Anonymous Referee #2

General comments. The manuscript presents results from studies probing the effects of liquid-liquid phase separations on the loss rate for methylglutaric acid signal through heterogeneous OH oxidation. A range of different analyses were combined with the flow tube studies to fully characterize the system including optical microscopy, an electrodynamic balance, and modeling studies. The authors found that the heterogeneous OH oxidation rate increased in LLPS particles, likely due to increased organic concentrations near the surface in the particles. Overall the paper is well written and the conclusions are supported by the data. There are a few places where additional information would enable a broader view of the results. I recommend this manuscript for publication in ACP after the following minor comments are addressed.

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.

Specific Comments

Reviewer's Comment #1
The effective heterogeneous OH rate constant was reported to vary from 1.01 x 10^-12 to 1.73 x 10^-12 cm^3 molecule^-1 s^-1. How does this scale to lifetimes in the atmosphere? How much of a difference might be expected for the lifetimes of organic compounds in LLPS systems in the atmosphere?

Authors' Response
Thanks for the comment. Using a 24-h averaged gas-phase OH concentration of 1.5×10^6 molecules cm^{-3}, the lifetime of 3-MGA against heterogeneous OH oxidation is estimated to decrease from 7.01 ± 0.13 days to 4.46 ± 0.05 days when the effective heterogeneous OH rate constant increases from $1.01 \pm 0.02 \times 10^{-12}$ to $1.73 \pm 0.02 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. These results would suggest that the lifetime of 3-MGA in phase-separated droplets would be shorter compared to that in single-phase aqueous droplets in the atmosphere. We also acknowledge that the presence of other organic and inorganic components in atmospheric aerosols is expected to further affect this estimated lifetime (e.g. if additional low-polarity organic components in the shell phase or air–liquid interface replace some of the 3-MGA exposed to the gas phase, the lifetime may prolong again).

We have added this information in the revised manuscript.
Conclusion, Line 543, "For instance, using the kinetic data and a 24-h averaged gas-phase OH concentration of 1.5×10^6 molecules cm^{-3}, the lifetime of 3-MGA against heterogeneous OH oxidation is estimated to decrease from 7.01 ± 0.13 days to 4.46 ± 0.05 days when RH decreases from 88% to 55%."

Reviewer's Comment #2
Where do the various error estimates come from? Are these from fits or from replicate measurements (or both)?

Authors' Response
The errors of effective OH uptake coefficient, γ_{eff} were determined according to the error propagation rule (Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results: http://physics.nist.gov/TN1297):

$$\sigma_{\gamma} = \gamma_{eff} * \sqrt{\left(\frac{\sigma_k}{k}\right)^2 + \left(\frac{\sigma_{D0}}{D_0}\right)^2 + \left(\frac{\sigma_{\rho 0}}{\rho_0}\right)^2 + \left(\frac{\sigma_{mf}}{mf}\right)^2} \qquad (1)$$

where σ_{γ} is the error of effective OH uptake coefficient, γ_{eff} is the best estimate of the effective OH uptake coefficient, k is the fitted effective heterogeneous OH rate constant, σ_k is the uncertainty of effective heterogeneous OH rate constant, **D_0** is the mean surface-weighted diameter, σ_{D0} is the uncertainty of the mean surface-weighted aerosol diameter (± 0.5 % uncertainty), *mf* is the mass fraction of 3-MGA in aqueous 3-MGA/AS droplet, σ_{mf} is the uncertainty of mass fraction of solute (± 5 % of *mf* predicted by AIOMFAC-LLE for given RH), ρ_0 is the estimated aerosol density based on the volume additivity rule, σ_{ρ_0} is the uncertainty of aerosol density determined using following equation.

$$\sigma_{\rho_0} = {\rho_0}^2 \frac{\rho_{*}\rho_w + \rho_w{*}\rho_{AS} - 2{*}\rho{*}\rho_{AS}}{\rho{*}\rho_w{*}\rho_{AS}} * \sigma_{mf} \qquad (2)$$

where ρ_w is the water density, ρ is the density of 3-MGA, ρ_{AS} is the density of AS.

