented here are to serve as a first approximation illustrating the possible effect of AS addition on the surface coverage of 3-MGA. Further investigations on the surfactant properties of 3-MGA and molecular dynamic simulation would be useful to better understand the surface composition of both 3-MGA and 3-MGA–AS particles."

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."

Specific Comments #5

Page 12, Line 24: Citations Petters et al. (2004) and Vereecken and Peeters (2009) are not given in bibliography and may be wrong as well?

Author Response:

We are sorry for the confusion. The first citation should be Peeters et al. (2004). These two citations are chosen as references for the SAR model developed for the decomposition of alkoxy radicals. We have corrected the typo and have added the two references in the revised manuscript.

Page 15, Line 20, "Furthermore, as proposed by Peeters et al. (2004) and Vereecken and Peeters (2009), the strong hydrogen bonding among the two terminal carboxyl groups might lower the decomposition rate of the alkoxy radical."

Specific Comments #6

Page 14, Line 15: ". . .over time.". Please add reference. Who has shown this?

Author Response:

This is an inference from the results of this study and previous studies. We have revised the sentence and clarified that there is a possibility, yet not verified, of phase behavior change in phase-separated particles upon oxidation.

Page 17, Line 13, "Furthermore, there is a possibility that the phase separation behavior (e.g. SRH) of the particles may change in response to the change in the particle composition over time."

Specific Comments #7

Page 14, Line 24: ". . .upon oxidation.". Please cite here the studies by Slade et al., ACP, 2015 and Slade et al., GRL, 2017.

Author Response:

We have cited the studies mentioned in the revised manuscript.

Page 17, Line 24: "Hence, it is of interest to investigate how the phase separation characteristics of organic–inorganic particles change in response to a change in the composition upon oxidation (Slade et al., 2015; Slade et al., 2017)."

References

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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.

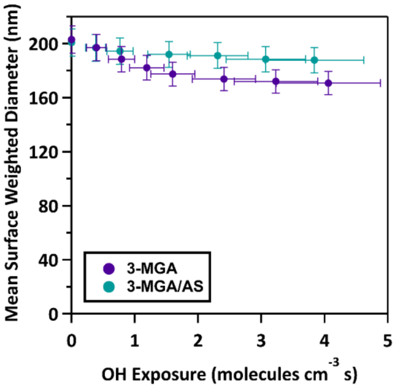

Figure S5. The change in surface-weighted mean diameter as a function of OH exposure for 3-MGA particles and 3-MGA–AS particles, respectively.

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

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Effects of Inorganic Salts on the Heterogeneous OH Oxidation of Organic Compounds: Insights from Methylglutaric Acid-Ammonium Sulfate

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Abstract

Atmospheric particles, consisting of inorganic salts, organic compounds and a varying amount of water, can continuously undergo heterogeneous oxidation initiated by gas-phase oxidants at the particle surface, changing the composition and properties of particles over time. To date, most studies focus on the chemical evolution of pure organic particles upon oxidation. To gain more fundamental insights into the effects of inorganic salts on the heterogeneous kinetics and chemistry of organic compounds, we investigate the heterogeneous OH oxidation of 3-methylglutaric acid (3-MGA) particles and particles containing both 3-MGA and ammonium sulfate (AS) in an organic-to-inorganic mass ratio of 2 in an aerosol flow tube reactor at a high relative humidity of 85.0 %. The molecular information of the particles before and after OH oxidation is obtained using the Direct Analysis in Real Time (DART), a soft atmospheric pressure ionization source, coupled to a

high-resolution mass spectrometer. Optical microscopy measurements reveal that 3-MGA-AS particles are in a single liquid phase prior to oxidation at high relative humidity. Particle mass spectra show that C_6 hydroxyl and C_6 ketone functionalization products are the major products formed upon OH oxidation in the absence and presence of AS, suggesting that the dissolved salt does not significantly affect reaction pathways. The dominance of C_6 hydroxyl products over C_6 ketone products could be explained by the intermolecular hydrogen abstraction by tertiary alkoxy radicals formed at the methyl-substituted tertiary carbon site. On the other hand, kinetic measurements show that the effective OH uptake coefficient, γ_{eff}, for 3-MGA-AS particles (0.99 ± 0.05) is smaller than that for 3-MGA particles (2.41 ± 0.13) by about a factor of ~2.4. A smaller reactivity observed in 3-MGA-AS particles might be attributed to a higher surface concentration of water molecules, and the presence of ammonium and sulfate ions, which are chemically inert to OH radicals, at the particle surface. This could lower the collision probability between the 3-MGA and OH radicals, resulting in a smaller overall reaction rate. 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.

~~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 particles.~~

1. Introduction

Atmospheric particles are chemically complex and are comprised of a large variety of organic compounds, inorganic salts and water. Organic compounds contribute a significant mass fraction (20-90 %) of atmospheric particles (Kanakidou et al., 2005; Zhang et al., 2007; Jimenez et al., 2009). Laboratory and modeling studies have revealed that organic compounds present at or near the particle surface can be efficiently oxidized by gas-phase oxidants such as hydroxyl (OH) radicals, ozone (O_3) and nitrate radicals (Rudich et al., 2007; George and Abbatt, 2010; Kroll et al., 2015; Estillore et al., 2016; Chapleski et al., 2016). The effective OH uptake coefficient, γ_{eff}, defined as the fraction of OH collisions with organic molecules that yields a reaction of a target organic molecule, has been commonly used to describe the kinetics and reported for a variety of pure organic compounds. The γ_{eff} in general has a value of ≥ 0.1 and even ≥ 1, indicating the occurrence of secondary chemistry (e.g. chain reactions induced by the hydrogen abstraction of organic molecules by alkoxy radicals) (Richards-Henderson et al., 2015). These heterogeneous oxidative processes can continuously alter the surface and bulk composition of the particles (Slade and Knopf, 2013; Li et al., 2018), and thus modify particle properties such as light extinction, hygroscopicity and cloud condensation nuclei activity (Petters et al., 2006; George et al., 2007; Lambe et al., 2007, 2009; Cappa et al., 2011; Slade et al., 2015; Slade et al., 2017). ~~These heterogenous oxidative processes can continuously alter the surface and bulk composition of the particles (Slade and Knopf, 2013; Li et al., 2018), and thus modify particle properties such as light extinction, hygroscopicity and cloud condensation nuclei activity (George et al., 2007; Lambe et al., 2007, 2009; Cappa et al., 2011).~~

While the transformation of pure organic particles has become more reasonably understood, the chemical transformation of organic particles in the presence of dissolved inorganic salts is largely unclear. Only a few laboratory studies have investigated the heterogeneous oxidation of organic-inorganic particles (McNeill et al., 2007, 2008; Dennis-Smither et al., 2012). In those studies, hydrophobic organic compounds (e.g. oleic acid and palmitic acid) have been chosen as model compounds. Due to the hydrophobic nature of these compounds, the particles tend to be phase-separated with a thin organic layer on the surface of aqueous inorganic core (e.g. aqueous sodium chloride or ammonium sulfate (AS) phases). For these phase-separated particles, the molecular structure and orientation of organic molecules at the particle surface are observed to alter the reactive uptake of gas-phase oxidants such as O_3 and OH radicals. The reaction products formed from the ozonolysis of oleic acid-AS particles are very similar to those found in pure oleic acid particles (McNeill et al., 2007). These observations are consistent with the hypothesis that a thin organic layer effectively shields the aqueous inorganic core from being oxidized at the particle surface.

