

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

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1. "Do authors have any information on particle or oxidant loss to the wall? The effects of wall might be larger in the large flow tube reactor compared to the small one because the residence time of particles is long. Do authors think this may potentially affect the observed reaction kinetics or this wall effects are negligible?"

The wall loss of particles, gas phase reference and oxidants can be ignored in these experiments. Unless the addition of the light into the flow tube changes the wall loss of the particles or gas reference (which is not to be expected), wall losses of these species are the same whether the reaction is occurring (light is on) or not. Therefore, when the

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reaction is initiated by introducing the light, the only change in the particle or gas phase reference signal is due to reaction. Wall loss of the oxidant is accounted for by use of the gas-phase reference; any wall loss of the oxidant will affect the concentration “seen” by the gas-phase reference and the particles and will cancel out. We will add explicit mention in the manuscript of the insensitivity of our uptake measurements to wall loss of the various species.

2. "I am concerned that the authors did not correct for gas-phase diffusion of the radical to the particle. The gas phase diffusion correction is indeed negligible if uptake coefficients is below  $10^{-3}$ , but it is significant with uptake coefficients over 0.1 for the particles larger than 100 nm (Pöschl et al., 2007 and see Fig. 2 in Shiraiwa et al., 2009). The authors should either apply a gas phase diffusion correction, or otherwise justify why this correction is not needed."

Correcting for gas phase diffusion of OH to the particle surface in the OH reactive uptake experiments changes the calculated reactive uptake coefficients by less than 10 % which is within the error bars of these measurements. Application of a gas phase diffusion correction to the chlorine atom initiated heterogeneous reactions may not be accurate due to the presence of secondary chemistry. Therefore, we have decided to omit the diffusion correction. In addition, the gas phase diffusion correction factor should be independent of O<sub>3</sub>/Cl<sub>2</sub> concentration as well as OH/Cl exposure and thus cannot explain the trends observed in the reactive uptake coefficient as a function of radical concentration or as a function of radical precursor concentration. Since the main conclusions from this paper are the trends observed as a function of radical and precursor concentrations, including the gas phase diffusion correction is unnecessary. We will add a more specific description of why we did not include gas-phase diffusion corrections in our reported uptake coefficients.

3. "The authors applied Langmuir-type isotherm to the experimental data. Do the authors implicitly assume that kinetics is limited by surface adsorption/reaction and ozone dose not diffuse into the bulk?"

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It is not assumed that ozone does not diffuse into the bulk, and diffusion of ozone into the bulk has not been ruled out. However, equilibrium solubility behavior cannot explain a high concentration of O<sub>3</sub> or Cl<sub>2</sub> at the particle surface. Assuming the equilibrium solubility of O<sub>3</sub> may be approximated by that of O<sub>3</sub> in cyclohexane (Ostwald coefficient,  $L = 1$  [1]), at the highest O<sub>3</sub> concentration used here ( $\sim 8 \times 10^{15}$  molecules/cm<sup>3</sup>) there would be less than one molecule of O<sub>3</sub> (on average) in a 1 nm thick layer at the surface of a 100 nm particle. Thus, we conclude that there would be insufficient O<sub>3</sub> to impede the reactive uptake of OH on the particle surface. We believe that another phenomenon, other than equilibrium solubility, such as O<sub>3</sub> adsorption onto the particle surface, must be responsible for the observed decrease in the OH-particle reactivity at high O<sub>3</sub> concentrations.

4. "The high  $K$  value of  $10^{15}$  cm<sup>3</sup> suggests the high surface coverage and long desorption lifetime (about millisecond to second) of O<sub>3</sub> (Kwamena et al., 2007; Shiraiwa et al., 2009). The molecular dynamic simulation predicts that desorption lifetime of O<sub>3</sub> on liquid particle should be only about nanoseconds (Vieceli et al. 2005). Recently, Shiraiwa et al. (2011) showed the formation of long-lived reactive oxygen intermediates (ROIs) upon heterogeneous reaction of ozone. The desorption lifetime of ozone is actually short (nanoseconds, but not seconds) and ozone decomposes into ROIs (O atom), which are long-lived leading to the high surface coverage. It may be worthwhile to discuss this aspect."