Reviewer's Comment #3

In the discussion of diffusivity, the comparison is made for laboratory studies. How would this extrapolate to temperatures found in the atmosphere? Could we still anticipate that diffusion would not be limiting, especially given the lower OH radical concentrations?

Authors' Response

It acknowledges that when the ambient temperature decreases, the aerosol viscosity generally increases (everything else being equal). This would lead to a decrease in the diffusion rate of species from the bulk to the surface where oxidation preferentially takes place, and the overall rate of the oxidation will become more likely controlled by the diffusion. This is an expected temperature effect in the boundary layer (e.g. in the cold season or cold climates). However, in the context of vertical air motions (e.g. when air parcels rise adiabatically), we expect that a decrease in temperature will be accompanied by changes in RH; in the case of adiabatic ascent RH tends to increase. This in turn would potentially limit the increase in viscosity of hygroscopic aerosols or even lower it while RH remains high (Gervasi et al., 2020).

To investigate the effect of gas-phase OH radical concentrations, [OH], on the rate of oxidation, we could determine the characteristic time between two successive collision events between gas-phase OH radical and the aerosol surface, τ_{coll}, as follow (Chim et al., 2018):

$$\tau_{coll} \cong \frac{4}{[OH]\,\overline{c_{OH}}\,A} \qquad (3)$$

where $\overline{c_{OH}}$ is the mean thermal velocity of gas-phase OH radicals, and A is the surface area of the droplets. From Eqn. 3, τ_{coll} is larger at a lower gas-phase OH radical concentration. This would suggest that the species would have more time to diffuse to the aerosol surface for oxidation. Hence, as commented by the reviewer, the overall rate of the oxidation becomes less likely limited by the diffusion at lower gas-phase OH radical concentrations.

We have discussed the potential effect of temperatures and gas-phase OH radical concentrations on the heterogeneous reactivity in the revised manuscript.

Line 478, "It also notes that ambient gas-phase OH radical concentration is lower than that used in this study. This suggests that the species would have more time to diffuse to the aerosol surface for oxidation. Hence, the overall rate of the oxidation will be less likely limited by the diffusion at lower gas-phase OH radical concentrations in the atmosphere."

Conclusion, Line 579, "On the other hand, our results show that aqueous organic–inorganic droplets with more hydrophilic organic compounds (e.g. 3-MGA) may not necessarily experience diffusion limitation during heterogeneous OH oxidation, even when phase-separated. The overall heterogeneous reactivity is likely governed by the surface concentration of organic molecules at room temperature. It acknowledges that when the temperature decreases, the aerosol viscosity generally increases (everything else being equal). This would lead to a decrease in the diffusion rate of species from the bulk to the surface where oxidation preferentially takes place, and the overall rate of the oxidation will become more likely controlled by the diffusion. This is an expected temperature effect in the boundary layer (e.g. in the cold season or cold climates). However, in the context of vertical air motions (e.g. when air parcels rise adiabatically), a decrease in temperature will be accompanied by changes in RH; in the case of adiabatic ascent RH tends to increase. This in turn would potentially limit the increase in viscosity of hygroscopic aerosols or even lower it while RH remains high (Gervasi et al., 2020). Overall, this work further emphasizes that the effects of phase separation and potentially distinct aerosol morphologies add further complexity to the quantitative understanding of the heterogeneous reactivity of organic compounds in aqueous organic–inorganic droplets in the atmosphere, motivating further experimental and process modeling studies for a variety of aerosol systems."

Reviewer's Comment #4
The kinetics were tracked by looking at the loss of the parent signal, and the same products appear to be formed in the experiments. However, the intensities of these products have some apparent differences in Figure S4. Was there any correlation of product ion signals to the decay rate of the parent ion? Either in terms of the relative intensities between C6H9O5- or C6H7O5- or the total product ion signal?