To date, there are still uncertainties on how salts affect the heterogeneous reactivity of organic compounds, in particular, the more oxygenated ones which exhibit moderate to high solubility in water. In this work, experiments were conducted to investigate the evolution of molecular composition of 3-methylglutaric acid (3-MGA) particles and particles containing 3-MGA and AS in an organic-to-inorganic mass ratio (water-free) (OIR) of 2 upon heterogeneous OH oxidation at a relative humidity (RH) of 85.0 % using an aerosol flow tube reactor coupled to the Direct Analysis in Real Time (DART) mass spectrometry. 3-MGA is chosen as a model compound for methyl-substituted dicarboxylic acids (**Table 1**), while AS is chosen as the model inorganic salt. The OIR of 2 used in this work is in the range of OIR commonly observed in atmospheric particles (Jimenez et al., 2009). The model system allows us to gain more insights into the physics and chemistry of heterogeneous reactions. The physical state of the particle is known to be a key factor in controlling the heterogeneous reactivity (Renbaum and Smith, 2009; Shiraiwa et al., 2011; Chan et al., 2014; Slade and Knopf, 2014; Fan et al., 2015; Marshall et al., 2018). Recent laboratory and modeling studies have shown that in addition to deliquescence and efflorescence, particles containing organic compounds and inorganic salts can undergo phase separation, depending on the particle composition and environmental conditions such as RH and temperature (Ciobanu et al., 2009; Reid et al., 2011; Song et al., 2012ab; Zuend and Seinfeld, 2012; Qiu and Molinero, 2015; Stewart, et al., 2015; You and Bertram, 2015; Freedman, 2017; Losey et al., 2018). Since whether particles are well-mixed or phase-separated governs the surface composition of particles and thus the heterogeneous reactivity, the phase separation behavior of 3-MGA-AS particles was investigated using an aerosol flow cell coupled to an optical microscope. By assessing the molecular transformation of 3-MGA and 3-MGA-AS particles upon oxidation together with phase separation data obtained from optical microscopy measurements, the effects of AS on the heterogeneous OH kinetics and chemistry of 3-MGA are examined. More recently, we have measured the heterogeneous OH reactivity of pure 2-MGA particles, a structural isomer of 3-MGA (Chim et al., 2017a). Given their similar structures, the results of this work together with 2-MGA data might provide some new aspects on how dissolved inorganic salts would alter the heterogeneous kinetics and chemistry of methyl substituted dicarboxylic acids.

2. Experimental Methods

2.1 Heterogeneous OH oxidation of 3-MGA and 3-MGA-AS particles

The OH-initiated heterogeneous oxidation of 3-MGA and 3-MGA-AS particles were performed in an aerosol flow tube reactor at 85.0 % RH. Details of the experimental methods have been described elsewhere (Chim et al., 2017ab). In brief, the particle stream did not pass through a diffusion dryer and was directly mixed with O_3, oxygen (O_2), dry nitrogen (N_2), humidified N_2 and hexane before being introduced into the reactor. 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. A water jacket around the reactor was used to maintain a constant temperature of 20 °C inside the reactor. ~~In brief, an aqueous solution of 3-MGA or 3-MGA-AS in an OIR of 2 was atomized using a TSI atomizer to generate aqueous droplets. The particle stream was then mixed with O_3, oxygen (O_2), dry nitrogen (N_2), humidified N_2 and hexane, and was introduced into the reactor. The RH within the reactor was controlled by varying the dry N_2 to humidified N_2 ratio. A water jacket was used to maintain a constant~~

~~temperature of 20 °C inside the reactor.~~ Inside the reactor, gas-phase OH radicals were generated via the photolysis of O_3 using UV lamps at 254 nm. The processes can be described by the following reactions:

$$O_3 \rightarrow O(^1D) + O_2 \tag{R1}$$

$$O(^1D) + H_2O \rightarrow 2\ OH \tag{R2}$$

The gas-phase concentration of OH radicals was controlled by varying the O_3 concentration introduced to the reactor and was determined by measuring the decay of hexane, a gas-phase tracer of OH radicals, using a gas chromatograph coupled with a flame ionization detector (GC-FID). The OH exposure, a quantity defined as the product of OH concentration and particle residence time (~1.3 min), can be determined by the following equation (Smith et al., 2009):~~The OH exposure, a quantity defined as the product of OH concentration and particle residence time, can be determined by the following equation (Smith et al., 2009):~~

$$\text{OH exposure} = -\frac{\ln\left(\frac{[\text{Hex}]}{[\text{Hex}]_0}\right)}{k_{\text{Hex}}} = \int_o^t [\text{OH}]dt \tag{Eqn. 1}$$

where k_{Hex} is the rate constant for the reaction of OH radicals with hexane (5.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}), $[\text{Hex}]_0$ is the initial hexane concentration entering the reactor, and [Hex] is the concentration of hexane leaving the reactor. The OH exposure was varied from 0 to a maximum of 4.06×10^{11} molecules cm^{-3} s in 3-MGA experiments and was varied from 0 to a maximum of 3.84×10^{11} molecules cm^{-3} s in 3-MGA-AS experiments. The oxidation levels are equivalent to about 3 days in the atmosphere under a moderate to high level of OH concentration (1.5×10^6 molecules cm^{-3}). Since the OH exposure (and OH concentration) was determined by the in situ measurement of the decay of hexane, 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. Upon exiting the reactor, the particle stream then passed through an annular Carulite catalyst denuder for O_3 removal and an activated charcoal denuder for the removal of organic gas-phase species remaining in the stream. Hence, only particle-phase reaction products were analyzed. 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. 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. ~~Size distribution of the particles was determined by sampling a small portion of the particle stream using a scanning mobility particle sizer (SMPS, TSI).~~ The remaining flow was directed to a heater at 250–300 ºC to fully vaporize the particles. 3-MGA and 3-MGA-AS particles were confirmed to be fully vaporized upon heating at 250 ˚C or above by measuring the size distribution of the particles leaving the heater with the SMPS in separate experiments. The resulting gas-phase species were then directed to an ionization region, a narrow open space between the DART ionization source (IonSense: DART SVP), and the inlet of the high-resolution mass spectrometer (ThermoFisher, Q Exactive Orbitrap) (Chan et al., 2013; Nah et al., 2013).

