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Atmospheric
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Discussions

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 2

We would like to thank the reviewer for his/her thoughtful comments. The referee’s specific comments are below in italics followed by our reply to each.

Questions and comments regarding experimental details:
1)*HO_2 radicals will be created from the reaction of OH with ozone at similar (if not higher) concentrations than OH. Might not the HO_2 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.

The reviewer is correct in pointing out that HO_2 radicals should be present in our flow tube reactor. Using a gas-phase kinetic model (mentioned in the manuscript) the HO_2 concentration is estimated to be 3-10% lower than the OH concentration over the range of conditions employed in our experiment. It is unlikely that HO_2 would react with any significant fraction of the squalane or its stable oxidation products since the reaction of HO_2 with most organics is extremely slow. For example, the room temperature gas-phase rate constant for the reaction of HO_2 with propane is 1.6 x 10^{-25} cm^3/molec·s (Tsang, 1988), which is $\sim$12 orders of magnitude slower than the equivalent reaction with OH (Atkinson, 2003). It is possible that HO_2 could react with the peroxy radical intermediate forming a hydroperoxide (ROOH) species. However, as pointed out in the manuscript we see no evidence for this reaction based on the elemental composition measurements, which indicates that only one O atom is added per reactive loss of squalane. Two oxygen atoms added per reactive decay of squalane would be observed if hydroperoxides were produced in appreciable quantities. It is expected that under these experimental conditions the RO_2 self reaction will be the primary fate of the particle-phase peroxy radicals. In addition, due to the relatively low HO_2 concentrations in our system, alkoxy radicals will preferentially react with O_2 and other particle-phase organics, and it is expected that the HO_2 + alkoxy reaction should represent only a very minor channel. We have added additional discussion of the possible role of HO_2 near the end of the Results and Discussion section of the manuscript.

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?*

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It is again unlikely that ozone plays any major direct role in the oxidation of squalane particles. The rate constant for alkyl radicals reacting with ozone and with O_2 should be similar (Paltenghi et al., 1984). However, in our experiments the concentration of O_2 is more than 4 orders of magnitude larger than ozone. In this large excess of O_2 it is unlikely that any measurable fraction of the alkyl radicals will react with the ozone. A similar argument can be made for the reaction of alkoxy radicals with ozone. The loss of alkoxy radicals will be dominated by the reaction with O_2 and other particle-phase organics (H abstraction reactions), which are both many orders of magnitude more concentrated than ozone in our system.

The Referee also suggests that ozone may impact the uptake measurements in a more indirect way by occupying surface sites, and thus reducing the amount of squalane available at the surface. During the kinetic measurements presented here the maximum ozone mixing ratio is 3 ppm. If we assume that the Henry's law solubility constant for ozone in squalane is the same as O_2 (4.4 x 10^{18} cm^{-3} atm^{-1}) (Vasenkov et al., 1991), the particle-phase concentration of ozone should be $\sim$4 x 10^{13} molec/cm^3. Based on the mean volume of the particles used in these experiments this particle-phase ozone concentration corresponds to an average of $<$ 0.1 ozone molecules per particle. For comparison, the concentration of organic molecules (squalane + oxidation products) in the particle-phase is approximately 10^{21} molec/cm^3, corresponding to 2 x 10^6 molecules per particle. Therefore, squalane and its oxidation products should be more than 7 orders of magnitude more concentrated in the particle-phase than ozone. Therefore, we do not expect that surface solvated ozone will limit the uptake of OH on the particle surface.

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 (r^3). 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.