We would like to thank Dr. Shiraiwa for pointing out the possible role of ROI's in our experiments.

The role of reactive intermediates as well as expected desorption lifetimes of O<sub>3</sub> from the particle surface is unclear in these studies. Vieceli et al. [2] use the radial distribution functions and dipole orientation distributions of water and ozone in the bulk and surface in order to determine the theoretical desorption lifetimes. It is not clear by what extent the desorption lifetime should change for O<sub>3</sub> interacting with a branched, saturated organic acid. Also, it is not clear if the type of ROI's (presumed to be O atoms)

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that are formed in the interaction of O<sub>3</sub> with aromatic surfaces, such as benzo[a]pyrene [3], are expected here. It is possible that the ozone may interact with the delocalized electrons on the carboxylic acid moiety. However, the identity of the ROI's and their respective lifetimes are unknown. It is possible, if formed, that these species may participate in blocking reactive sites for OH. Since no change in the particle species signal is observed upon addition of O<sub>3</sub>, the intermediate species formed from the interaction of O<sub>3</sub> with the 2-ODA particle surface would have to be a) unreactive with 2-ODA or b) formed in small yields and c) be formed from a mechanism that involves no net loss of the particle phase species.

Given the uncertainty as to the nature of the potential ROI's that may be formed, we do not feel comfortable making any statement about their lifetimes. However, we will add mention of the possibility that they may be playing a role, here, citing the recent work by Dr. Shiraiwa and co-workers [3] supporting this possibility.

5. "The authors conclude that time and concentration are interchangeable variables. I am concerned how robust this conclusion is. The reaction time of 66 s is still too short compared to atmospheric oxidation time of hours to days. Therefore, the reactants were consumed only 20%. Are the authors sure that the conclusions hold if the reactants are consumed for example 90% or more? Please note that uptake coefficients are not constant but function of reaction time and concentration of reactants (Ammann and Pöschl, 2007). I do agree with the authors that more work is needed to explore the effects of chemical and physical properties of particles such as phase state (e.g., liquid vs. semi-solid vs. solid)."

We conclude that concentration and time are interchangeable variables when the oxidant concentration, and thus reaction time, for a given exposure is changed by over an order of magnitude (factor of 33) and suggest using caution when extrapolating reactive uptake coefficients measured in the lab to the troposphere. We agree with the reviewer that the uptake coefficient is a function of the particle composition, and therefore of the extent of reaction. This is precisely why we controlled the oxidant exposure to al-

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low only ~20% reaction. If we had allowed the reaction to proceed further we would not be measuring the rate of reaction of 2-ODA, for example, but the partially-reacted particles. In short, we are not claiming that the conclusions hold if the particles are consumed 90% or more. Our hypothesis that inert species (i.e. O<sub>3</sub> or Cl<sub>2</sub>) are adsorbing to the surface and affecting the observed rate of loss of the particle species would have to be tested on more complex particles containing mixtures or having already been reacted significantly.

[1] Gomez, A.L., Lewis, T.L., Wilkinson, S.A. & Nizkorodov, S.A. Stoichiometry of ozonation of environmentally relevant olefins in saturated hydrocarbon solvents. *Environ Sci Technol* 42, 3582-3587 (2008).

[2] Vieceli, J. et al. Molecular dynamics simulations of atmospheric oxidants at the air-water interface: solvation and accommodation of OH and O<sub>3</sub>. *J Phys Chem B* 109, 15876-15892 (2005).

[3] Shiraiwa, M. et al. The role of long-lived reactive oxygen intermediates in the reaction of ozone with aerosol particles. *Nat Chem* 3, 291-295 (2011).

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