Details of the DART operation have been described in the work of Cody et al. (2005). The DART ionization source was operated in negative ionization mode with helium (He) as the ionizing gas. The formation of gas-phase ions in the ionization region can be described by below (Cody, 2009):

$$e^- + O_2(g) \rightarrow O_2^-(g) \qquad \text{(R3)}$$

$$O_2^-(g) + M(g) \rightarrow [M-H]^-(g) + HO_2(g) \qquad \text{(R4)}$$

Atmospheric O_2 molecules abstract the electrons (e^-) produced by the Penning ionization of metastable He in the DART ionization source to form anionic oxygen ions (O_2^-) which then react with the gas-phase species (M) to form deprotonated molecular ions ($[M-H]^-$) by proton abstraction. Previous studies have shown that the acidic proton of the carboxyl group can be abstracted by the O_2^- ions to generate the $[M-H]^-$, which was observed dominantly in the mass spectra (Cheng et al., 2015; Chim et al., 2017ab). In this work, it is likely that proton abstraction from the carboxyl group of 3-MGA and its reaction products occurred to produce the $[M-H]^-$. These ions were sampled by the high-resolution mass spectrometer. Mass spectra, over a scan range from *m/z* 70–400 at a mass resolution of about 140000, were collected. The mass spectra were analyzed using the Xcalibur software (Xcalibur Software, Inc., Herndon, VA, USA). 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. Two control experiments were conducted: one in the presence of O_3 without the UV light and another one in the absence of O_3 with the UV light on. No compositional changes were observed for 3-MGA and 3-MGA-AS particles in both control experiments, indicating that the reaction of 3-MGA with O_3 is insignificant and that 3-MGA is not likely to be photolyzed.

The hygroscopicity data of 3-MGA has been reported in the work of Marsh et al. (2017) with a growth factor of ~1.2 at 85 % RH. As shown by the hygroscopicity curve measured, 3-MGA particles absorb and desorb water reversibly as the RH increases or decreases, indicating that they are likely aqueous droplets prior to oxidation. Optical microscopy measurements have been carried out (**Figure S1**, *supplementary material*) and show that 3-MGA-AS particles are in a single liquid phase prior to oxidation at 85.0 % RH as the particles become phase-separated when the RH is below the separation

RH (SRH = 72.7–73.6 %) (**Figure S2**, *supplementary material*). Details of the optical microscopy measurements have been given in the *Supplementary Material*.

~~_Optical microscopy measurements have been carried out (**Figure S1,** *supplementary material*) and show that 3-MGA-AS particles are in a single liquid phase prior to oxidation at 85.0 % RH as the particles become phase-separated when the RH is below the separation RH (SRH = 72.7–73.6 %) (**Figure S2,** *supplementary material*). Details of the optical microscopy measurements have been given in the *Supplementary Material*.~~ Since the particles were always exposed to high humidity and the experiments were carried out at 85.0 % RH, which is higher than the SRH, 3-MGA-AS particles are likely to be single-phase liquid droplets prior to oxidation.

3 Results and Discussion

3.1 Particle mass spectra of 3-MGA and 3-MGA-AS before and after OH oxidation

Figure 1 shows the mass spectra of 3-MGA and 3-MGA-AS before and after OH oxidation at 85.0 % RH, respectively. For 3-MGA, a dominant peak is observed before oxidation at *m/z* = 145 which corresponds to the deprotonated molecular ion of 3-MGA ($C_6H_9O_4^-$). After oxidation, two major product peaks evolve, corresponding to two C_6 functionalization products (C_6 hydroxyl products ($C_6H_{10}O_5$) and C_6 ketone products ($C_6H_8O_5$)). A few minor product peaks, such as $C_4H_5O_3^-$, $C_5H_5O_3^-$, $C_5H_7O_3^-$, $C_5H_7O_4^-$ and $C_5H_7O_5^-$, are also observed. Each of these peaks contributes less than 2.5 % of the total ion signal at the maximum OH exposure. The mass spectra of 3-MGA-AS particles in OIR = 2 are very similar to those of 3-MGA particles, except for the two inorganic sulfate peaks that originate from dissolved AS. Before oxidation (**Figure 1**), three peaks at *m/z* = 97, *m/z* = 145 and *m/z* = 195 are observed, corresponding to the bisulfate ion (HSO_4^-), the deprotonated molecular ion of 3-MGA and $H_3S_2O_8^-$, respectively. One possibility is that HSO_4^- is likely the dissolved ion from aqueous AS that became acidified by the evaporative loss of ammonia (NH_3) into gas phase and can be detected via direct ionization in the negative ion mode (Hajslova et al., 2011). HSO_4^- has been detected when aqueous AS particles are ionized by the DART ionization source as well as when being a reaction product formed in the heterogeneous OH oxidation of sodium methyl sulfate, sodium ethyl sulfate and methanesulfonic acid particles (Kwong et al., 2018ab). However, we do not have a clear explanation for the formation of $H_3S_2O_8^-$ which is likely an adduct of HSO_4^- and H_2SO_4. After oxidation, the deprotonated ions of C_6 hydroxyl ($C_6H_9O_5^-$) and C_6 ketone products ($C_6H_7O_5^-$) are observed in addition to the unreacted 3-MGA. Some small product peaks are detected ($C_4H_5O_3^-$, $C_5H_5O_3^-$, $C_5H_7O_3^-$, $C_5H_7O_4^-$ and $C_5H_7O_5^-$); with each contributing less than 2.5 % of the total ion signal.

As shown in **Figure 2**, the chemical evolution in the composition of 3-MGA and 3-MGA-AS particles upon oxidation are very similar. At the maximum OH exposure, the C_6 hydroxyl products are the most abundant species, which accounts for 38.0−48.2 % of the total organic ion signal, followed by unreacted 3-MGA (37.3−47.9 %), and the C_6 ketone products (7.3−7.6 %). For 3-MGA-AS, the intensities of HSO_4^- and $H_3S_2O_8^-$ remain about the same before and after OH oxidation (**Figure S3,** *supplementary material*). This could be attributed to the fact that dissolved AS does not react effectively with gas-phase OH radicals at the particle surface (George and Abbatt, 2010). In general, the same reaction products are observed for both 3-MGA and 3-MGA-AS particles after oxidation, suggesting that AS does not significantly affect the reaction pathways.

3.3 Oxidative Kinetics of 3-MGA and 3-MGA-AS

The normalized parent decay in 3-MGA and 3-MGA-AS particles as a function of OH exposure at 85.0 % RH is shown in **Figure 3**. For both systems, the OH-initiated decay of 3-MGA follows an exponential trend and can be fit with an exponential function to obtain an effective second order OH reaction rate constant (k):

$$\ln\frac{I}{I_0} = -k\,[\mathrm{OH}]\,t \qquad \text{(Eqn. 2)}$$

where I_0 is the ion signals of 3-MGA before oxidation, I is the ion signals of 3-MGA at a given OH exposure, [OH] is the gas-phase concentration of OH radical and t is the reaction time. The fitted value of k for the 3-MGA and 3-MGA-AS are (3.26 ± 0.065) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1} and (2.72 ± 0.064) × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, respectively. Using the fitted k value, the effective OH uptake coefficient, γ_{eff}, defined as the fraction of OH collisions with particles that yields a reaction, can be computed by the following equation (Davies and Wilson, 2015):