The geometric standard deviation found from the particle distributions used in these studies is ∼1.3. This value has been added to the experimental section of the manuscript. However, we find that if the polydisperse distribution of particles is correctly accounted for very little error is incurred in the calculation of the uptake coefficient. This is the case even for very broad particle distributions (i.e large geometric standard deviations). As discussed in the manuscript the uptake coefficient is proportional to V/A, where V is the volume of the particles ((1/6)$\cdot\pi\cdot D^3$) and A is the surface area ($\pi\cdot D^2$). Here D is the geometric diameter of the particles. Although calculating the volume to surface ratio (V/A) is straightforward for a single particle size, it is slightly more complicated for a distribution of particles and is given by

$$\frac{V}{A} = \frac{\int D^3 f(D) dD}{6 \cdot \int D^2 f(D) dD} \tag{1}$$

Where *f(D)* is the normalized diameter distribution function describing the particles. In the studies presented here we have found that the particles are well described by a log-normal distribution function such that

$$f(D) = \frac{1}{\sqrt{2\pi} D \ln\sigma} \exp\left[\frac{-[\ln(D/\bar{D})]^2}{2(\ln\sigma)^2}\right] \tag{2}$$

Here σ is the geometric standard deviation (∼1.3), and $\bar{D}$ is the median diameter (∼130 nm) of the distribution. By substituting Eq. (2) into Eq. (1), and integrating over all particle diameters, it is found that the volume to surface ratio for a log-normal distribution is equal to surface weighted diameter (D_{surf}) divided by 6, as shown below

$$\frac{V}{A} = \frac{\int_0^\infty D^2 \cdot \exp\left[\frac{-[\ln(D/\bar{D})]^2}{2(\ln\sigma)^2}\right] dD}{6 \cdot \int_0^\infty D \cdot \exp\left[\frac{-[\ln(D/\bar{D})]^2}{2(\ln\sigma)^2}\right] dD} = \frac{\bar{D}\exp\left[\frac{5(\ln\sigma)^2)}{2}\right]}{6} = \frac{D_{surf}}{6} \qquad (3)$$

We note that for a distribution with a geometric standard deviation of 1.3 using the mean number weighted diameter, instead of surface area weighted diameter, to calculate the uptake coefficient leads to a value that is 13% too small. Furthermore, if the mean mass weighted diameter is used, the computed uptake coefficient would be 8% too large. Furthermore, the error incurred by using the mean number weighted or mass weighted diameters becomes far larger as the geometric standard deviation of the particle distribution increases. Eqs. (1) and (2) have been added to the manuscript after Eq. (7) along with a short discussion of why the surface weighted diameter is used.

4) *Why is the surface-weighted diameter used here?*

Please see the previous discussion. We now explain why we use the surface weighted diameter in the Results and Discussion section of the manuscript (after Eq. (7)).

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?*

The flow tube is actively cooled using pressurized air directed perpendicularly at three points along the length of the tube. However, even with this active cooling the flow tube warms up to approximately 35° C. We regret that this information was not included in the original manuscript, and it has been added to the Experimental section

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of the manuscript. Based only on Eq. (7) in the manuscript this elevated temperature would lead to less than a 2% decrease in the calculated uptake coefficient, relative to room temperature, due to the increased collision frequency of OH with the particles.
In general it is difficult to speculate on any additional temperature dependencies of the reactive uptake coefficient. It is possible that there is an energetic barrier to the heterogeneous OH + squalane reaction which would lead to a small increase in the uptake coefficient with increasing temperature. For example, based on the dependence of the activation energy of the OH + n-alkane reaction on carbon number in the gas-phase, the barrier to the OH + squalane reaction is likely less than 3 kJ/mol (Manion et al., 2008). Therefore, an increase in temperature of 10° C would lead to an increase in the reaction rate of less than 7%. However, this barrier may be significantly reduced for a heterogeneous surface reaction, as suggested by the large uptake coefficient, which would lead to an even weaker temperature dependence. In contrast, the sticking coefficient of OH on an organic surface may be reduced at elevated temperatures potentially resulting in what would likely be a weak inverse temperature dependence of the reactive uptake coefficient. Therefore, in general we expect the effect of the elevated temperature to be relatively small, and much less than our stated error in the measured uptake coefficient. We currently do not have the means to control the temperature of the flow tube, but temperature dependent studies may represent an interesting direction for future studies.

