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

Atmospheric Chemistry and Physics
Discussions

# *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**

Received and published: 3 April 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.

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.

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?

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.

Specific comments:

p. 3, l. 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.

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

p. 9, Eqn. 3: Please discuss particle diameter applied.

p. 9, l. 15-20 and p. 10, l. 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. SO42- 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.

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

p. 14, l. 15: "…over time.". Please add reference. Who has shown this?

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

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Petters, M., Prenni, A. J., Kreidenweis, S. M., DeMott, P. J., Matsunaga, A., Lim, Y. B., Ziemann, P. J., Chemical aging and the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol, Geophys. Res. Lett., 33, L24806, 2006.

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