$$\gamma_{\mathrm{eff}} = \frac{2\,\rho_0 D_0\, mfs\, N_A\, k}{3\, M_w\, \overline{c_{OH}}} \qquad \text{(Eqn. 3)}$$

where ρ_0 is the density of particle, D_0 is the particle diameter, mfs is the mass fraction of 3-MGA in the particle, M_w is the molecular weight of 3-MGA, N_A is Avogadro's number, and $\overline{c_{OH}}$ is the mean speed of gas-phase OH radicals. The mean surface weighted 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 mean surface weighted diameter 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 Meng and Seinfeld (1996). We thus postulate that the spread of particle size and the mixing timescale would not play a substantial role in the evaporation of fragmentation products during oxidation. As the change in particle size upon oxidation is not very significant, the change in particle diameter was not accounted for in the γ_{eff} calculation. The γ_{eff} may thus be considered as an initial uptake coefficient (Chim et al., 2018). We acknowledge that the spread of particle size could potentially affect the uncertainty and determination of γ_{eff}, but we could not quantify it since the particles are polydisperse in our study. Future investigations can be carried out to measure the γ_{eff} for both monodisperse (size-selected) and polydisperse particle populations. The γ_{eff} assembled from different monodisperse particle sizes can be compared with that obtained from polydisperse populations using the surface-weighted mean diameter in order to assess how the spread and uncertainty in the particle size distribution of polydisperse particle populations affect the determination of γ_{eff}. ~~Before oxidation, the diameter of 3-MGA and 3-MGA-AS particles were measured to be 203.0 nm and 200.8 nm, respectively.~~ The *mfs* values were obtained from equilibrium composition calculations using the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) model available online (https://aiomfac.lab.mcgill.ca) (**Table 1**) (Zuend et al., 2008; Zuend et al., 2011). Based on the composition (i.e. *mfs*), the densities of 3-MGA and 3-MGA-AS particles were estimated using the volume additivity rule with the density of water, 3-MGA and AS (Chim et al., 2017a). Using Eqn. 3, the γ_{eff} for 3-MGA and 3-MGA-AS are calculated to be 2.41 ± 0.13 and 0.99 ± 0.05, respectively. The value of γ_{eff} for 3-MGA particles is larger than that of 3-MGA-AS particles by about 2.4 times.~~The values of γ_{eff} for 3-MGA-AS particles is smaller than that of 3-MGA particles by about 59 %.~~ One possible explanation is that the mass fraction of 3-MGA in 3-MGA-AS particles (*mfs* = 0.344) is smaller than that in 3-MGA particles (*mfs* = 0.707) at 85.0 % RH before oxidation (**Table 1**), likely resulted from the presence of AS and the concomitant increase in particle hygroscopicity. A simple analysis shows that the surface coverage of 3-MGA in 3-MGA particles and 3-MGA-AS particles are roughly estimated to be 51.4% and 21.6%, respectively (*Supplementary material*). A smaller surface concentration of 3-MGA in 3-MGA-AS particles might reduce the collision probability between 3-MGA and gas-phase OH radicals at the air-particle interface and thus lower the overall reactivity, as compared to 3-MGA particles. It should acknowledge that dissolved inorganic ions (e.g. SO_4^{2-}) may not be homogeneously distributed in the droplets with reference to the work of Jungwirth et al. (2003) and Jungwirth and Tobias (2006). Furthermore, the surface activity of 3-MGA is not known and slight surfactant behavior could drastically alter the surface concentration. Thus the numbers presented here are to serve as a first approximation illustrating the possible effect of AS addition on the surface coverage of 3-MGA. Further investigations on the surfactant properties of 3-MGA and molecular dynamic simulation would be useful to better understand the surface composition of both 3-MGA and 3-MGA–AS particles.

A similar result has also been observed for the OH oxidation with methanesulfonic acid (MSA) reported in the literature. Mungall et al. (2017) have investigated the heterogeneous OH oxidation of MSA-AS particles with a mass fraction of MSA = 0.16 at 75 % RH. The γ_{eff} was reported to be 0.05 ± 0.03, which is smaller than that of pure MSA particles (γ_{eff} = 0.45 ± 0.14) measured at a slightly higher RH (90 %) (Kwong et al., 2018b). The results obtained in this work and in the literature suggest that for a given RH, inorganic salts (e.g. AS) might lower the heterogeneous reactivity of organic compounds toward gas-phase OH radicals due to the smaller surface concentration of 3-MGA resulting from the presence of AS and concomitant increase in water uptake. It acknowledges that ammonium (NH_4^+) and sulfate (SO_4^{2-}) ions, which are chemically inert to OH radicals, present at or near the surface could lower the overall reaction rates by reducing the surface concentration of organic compounds. However, the additional effects of NH_4^+ and SO_4^{2-} ions on the surface activity and configuration of organic molecules, which could play a role in determining the heterogeneous activity, are not yet well understood and warrant further investigations.

Kinetic measurements show that γ_{eff} for both 3-MGA and 3-MGA-AS particles are close to or greater than one. This indicates that more than one 3-MGA molecule is reacted away per OH radical collision with the particle surface, suggesting the occurrence of secondary chemistry in the particle phase. In the following sections, reaction mechanisms are tentatively proposed and discussed to explain the formation of major products detected in the particle mass spectra and the reaction pathways likely responsible for the secondary chemistry.

3.4 Reaction Mechanisms

As shown in **Figure 2**, the reaction products observed in 3-MGA and 3-MGA-AS particles are about the same upon oxidation. A generalized reaction scheme is thus proposed for both systems based on well-known particle-phase reactions previously published in the literature (Russell, 1957; Bennett and Summers, 1974; George and Abbatt, 2010). As shown in **Scheme 1,** the OH oxidation with 3-MGA can be initiated by the hydrogen abstraction at three different carbon sites: tertiary backbone carbon site (**Path A),** secondary backbone carbon site (**Path B**) and the primary carbon site of the branched methyl group (**Path C**). Depending on the initial OH reaction site, a variety of reaction products can be formed and broadly classified into two groups: functionalization and fragmentation products.

3.4.1 Functionalization products

At the first oxidation step, a hydrogen atom is abstracted from a 3-MGA molecule by an OH radical, forming an alkyl radical that reacts quickly with an O_2 molecule to form a peroxy radical. The major C_6 hydroxyl ($C_6H_{10}O_5$) and C_6 ketone ($C_6H_8O_5$) products can be generated from the self-reactions of two peroxy radicals through the Russell mechanism (**R1**) and/or Bennett-Summers reactions (**R2**). Alternatively, the self-reactions of two peroxy radicals can form two alkoxy radicals which can then abstract hydrogen atoms from the neighboring organic molecules (**R3**) to form C_6 hydroxyl products or react with O_2 molecules (**R4**) to form C_6 ketone products. However, when the hydrogen abstraction occurs at the tertiary carbon site (**Scheme 1, Path A**), only the C_6 hydroxyl product can be formed because only a hydroxyl group can be added to the tertiary carbon site. Depending on initial reaction site, structural isomers of these C_6 hydroxyl and ketone products are likely formed during oxidation.

