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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 #2

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This manuscript describes laboratory experiments of the reaction of OH radicals with squalane particles. This system is used as a model for the OH-initiated oxidation of organic aerosols in the troposphere. Using a combination of aerosol mass spectrometry techniques and particle sizing, the authors conclude that the reaction proceeds quickly with an OH uptake coefficient of 0.3 and by sequentially adding one oxygen atom per reaction. It is a nice result that the observed rate constant, k, for the decay of squalane can be used to fit the appearance of the SqO, SqO2 and SqO3 products using the sequential oxidation model. Furthermore, it is determined that no appreciable

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volatilization occurs until after several oxidative lifetimes with the implication being that evaporation of oxidation products is not significant under atmospheric conditions. This work appears to have been carried out and interpreted carefully, provides some insight into the oxidation mechanism of organic aerosols and should be published after some revision.

Questions and comments regarding experimental details:

1. HO2 radicals will be created from the reaction of OH with ozone at similar (if not higher) concentrations than OH. Might not the HO2 react with squalane, the oxidation products or the intermediates (such as the peroxy and alkoxy radicals)? Such reactions could affect the types of products observed.

2. With such a high concentration of ozone in the gas phase, it seems like it could play a role after the initial H-abstraction by OH. For example, couldn’t the alkyl radicals react with ozone? Or, could the alkoxy radicals react with ozone? Would such a large concentration of ozone reduce the uptake of OH by occupying surface sites?

3. What is the geometric standard deviation of the particle size distribution? The observed rate of loss of the squalane in the particles is proportional to the surface area to volume ratio (˜ 1/r), but the squalane mass spectrometer signal is proportional to the mass (˜ r3). Consequently, if the particle size distribution is too wide then the calculation of the uptake coefficient from the observed rate of loss of the squalane signal is not straightforward and cannot be calculated from equations 3 and 7 directly.

4. Why is the surface-weighted diameter used here?

5. What is the temperature in the flow tube? The four 130-cm long Hg lamps surrounding the flow tube probably heat it up. What impact would this increased temperature have on the results and their interpretation?

6. The explanation of how the O/C and H/C ratios are calculated from the EI spectra would benefit from additional details. It is not clear how these are derived, and given

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that the O/C ratio is such an important measurement in this manuscript, it should be explained in more detail. It is not at all clear why the correction factors are necessary, how they have been chosen or why the H/C correction can be ignored. The reader should not have to read the works of Aiken et al. to understand how this important measurement is made.

7. To measure hexane loss with the larger concentrations of OH, the hexane is introduced near the end of the flow tube and the squalane decay is scaled accordingly. How far down the flow tube is this point and what is the shorter OH + hexane residence time?

Questions and comments regarding results:

1. The new definition of the uptake coefficient introduced here, gamma_OH_Sq is confusing and does not seem necessary or appropriate. Instead of normalizing the squalane loss to the number of OH-particle collisions, it is normalized to the number of OH-squalane collisions. No other studies have used this definition as far as I am aware. It includes an additional assumption, namely that the number of OH-squalane collisions can be calculated from the squalane concentration (f = [Sq]/[Sq]_0 in equation 4). This amounts to assuming that d[Sq]/dt is proportional to [Sq] and that the particle is well mixed. In other words, the squalane decay is assumed to be exponential a priori. These assumptions cannot be made in a general sense; what if the reaction is diffusion limited, in which case d[Sq]/dt is proportional to [Sq]ˆ1/2, or if the particle is not well mixed?

In essence, the initial uptake coefficient, gamma_0, is replaced by this new uptake coefficient, gamma_OH_Sq. However, as the authors point out, these two values will be identical when most of the particle remains unreacted. So, then, what is the value of redefining the uptake coefficient, here?

The authors claim that fitting to equation 7 (the exponential fit) allows them to use a larger range of the experimental decay data, but this is valid only if the reaction between OH and squalane is the same initially (when no squalane has reacted) as it is when the particle is only 20% squalane. On the contrary, calculating an initial uptake coefficient from the initial slope of the decay does not require such an assumption and is a direct representation of the rate of reaction of squalane (not a mixture of squalane and oxidation products).

2. In re-fitting the OH + DOS data of George et al. (incorrectly referenced as Figure 5; it is in fact Figure 4) to an exponential function, the authors claim a better agreement between the calculated uptake coefficients. Please specify what the value obtained from re-fitting their data is. Also, the validity of using an exponential fit is questionable since George et al. state in their paper that it doesn’t fit their data! In doing so, the initial rate of reaction (when very little DOS has reacted) is not described well. There does not appear to be a strong case for quantitative agreement between these two studies. Furthermore, the OH + DOS data of Hearn et al., 2006, yields an uptake coefficient of 2.0, and fitting it to an exponential does not appear to change this value appreciably. The authors don’t mention this, however. I suggest that the comparison with these two OH + DOS studies be reconsidered.

Likewise, in re-fitting the OH + palmitic acid data of McNeill et al. to an exponential, the authors claim that three of the four curves show quantitative agreement with the current measurement. The values of the uptake coefficient obtained from this re-fitting need to be stated.

3. Hearn et al. (2007) also observed similar oxidation products from the reaction of Cl + DOS and measured their yields. This work should be cited when discussing the similarity of the squalane and DOS oxidation products.

4. In Figure 7 there appears to be no alcohol product at m/z = 438 or the corresponding alcohol products in the 2nd, 3rd and 4th generation products. It seems as if the absence of these products provides further insight into the oxidation scheme of Figure 6. Specifically, it infers that the Russell mechanism, the alkoxy radical isomerization and

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the chain propagation are not present. The implications of the lack of alcohol products should be addressed.

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