

## ***Interactive comment on “Artifacts in measuring aerosol uptake kinetics: the roles of time, concentration and adsorption” by L. H. Renbaum and G. D. Smith***

**L. H. Renbaum and G. D. Smith**

gsmith@chem.uga.edu

Received and published: 23 May 2011

1. We thank the reviewer for drawing our attention to the need for more description of the supercooled 2-ODA. This will be added in the revised manuscript. Briefly, we are confident that the 2-ODA particles are supercooled after having cooled to room temperature for several reasons: 1) bulk samples (i.e. in beakers) remain liquid after warming for several hours, 2) our experience with other organic solids with melting points within 30 degrees C of room temperature (2-ODA's is only  $\sim 10$  degrees C above room temperature) indicates that it should remain supercooled in the aerosol form over the course of the experiment (i.e.  $\sim$  two minutes), 3) uptake kinetics and product distri-

C3809

butions from the OH or Cl reactions are identical whether the particles are pre-cooled in a -78 degree C bath or not (no evidence for a phase change). We believe that the supercooled 2-ODA particles are good mimics for liquid organic particles because at room temperature the bulk supercooled liquid does not appear to be any more viscous than 2-ODA when it is warmed above its melting point or than other organic liquids (e.g. squalane). This observation is only qualitative, but it does confirm that the viscosity of the supercooled liquid is not drastically different than other liquids that we use for model organic aerosols.

2. We will add a range of lines representing the uncertainty in the slopes of the linear fits to the large flow tube decays in Figure 2. We will also add more discussion of how the error bars for the small and large flow tube measurements were derived. The noise in the large flow tube data at each point is larger than the small flow tube error bar because the single small flow tube data point is really the average of over 100 data points. This aspect of the measurements will be explained in more detail in the revised manuscript. With regards to the suggestion that the data in Figure 2a for the small and large flow tubes are indistinguishable at low exposure ( $< 10^{10}$  molecules/cc), we disagree since the data are not as robust there. In essence, we would be looking for a very small change ( $< 5\%$ ) on a large ion signal. We have concluded that a more accurate measure of the rate of change of the ion signal is made by including more data points representing up to 20% reaction. We feel that that level provides enough data points to fit while still representing the rate of reaction of a particle that hasn't changed in composition too much.

3. We agree with the reviewer that it would be nice to compare results for OH uptake from as many other studies as possible. However, we chose not to do because we don't think that these experiments are all comparable for a variety of reasons. We describe these for each study, below.

OH uptake studies:

C3810

In Lambe et al. [1] they studied OH + hexacosane particles and found  $\gamma = 1.04$ . Since OH gas-phase diffusion limitation apparently was not accounted for, this makes it difficult to compare to. The diffusion-corrected  $\gamma$  becomes  $> 4$  which indicates a significant gas-phase reaction or secondary chemistry. Also, hexacosane is a solid at room temperature, and we chose not to compare to solid particles since we focused on liquid and supercooled particles in the present study.

In Weitkamp et al. [2] they studied OH + aerosolized motor oil and found efficient reaction of alkanes and other hydrocarbons. Because the compositions of these particles were unknown, it was not possible to calculate uptake coefficients, and instead they measured effective second-order rate constants and relative rates. They did estimate effective uptake coefficients and report them to range from 0.1 to 8, but we feel that we could not include these values in our comparison because they were based on an assumption that all of the organics reacted at the same rates. Also, these values weren't attributed to specific species.

In McNeill et al. [3] they studied OH + palmitic acid particles and found  $\gamma = 0.8 - 1$ . We did not include this study in our comparison because these particles are solid at room temperature.

In George et al. [4] they measured OH + BES (or DOS, dioctyl sebacate) particles and found  $\gamma = 1.3 (+/- 0.4)$ . The value  $> 1$  indicates a potential secondary loss of BES molecules, perhaps through a radical chain. In fact, we previously measured the OH + BES uptake coefficient to be 2.0 (+0.6/-0.1) [5], also indicating a potential radical chain. Since such secondary chemistry could be a function of radical concentration, as well as other conditions, we chose not to compare these values to those for OH + 2-ODA and OH + squalane, for which no evidence for secondary chemistry was observed.