3.4.2 Fragmentation products

The fragmentation products can be generated from the decomposition of alkoxy radicals (**R5**). For instance, when the initial hydrogen abstraction occurs at the secondary carbon site (**Scheme 1, Path B**), the decomposition of the secondary alkoxy radical can yield either a C_2 ($C_2H_2O_3$) or a C_5 fragmentation product ($C_5H_8O_3$). On the other hand, a C_4 fragmentation product ($C_4H_6O_3$) can be yielded from the decomposition of the alkoxy radical formed at the tertiary carbon site (**Scheme 1, Path A**) while oxidation at the primary carbon site (**Scheme 1, Path C**) can yield a C_3 fragmentation product ($C_3H_4O_3$). For both 3-MGA and 3-MGA-AS, the ion signal intensity of fragmentation products is small (**Figure 1**). For example, only a small signal of C_4 fragmentation product ($C_4H_6O_3$), which is formed from the oxidation at the tertiary carbon site (**Scheme 1, Path A**), is detected. It contributes less than 2% of the total ion signal at the maximum OH exposure. The observed low abundances of fragmentation products could be explained by their higher volatilities (**Tables S1 and S2,** *supplementary material*) and some (e.g. $C_5H_8O_5$) may be explained by the preference on initial OH reaction site as discussed below. It is noted that for 3-MGA-AS particles, the presence of AS increases the activity coefficients of fragmentation products in the particle phase based on the thermodynamic model predictions and thus increases their volatilities in general (**Table S3,** *supplementary material*).

3.4.3 Large C_6 hydroxyl-to-C_6 ketone product ratio: Implications for secondary chemistry

From the particle composition data, a large C_6 hydroxyl-to-C_6 ketone product ratio is observed. At the maximum OH exposure, the relative abundance of C_6 hydroxyl products is about 5.0–6.6 times that of C_6 ketone products for both 3-MGA and 3-MGA-AS particles. We acknowledge that although the ionization efficiencies are not corrected for these products in this study, the ionization efficiency of

C_4 hydroxyl products is found to be about the same or even lower than that of C_4 ketone products during the DART ionization processes (Chan et al., 2014). The abundance of C_6 hydroxyl products might be even larger than that of C_6 ketone products after correcting their ionization efficiencies, supporting the statement above. One possible explanation for the dominance of C_6 hydroxyl products is that the OH abstraction may preferentially occur at the tertiary carbon site (**Scheme 1, Path A**) since the tertiary alkyl radicals are more stable than secondary and primary alkyl radicals (Cheng et al., 2015). Only an addition of a hydroxyl group at the tertiary carbon site is allowed via the alkoxy or peroxy radical reactions.

Another possibility is that the branched methyl group may sterically hinder the two peroxy radicals from arranging into a cyclic tetroxide intermediate, which is essential for the formation of hydroxyl and ketone functionalization products through the Russell and the Bennett-Summers mechanisms (Cheng et al., 2015). Alternatively, alkoxy radicals are more likely formed through the self-reaction of two peroxy radicals and can react with neighboring organic molecules (e.g. unreacted 3-MGA) by intermolecular hydrogen abstraction to form the C_6 hydroxyl products. Furthermore, as proposed by Peeters et al. (2004) and Vereecken and Peeters (2009), the strong hydrogen bonding among the two terminal carboxyl groups might lower the decomposition rate of the alkoxy radical. ~~Furthermore, as proposed by Petters et al. (2004) and Vereecken and Peeters (2009), the strong hydrogen bonding among the two terminal carboxyl groups might lower the decomposition rate of the alkoxy radical.~~ This could increase the competitiveness of the intermolecular hydrogen abstraction by the alkoxy radicals. It is worthwhile to note that the intermolecular hydrogen abstraction can regenerate an alkyl radical and eventually produce peroxy radicals. These peroxy radicals can react again with other peroxy radicals to regenerate alkoxy radicals. This allows the chain reactions to propagate and increases the overall reactivity (i.e. more than one 3-MGA molecule can be reacted per initial OH collision via secondary chemistry and, thus γ_{eff} is larger than one). Overall, the alkoxy radical chemistry, originating from the OH abstraction at the tertiary carbon site at the first oxidation step

(**Scheme 1, Path A**) is likely the important reaction pathway for the OH reactions with 3-MGA.

4. Conclusions and Atmospheric Implications

Atmospheric particles can keep colliding with gas-phase oxidants, allowing continuous oxidation to occur at or near the particle surface. To better understand how dissolved inorganic salts affect the heterogeneous chemistry and kinetics of organic compounds with gas-phase OH radicals, we investigated the kinetics, products and mechanisms of particles comprised of 3-MGA and 3-MGA-AS in an OIR of 2 upon heterogeneous OH oxidation at 85.0 % RH. Optical microscopy measurements for the detection of phase separation reveal that 3-MGA-AS particles exhibit a single liquid phase prior to oxidation. Same major reaction products are formed as a result of ~~heterogenenous~~heterogeneous OH oxidation with both 3-MGA and 3-MGA-AS particles. These data suggest that the presence of aqueous AS does not significantly affect the formation pathways of major reaction products. On the other hand, in the presence of AS, the heterogeneous reactivity of 3-MGA toward gas-phase OH radicals is slower in 3-MGA-AS particles compared to that in 3-MGA particles. It is likely attributed to a lower concentration of 3-MGA at the surface of 3-MGA-AS particles relative to 3-MGA particles, reducing the collision probability between 3-MGA and gas-phase OH radicals. The results from this work and the literature suggest that the presence of dissolved salts could reduce the overall heterogeneous reactivity of organic compounds with gas-phase OH radicals at the surface by lowering the surface concentration of organic compounds at a given RH and temperature. Until recently, the kinetic parameters (e.g. γ_{eff}) reported in the literature were mostly measured based on experiments with salt-free organic particles. The chemical lifetime of organic compounds or chemical tracers against heterogeneous OH reaction in the atmosphere could be longer than expected when the salts are present. Further investigations on how the amount and types of inorganic salts alter heterogeneous kinetics and chemistry are highly desirable.