Authors' Response
Thanks for the comment. We introduced a figure to show the change in the relative abundance of the two major functionalization products (alcohol product, $C_6H_9O_5^-$ and carbonyl product, $C_6H_7O_5^-$) as a function of OH exposure at different RH. As shown in Figure R1, the relative abundance of these two products increases with increasing OH exposure and does not significantly vary with the RH. To represent the correlation of major product ion signal to the decay of parent ion (i.e. 3-MGA), we calculated the change in relative abundance of the major product ion (i.e. $C_6H_9O_5^-$ or $C_6H_7O_5^-$) relative to that of parent ion (i.e. 3-MGA, $C_4H_9O_4^-$) at a given OH exposure as follow

$$Ratio = \frac{\Delta\,[product\ ion]}{\Delta\,[parent\ ion]} \qquad (4)$$

Table R1 shows that at the maximum OH exposure, the ratio for $C_6H_7O_5^-$ ranges from 0.23±0.06 to 0.33±0.11, while the ratio for $C_6H_9O_5^-$ ranges from 0.58±0.18 to 0.70±0.21 over the experimental RH. These results suggest that considering the uncertainties, the formation of the two major products does not strongly depend on the RH.

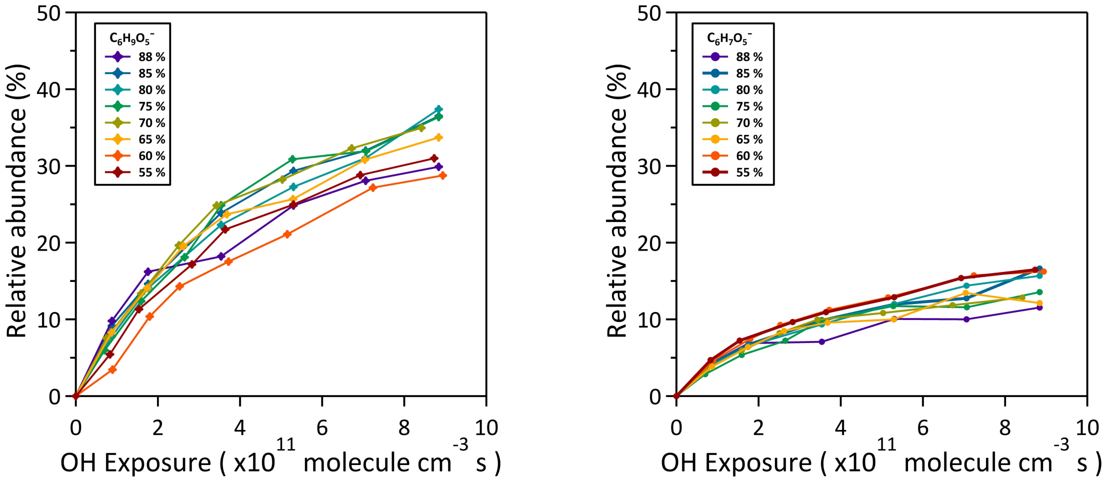


Figure R1. The relative abundance of carbonyl functionalization product ($C_6H_7O_5^-$, left panel) and alcohol functionalization product ($C_6H_9O_5^-$, right panel) under different relative humidities indicated by curve colour (legend) as a function of OH exposure.

Table R1. The change in relative abundance of the major product ion ($C_6H_9O_5^-$ and $C_6H_7O_5^-$) relative to that of parent ion at the maximum OH exposure at different RH

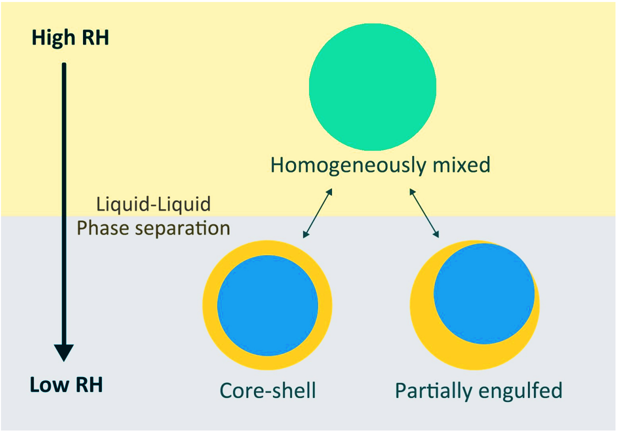
RH (%)	**88**	**85**	**80**	**75**	**70**	**65**	**60**	**55**
Ratio for $C_6H_7O_5^-$	0.25±0.08	0.32±0.10	0.29±0.08	0.23±0.06	0.25±0.08	0.25±0.08	0.33±0.11	0.31±0.09
Ratio for $C_6H_9O_5^-$	0.64±0.22	0.70±0.21	0.68±0.20	0.61±0.17	0.67±0.21	0.69±0.23	0.58±0.19	0.58±0.18