Cl uptake studies:

In Hearn & Smith [5] and Hearn et al. [6], we studied the reaction of Cl with DOS particles with and without O<sub>2</sub> and found the uptake coefficient to be fast, i.e. 1.7 and

C3811

1.8. In the present manuscript, we have measured Cl + 2-ODA uptake coefficients to range from 0.9 to 1.4 (with 20% O<sub>2</sub>) depending on [Cl<sub>2</sub>]. We feel that these measurements are in fairly good agreement with each other, but we don't include the previous measurements in our figures because we didn't measure  $\gamma$  as a function of [Cl<sub>2</sub>] explicitly. Consequently, it would be difficult to infer a dependence on [Cl<sub>2</sub>] which was the primary result of this part of the manuscript. In short, including the previous measurements would not add to the interpretation of the present results and may, in fact, confuse the issue.

In summary, for a variety of reasons we feel that the previous measurements of OH and Cl uptake on model organic aerosols by our group and others are not directly relevant to the work presented here. We will add mention of these previous studies in the revised manuscript along with a brief explanation as to why they were not included in the quantitative comparison.

4. There is no measurable change in the 2-ODA signal when the light is turned on with only Br<sub>2</sub> (i.e. no Cl<sub>2</sub>) in the flow tube. This tells us that Br radicals are not formed at a large enough concentration to affect the Cl uptake measurements. We will add this observation to the Br<sub>2</sub> discussion to make it clear that the decrease in the rate of 2-ODA loss observed when Br<sub>2</sub> was added cannot be attributed to a Br + 2-ODA reaction. We did not measure [Br] because it does not react with the gas-phase reference, acetone.

The gas-phase reaction,  $\text{Cl} + \text{Br}_2 \rightarrow \text{BrCl} + \text{Br}$ , is indeed fast ( $k \sim 10^{-10} \text{ cm}^3/\text{molecule}/\text{sec}$ . [7]), and we do observe a reduced extent of reaction with Cl radicals in the presence of Br<sub>2</sub>. However, [Cl] will be reduced for both the reaction with the 2-ODA particles and the gas-phase reference, acetone. Thus, any reduction in [Cl] is accounted for by using the mixed-phase relative rates approach to measure the rate of the Cl + 2-ODA reaction.

References

[1] Lambe, A., Zhang, J., Sage, A. & Donahue, N.M. Controlled OH Radical Production

C3812

via Ozone-Alkene Reactions for Use in Aerosol Aging Studies. *Environ Sci Technol* 41, 2357-2363 (2007).

[2] Weitkamp, E., Lambe, A., Donahue, N.M. & Robinson, A.L. Laboratory Measurements of the Heterogeneous Oxidation of Condensed-Phase Organic Molecular Markers for Motor Vehicle Exhaust. *Environ Sci Technol* 42, 7950-7956 (2008).

[3] McNeill, V. et al. The heterogeneous OH oxidation of palmitic acid in single component and internally mixed aerosol particles: vaporization, secondary chemistry, and the role of particle phase. *Atmos Chem Phys* 8, 5465 (2008).

[4] George, I., Vlasenko, A., Slowik, J., Broekhuizen, K. & Abbatt, J. Heterogeneous oxidation of saturated organic aerosols by hydroxyl radicals: uptake kinetics, condensed-phase products, and particle size change. *Atmos Chem Phys* 7, 4187-4201 (2007).

[5] Hearn, J. & Smith, G.D. A mixed-phase relative rates technique for measuring aerosol reaction kinetics. *Geophysical Research Letters* 33, L17805, doi:10.1029/2006GL026963 (2006).

[6] Hearn, J.D., Renbaum, L.H., Wang, X. & Smith, G.D. Kinetics and products from reaction of Cl radicals with dioctyl sebacate (DOS) particles in O(2): a model for radical-initiated oxidation of organic aerosols. *Phys Chem Chem Phys* 9, 4803-4813 (2007).

[7] NIST Chemical Kinetics Database, Standard Reference Database 17, Version 7.0, Release 1.3, <http://kinetics.nist.gov>. (2000).

---

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 11, 7971, 2011.