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Interactive Comment

Interactive comment on "The heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidative aging of ambient aerosols" by J. D. Smith et al.

J. D. Smith et al.

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Reply to Referee 1

We would like to thank Referee 1 for his/her thoughtful comments. Many of the comments and questions raised here were the same ones raised by Referee 2, and in these instances we refer the reader to our reply to Referee 2. The Referee's specific comments are below in italics followed by our reply.

1) Do the lamps influence temperature in the flow tube?



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For a discussion of the effect of lamps on the temperature of the flow tube please see the reply to Referee 2.

2) Page 3955, lines 1-5: "It is found that the total ion signal in the AMS when normalized to the SMPS particle volume and the VUV photon flux is constant to within 10% over the entire range of OH exposures employed in the kinetic analysis presented here." Does this data give proof that the particles are completely vaporized at the lowest temperature? As the particles are oxidized the VUV cross-sections will likely change. Hence, it is not clear that a constant VUV-mass spectrum signal (within 10%) indicates that complete vaporization has occurred.

We concede that it is possible that the VUV cross-sections of the oxidation products could be larger than that of squalane leading to an increase in the total ion signal. However, it seems unlikely that the potential decrease in vaporization efficiency at low temperature would exactly compensate for this effect leading to the observed constant total ion signal. The fact that the VUV squalane decays measured at low temperature is equivalent to the EI squalane decay measured at 600° C indicates that partial vaporization of the particles is unlikely. We have included this discussion of the potential effects of partial vaporization to the beginning of the Results and Discussion section of the manuscript in order to clarify this point.

3) Page 3955, line 25-30. The authors redefined the reactive uptake coefficient to take into account the fraction of OH-squalane molecular collisions. This is different from the standard definition in the literature, and I do not see why it is necessary to develop a new definition here. Either use the standard definition, or justify very clearly why the new one is more appropriate.

For a discussion of the utility of our modified definition of the uptake coefficient please see the reply to Referee 2.

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4) Also the equations developed by the authors assume that the reactant decays exponentially, which would not be the case if there was competition between diffusion into the particle and reaction. See for example, Hearn and Smith, GRL, 2006. Please justify why an exponential decay is valid.

Our assumption that the squalane decay is exponential is discussed in the reply to Referee 2.

5) As the authors pointed out, it is conventional to report an initial uptake coefficient where the initial uptake coefficient is obtained from a linear fit to a small subset of the decay data. This seems like an appropriate method, since after the particles have decayed by more than approximately 25%, the uptake is on a relatively different particle. Nevertheless the authors use the decay data over a wide range to determine the reactive uptake coefficient. I think this uptake coefficient is less appropriate to a pure squalane particle. I suggest the authors determine an initial uptake coefficient from a linear fit to a small subset of decay data, similar to what has been done in the literature, and then compare this with literature results. Alternatively, the authors should provide a convincing argument why it is better to use the decay data over a wide range to determine the reactive uptake coefficient. The current manuscript was not convincing on this point.

For a discussion of the utility of our modified definition of the uptake coefficient please see the reply to Referee 2.

6) Page 3960, lines 20-25: "Based on the mass of the observed oxidation products it appears that the products primarily correspond to carbonyls and alcohols." However, the mass spectrum in Figure 7 is only consistent with the formation of carbonyls. Please explain. If there are no alcohols, this has significant implications for ACPD

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the reaction mechanism, as referee 2 has pointed out.

Using the relative peak intensities in the aerosol mass spectrum to estimate the relative population of specific product species is discussed in the reply to Referee 2.

7) Page 3966, line 1-5: "It is also very likely that RO radicals are present at lower O/C ratios, but do not readily fragment, reacting instead via the other reaction pathways shown in Figure 6." What is the support for this statement?

This statement is speculation based on the fact that in the gas-phase decomposition rates of alkoxy radicals are known to increase with β -substitution. We have rewritten this statement to emphasize that it is speculative.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3945, 2009.

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