Reviewer's Comment #5

Figure 1 is not interpretable in black and white, I suggest a different color scheme, or more gradation.

Authors' Response

Thanks for the suggestion. We have revised the color scheme for Figure 1.



Reviewer's Comment #6

What are the error bars on Figure 5a (how are they estimated)? Are there error bars that can be applied to Figure 5b?

Authors' Response

In Figure 5a, the error bar for the x-axis represents the calculated error of OH exposure. The OH exposure, defined as the product of gas-phase OH radical concentration, [OH], and the particle residence time, t, was determined by measuring the decay of the hexane concentration (Smith et al., 2009):

$$\text{OH } exposure = -\frac{ln([\text{Hex}]/[\text{Hex}]_0)}{\text{k}_\text{Hex}} = \int_0^t [\text{OH}]dt \qquad (5)$$

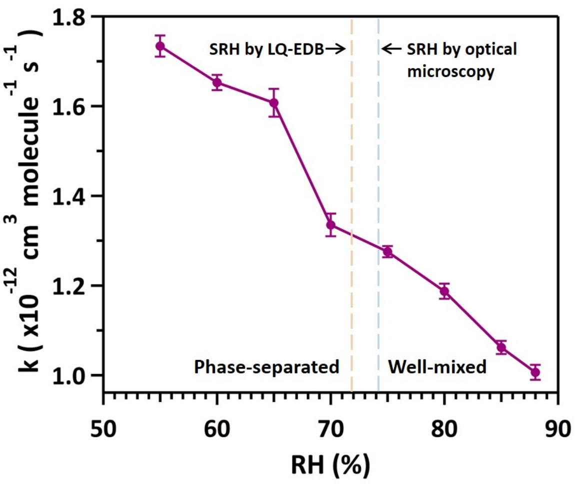
where [Hex] is the hexane concentration leaving the reactor after oxidation, $[\text{Hex}]_0$ is the initial hexane concentration before oxidation, and k_{Hex} is the second-order rate constant of the gas-phase OH−hexane reaction). Based on Eqn.6 and the error propagation rule, the uncertainty for OH exposure, $\sigma_{OH\ exp}$,was derived from Eqn.7:

$$\sigma_{exp} = 0.005\ (\text{OH exposure})\sqrt{\left(16 + \frac{2}{(\text{OH exposure}\times\text{k}_\text{Hex})^2}\right)} \qquad (6)$$

where 0.005 is the precision of the hexane concentration measurement (0.5 % of the reading). The error for the parent decay, $\sigma_{\frac{I}{I_0}}$, is determined from the following equation when the uncertainty of ion signal intensity was assigned to be 0.1 %:

$$\sigma_{\frac{I}{I_0}} = \frac{I}{I_0} \times 0.1 \times \sqrt{2} \qquad (7)$$

where *I* is the signal intensity of 3-MGA at a given OH exposure and I_0 is the signal intensity before oxidation. In Figure 5b (right panel), the x-axis represents the relative humidity (RH), which has been measured by a calibrated RH and temperature sensor. The uncertainty of RH was estimated to be ± 1.5 % RH. The uncertainties of derived effective OH rate constants have been given in **Table 1**. The uncertainties have been included in Figure 5b (right panel) but they appear to be not obvious due to their smaller values. We have revised the Figure 5b (right panel) for better illustration.



References

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