6) *The explanation of how the O/C and H/C ratios are calculated from the EI spectra would benefit from additional details.*

The methods employed to determine the particle-phase O/C ratio have been explained in more detail in the Experimental section of the manuscript.

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?
For the high OH concentration measurements the hexane was added approximately 10 cm from the end of the flow tube. We have now included this information in the discussion of the high oxidation measurements. We again note that for the product analysis presented in Fig. 8 we do not report absolute reaction rates, and instead focus on the product reaction rates relative to squalane. Therefore, the quality of fit to the sequential oxidation model is independent of the OH exposure axis used.

Responses to the questions and comments regarding results:
1) *The new definition of the uptake coefficient introduced here,* γ_{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.*

We are not the first group to use this definition of the uptake coefficient. For example, Eq. (7) in the manuscript is identical to Eq. (10) in Lambe et al. (2007), which they used to calculate the uptake coefficient of OH on hexacosane particles.

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]*$^{1/2}$*, or if the particle is not well mixed?*

Since OH is known to react rapidly with most organic compounds in the gas-phase, it can safely be assumed that the heterogeneous OH reaction with squalane should represent a fast surface reaction (Rudich et al., 2007). Such a rapid surface reaction should result in an exponential decay (Hearn et al., 2005). In the case of a reaction that is limited by OH diffusion we would instead expect a quadratic decay of the squalane as a function of OH exposure, which is not observed here (see Figs. 5 and 8). Furthermore, if the particles are not well mixed and the reaction is limited by squalane diffusion to the surface we would also expect an exponential decay, but not as a function of OH exposure (Hearn et al., 2005). However, a simple time constant analysis suggests that the squalane reaction is not limited by squalane diffusion. For example, the time constant (τ) for the decay of squalane at the highest OH concentration used in the kinetic studies is

$$\tau = \frac{1}{k_{Sq} \cdot [OH]} \sim 26s \tag{4}$$

where k$_{Sq}$ is the second order rate constant for the decay of squalane and [OH] is the OH concentration. We can also estimate the time constant for the diffusive mixing of the particles (τ_D) (Docherty and Ziemann, 2006) using

$$\tau_D = \frac{d^2}{4 \cdot \pi^2 D_c} \sim 9 \times 10^{-6} s \tag{5}$$

where d is the particle diameter and D$_c$ is the self-diffusion coefficient. Eq.(6) is only an estimate for squalane particles because we have used the self-diffusion coefficient for triacontane (7.5 x 10^{-7} cm^2/s) (Vardag et al., 1991) a straight chain isomer of squalane. Even if the actual diffusion constant for squalane is an order of magnitude smaller than for triacontane, which is very unlikely, the decay time constant for the squalane reaction is still many orders of magnitude slower than the mixing time. Therefore, the squalane particles should be well mixed on the timescales of the reaction, which is confirmed by the fact that the sequential oxidation model

simultaneously fits the squalane decay as well as the product evolutions (see Fig. 8) as discussed in the manuscript.
Therefore since OH reacts rapidly at the surface of the well mixed particles, our assumption of an exponential decay of the particle-phase squalane is well founded, and, importantly, is also supported by the data. We have added short discussion of why an exponential decay is expected soon after we introduce Eq.(7) in the manuscript.

In essence, the initial uptake coefficient, γ_0*, is replaced by this new uptake coefficient,* γ_{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).*

Given that the observed squalane decay is in fact exponential (see Figs. 5 and 8) we see no reason to limit ourselves to an initial rate analysis. It is important to keep in mind that an initial rate analysis is a method of approximating the exponential decay constant, and only seems appropriate if the observed data is non-exponential. Such non-exponential behavior could indicate that the reaction of the particle-phase reactant changes upon the formation of products. However, since squalane decays exponentially, even after much of it has reacted away, the uptake of OH appears to be unchanged by the formation of products. Thus the reaction between OH and squalane is indeed the same initially as it is when the particle is only 20% squalane. Therefore, an initial rate analysis is unnecessary and can potentially result in avoidable errors. However, as expected for an exponential decay, if we employ an initial rate analysis of the squalane decay data we find that the calculated uptake coefficient is within 5% of the value reported in the manuscript. This point is more clearly emphasized in the revised manuscript.