Over the past decade, laboratory and modeling studies have demonstrated that atmospheric particles can undergo phase separation and exhibit different morphologies, which play a role in many atmospheric processes. For example, the inhomogeneous distribution of inorganic and organic species within phase-separated particles can affect the reactive uptake of gas-phase species (e.g. N_2O_5) (Gaston et al., 2014) and water uptake of organic-inorganic particles (Chan and Chan, 2007; Zuend and Seinfeld, 2012; Hodas et al., 2015). It is still unclear how the occurrence of liquid-liquid phase separation alters the heterogeneous reactivity of organic-inorganic particles over time. As shown in **Figure S2** (*supplementary material*), 3-MGA-AS particles become phase separated when the RH is below the SRH (72.7–73.6 %). The phase-separated particles might exhibit different reactivity compared to those in a single liquid phase investigated in this work since the surface composition of the particles are different in these two phases. Furthermore, there is a possibility that the phase separation behavior (e.g. SRH) of the particles may change in response to the change in the particle composition over time. ~~Furthermore, the phase separation behavior (e.g. SRH) of the particles can change in response to the change in the particle composition during oxidation over time.~~ Although the phase of oxidized 3-MGA-AS particles has not been determined experimentally in this work, the overall $\langle O/C \rangle$ is found to increase slightly from 0.67 to ~0.75 (*supplementary material*), and the SRH is expected to decrease slightly after oxidation (Bertram et al., 2011; Song et al., 2012b; You et al., 2013, 2014). Since the experimental RH inside the reactor was fixed at 85.0 %, it is very likely that 3-MGA-AS particles remain in a single liquid phase state during oxidation. During oxidation, the degree of aerosol oxidation state (e.g. expressed by $\langle O/C \rangle$) typically increases due to the formation of more oxygenated reaction products and, consequently, the SRH is expected to decrease. As shown in **Figure 4**, it is hypothesized that initially phase-separated particles might transition to a homogeneous, single liquid phase state, depending on the extent of oxidation and the environmental thermodynamic conditions. Hence, it is of interest to investigate how the phase separation characteristics of organic–inorganic particles change in response to a change in the composition upon oxidation (Slade et al., 2015; Slade et al., 2017). ~~Hence, it is of interest to investigate how the phase separation characteristics of organic-inorganic particles change in response~~

~~to a change in the composition upon oxidation.~~ Moreover, with respect to future work, it would be interested in understanding the dynamic interplay between the particle composition, heterogeneous reactivity, liquid-liquid phase separation and effects on particle morphology under different environmental conditions and extents of oxidation.

Author contributions

HKL, SMS, and MNC designed and ran the experiments. HKL, SMS, and MNC prepared the manuscript. All co-authors provided comments and suggestions to the manuscript.

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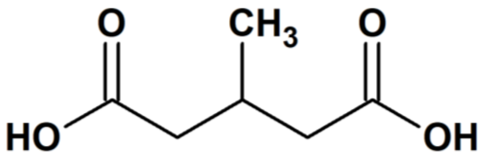
Table 1. Chemical structure, properties, effective heterogeneous OH rate constant, effective OH uptake coefficient of 3-methylglutaric acid (3-MGA) and 3-MGA mixed with ammonium sulfate (AS) in an organic-to-inorganic dry mass ratio (OIR) = 2.

Chemical structure		
Chemical formula	$C_6H_{10}O_4$	
O/C ratio	0.67	
H/C ratio	1.67	
	3-MGA	**3-MGA-AS (OIR =2)**
Separation RH (SRH)	–	72.7–73.6 %
Mass fraction at 85 % RH		
3-MGA	0.707	0.344
AS	0	0.172
H_2O	0.293	0.484
Effective second order heterogeneous OH rate constant, *k* (× 10^{-12} cm^3 $molecule^{-1}$ s^{-1})	3.26 ± 0.065	2.72 ± 0.064
Effective OH uptake coefficient, γ_{eff}	2.41 ± 0.13	0.99 ± 0.05

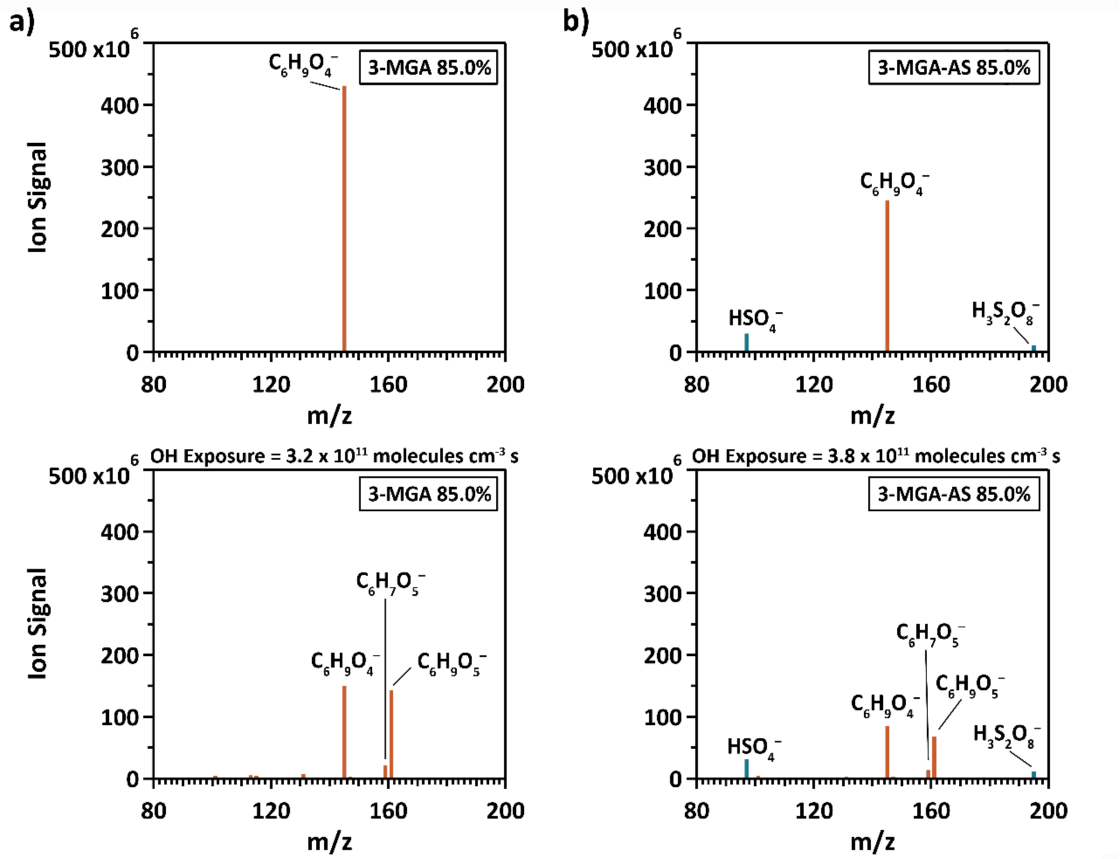


Figure 1. The particle mass spectrum of a) 3-MGA and b) 3-MGA-AS before (upper panels) and after (lower panels) heterogeneous OH oxidation at 85.0 % RH, respectively. Color scheme: brown = organic species, blue = inorganic species.

