

***Interactive comment on “The heterogeneous OH oxidation of palmitic acid in single component and internally mixed aerosol particles: vaporization, secondary chemistry, and the role of particle phase” by V. F. McNeill et al.***

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Received and published: 5 July 2008

We thank the reviewer and the editor for their constructive comments. We have taken their suggestions into account and revised the manuscript accordingly. Our responses to the their comments are listed below, indicated by \*\*\*.

Reviewer: 1. Pages 6044-6045, Section 3.1: I suggest explicitly stating the relationship between  $k''$  and  $k'$ ; or the uptake coefficient, and also stating something to the effect that  $S/S_o$  is proportional  $[PA]/[PA]_o$ , which in turn is proportional to  $[PA]_{surf}/[PA]_{surf,o}$  because the surface area/mass is approximately constant.

\*\*\*We have followed the suggestions to clarify that section of the manuscript.

2. Page 6049, lines 2-4: If the alkoxy radical isomerizes it forms a hydroxylalkyl radical, which then reacts with O<sub>2</sub> to form a hydroxyperoxy radical. A stable carbonyl is formed by the reaction of an alkoxy radical with O<sub>2</sub>.

\*\*\*The correction has been made.

3. I have one major concern that could unfortunately impact many aspects of the data interpretation. The concern is in regards to the formation (and possible photolysis) of hydroperoxides, which may dominate the chemistry of this system but has not been included in the reaction mechanism, model, or discussion.

\*\*\*We thank the reviewer for pointing this out. We agree that this chemistry could be occurring, but we initially chose a simpler model that neglects specific mechanisms because a number of the necessary parameters are poorly known. Additionally, in the case of ROOH, we had no direct observational evidence that it was occurring. That is, we did not observe signals in our mass spectra that would correspond to ROOH species in the aerosol, and neither did the work of George, et al (see ref in paper) which used a very similar apparatus but with a different aerosol composition.

\*\*\*In our revised manuscript, we now include an evaluation of peroxide formation and photolysis in the context of our model. We discuss the ROOH chemistry model results in detail in section 4.3 of the revised manuscript. To summarize, this chemistry does not impact our main conclusions: namely, gOH >0.8 on pure palmitic acid particles, and mass loss by volatilization due to heterogeneous OH oxidation is unlikely to be important in the atmosphere.

\*\*\*The results demonstrate that if ROOH production occurs as efficiently as possible, and ROOH photolysis leads to the oxidation of a palmitic acid molecule, then ROOH chemistry could explain a significant fraction, but not all, of the inferred secondary chemistry required in the simpler model.

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\*\*\*We ran simulations where every HO<sub>2</sub> collision with RO<sub>2</sub> produces ROOH, and where ROOH photolysis frequencies were 10 percent of those for O<sub>3</sub> + hν → O<sup>1</sup>D + O<sub>2</sub>. For comparison, CH<sub>3</sub>OOH photolysis frequencies at 254 nm should be about 0.1 percent of those for O<sup>1</sup>D production by O<sub>3</sub>. Thus, we feel we pushed this chemistry as hard as is reasonably possible for the information we currently have about such processes.

\*\*\*When including ROOH chemistry, we still require gOH > 1 to best match the data, consistent with our conclusion in the submitted version. With that said, the level of secondary chemistry unaccounted for by ROOH chemistry is likely small enough that uncertainties in OH concentration could allow for the remaining offsets between the model and observed decays. For this reason we have opted to remove the phrase -secondary chemistry- from the manuscript title, and to add comments suggesting that the degree of volatilization we observe is at best an upper-limit on what could be expected in the atmosphere because of the potential for ROOH chemistry to enhance passage through the RO decomposition channel in our system. This latter conclusion is directly in-line with the conclusions we had presented in the submitted version.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6035, 2008.

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