

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

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Overview

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

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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.

Comments

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.

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 ($2.72\text{--}3.26 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are competitive with that for hexane ($5.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) (Atkinson, 2003). Please specify. If mixed, how would this affect the determination of [OH]?

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.

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 decom-

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pose 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.

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).

Page 9, lines 11-12: Isn't γ_{eff} 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 γ_{eff} 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?

References

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