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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.

Anonymous Referee #1

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Review of "the heterogeneous reaction of hydroxyl radicals with sub-micron squalane particles: a model system for understanding the oxidation aging of ambient aerosols" by Smith et al.

This manuscript using an EI-AMS and VUV-AMS to look at the reaction between OH radicals and squalane particles. The oxidation of organic particles by OH and other atmospheric radicals is an important topic and has been studied by several groups recently. The current paper adds very nicely to the growing body of data on this topic.

Some of the main conclusions include the reaction appears to proceed sequentially by adding an average of one oxygenated functional group per reactive loss of squalane. The reactive uptake coefficient was found to be approximately 0.3. And volatilization of squalane is not important under atmospheric conditions, but once the particles are highly oxidized, volatilization becomes more important. From this the authors conclude that volatilization may be more important for highly oxidized organic particles such as SOA. I support publication after the authors have addressed the following comments:

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

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.

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.

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.

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 de-

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cayed 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.

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 the reaction mechanism, as referee #2 has pointed out.

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?

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

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