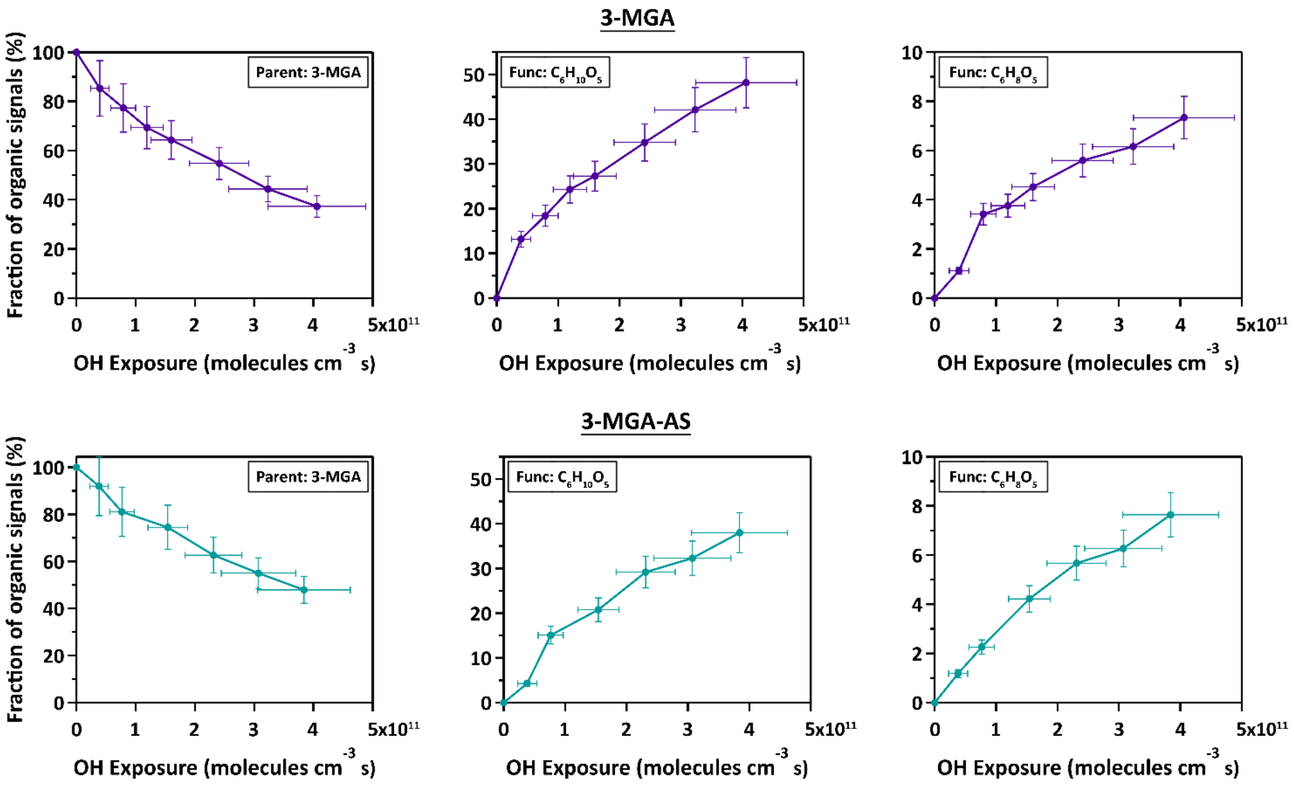


Figure 2. Upper panels: The fraction of the organic ion signal attributed to the parent 3-MGA, the major C_6 hydroxyl and C_6 ketone products of 3-MGA particles during the heterogeneous OH oxidation shown against OH exposure. Lower panels: analogous to the above, but for the case of mixed 3-MGA-AS particles.

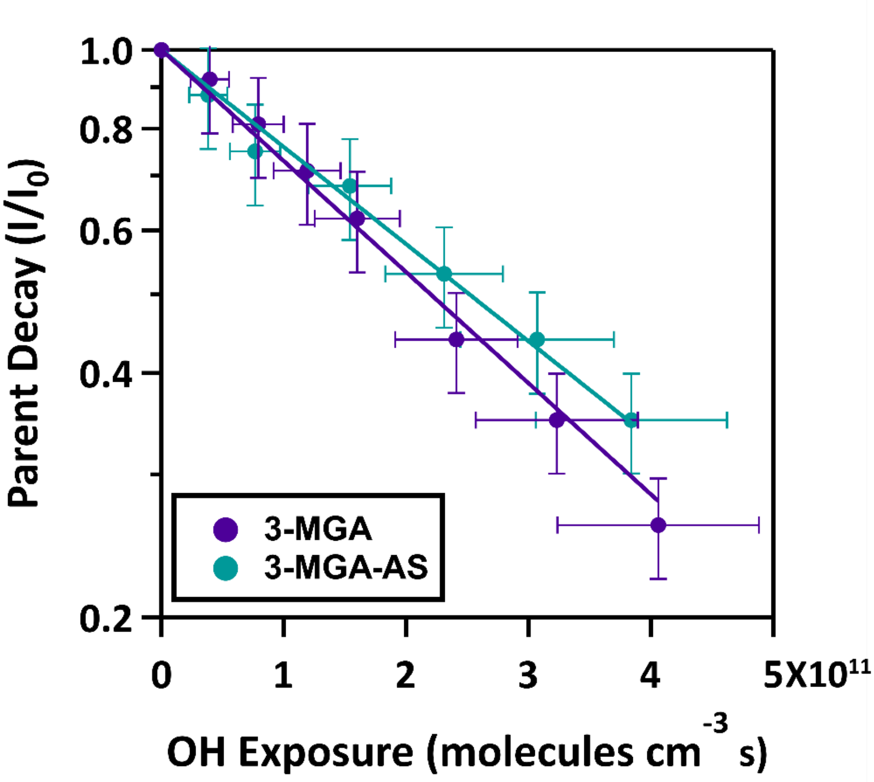


Figure 3. The normalized parent decay for the heterogeneous OH oxidation of 3-MGA and 3-MGA-AS particles at 85.0 % RH. Note the logarithmic scale of the ordinate.