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.*

The incorrectly referenced figure has been corrected in the revised draft. The uptake coefficient we calculate from an exponential fit to the George et al. (George et al., 2007) data is 0.23, which again is well within error of the value found here. We have included this value in our discussion of the George et al. results. The R^2 from an exponential fit to the George et al. data is 0.93. As discussed in the manuscript an exponential fit reasonably represents the George et al. decay data, except for the first few points at low OH exposure. As discussed in the manuscript we do not observe this type of bi-exponential decay, and currently cannot explain its origin. The purpose of re-fitting the George et al. data was simply to show that over a large OH exposure range the differences between the data reported in our manuscript and that of George

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et al. are relatively small. With regard to the Hearn and Smith (Hearn and Smith, 2006) measurements, we suspect that the large uptake coefficient reported in that study may be the result of the specific experimental conditions employed. Therefore, a straightforward comparison of the measurements presented in our manuscript, and those presented in Hearn and Smith could be difficult. In the experiments of Hearn and Smith pure ozone was used to generate OH without the explicit introduction of O_2 to the flow tube reactor. Under these conditions the particle-phase alkyl radicals will react with ozone resulting in the production of an alkoxy radical and an O_2 molecule (Paltenghi et al., 1984). This is different than for a system containing an excess of O_2 since alkyl radicals are rapidly converted to peroxy radicals. In the absence of O_2 the resulting alkoxy radical will likely abstract a hydrogen atom from another particle-phase DOS molecule to form an alcohol and another alkyl radical. This alkyl radical will in turn react with another ozone starting the cycle over again. This process could remove many DOS molecules per OH reaction leading to a chain reaction and very large apparent uptake coefficients. However, as pointed out by Hearn and Smith, some O_2 is produced from the photolysis of ozone. It is difficult for us to calculate the amount of O_2 generated by the photolysis of ozone because the laser fluence used in the Hearn and Smith experiments is not reported. However, if we estimate the photolysis rate of ozone in order to give to give OH concentrations in the range reported by Hearn and Smith we estimate that ozone is still more than an order of magnitude more concentrated than the O_2. As a result we would expect significant ozone chemistry under these conditions, which we believe could be the origin of the relatively large uptake coefficient observed by Hearn and Smith. In the revised manuscript we have added a brief discussion of the Hearn and Smith experiments where we discuss uptake values obtained by other groups.
The uptake coefficients calculated from the McNeil et al. data, which range between 0.28 and 0.39, have been included in the revised manuscript.

3) *Hearn et al. (2007) also observed similar oxidation products from the reac-*

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tion of Cl + DOS and measured their yields. This work should be cited when discussing the similarity of the squalane and DOS oxidation products.

We have added the Hearn et al. (2007) citation to the discussion of the observed oxidation products in our revised manuscript.

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

As mentioned in the manuscript it is difficult to draw quantitative conclusions about the relative populations of specific species (e.g. alcohols vs. ketones) based on the relative peak intensities in the mass spectrum. In our experience organic alcohols tend to fragment upon ionization more readily than ketones, which would make alcohols appear to be less abundant than ketones even if they are not. For example, a relatively large product peak is observed at 2 mass units less than squalane (m/z = 420). This peak shows the same kinetic behavior as the first generation oxidation products, and probably corresponds to an alcohol fragment produced by water elimination during dissociative photoionization. Therefore, we are hesitant to draw conclusions about the reaction mechanism based solely on the relative intensity of the alcohol peak. In order to emphasize this point we have added an additional discussion to the Results and Discussion section of the manuscript.

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