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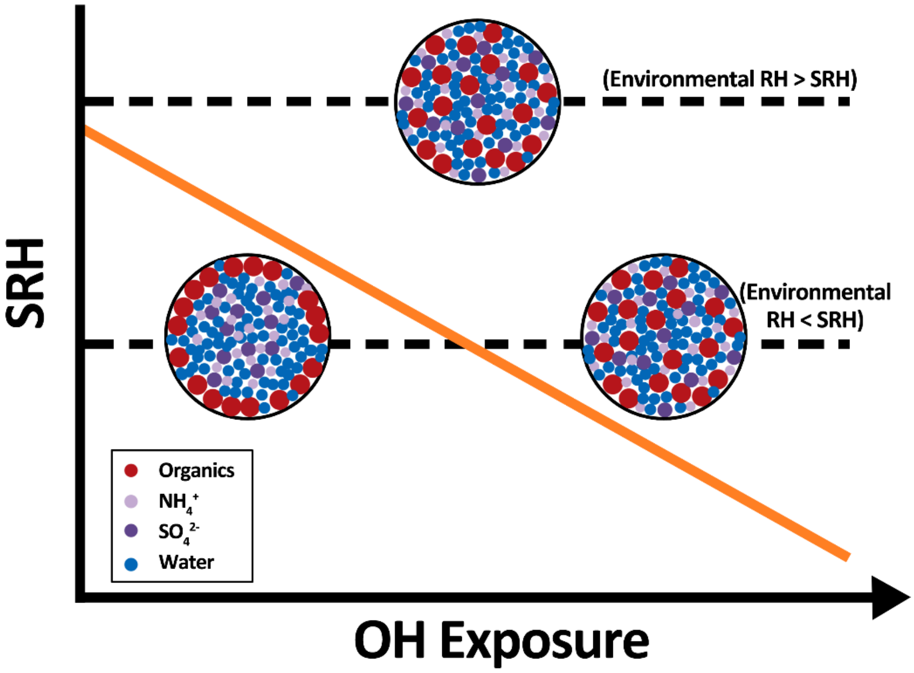
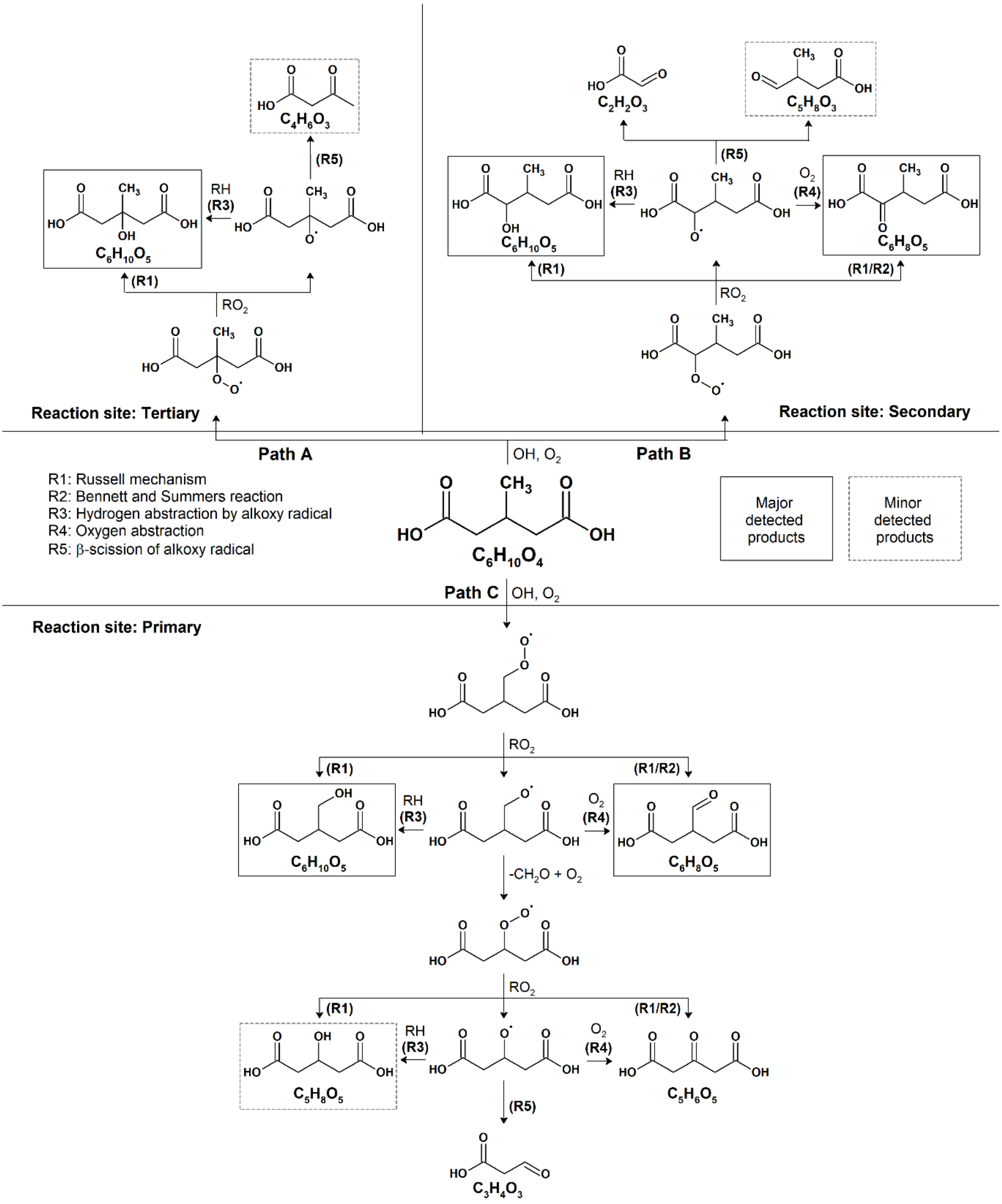
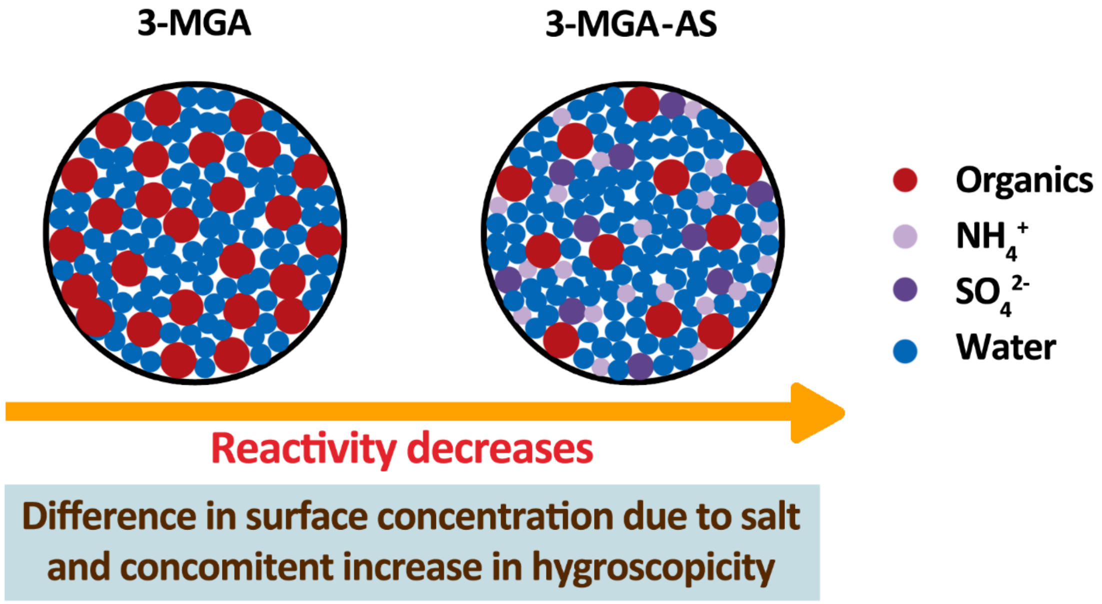


Figure 4. A simplified diagram illustrating the change in separation relative humidity (SRH, orange solid line) and phase composition of droplets containing inorganic salts and organic compounds (single liquid phase vs. liquid-liquid phase separated) upon heterogeneous oxidation at two different environmental RH.



Scheme 1. Proposed reaction mechanisms for the heterogeneous OH oxidation of 3-MGA and 3-MGA-AS particles.

TOC.


3-MGA
3-MGA-AS
Organics
NH_4^+
SO_4^{2-}
Water
Reactivity decreases
Difference in surface concentration due to salt and concomitent increase in hygroscopicity