

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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The authors present some very interesting work on the role that the radical precursor (O₃ and Cl₂) plays in the heterogeneous reaction of OH and Cl with organic aerosols. They conclude that physical absorption of the precursors either blocks the surface reaction in the case of OH or enhances the reaction in the case of Cl₂. They interpret the functional dependence of the measured uptake coefficient on [Cl₂] and [O₃] using a Langmuir absorption isotherm. The authors then discuss how time and concentration, due to the adsorption of these precursors, may not be interchangeable kinetic quantities, which clearly has important implications for extrapolating laboratory data to the

C2681

real atmosphere.

We recently published a study of secondary chain chemistry in the Cl + squalane heterogeneous reaction.[1] In this study, we concluded that the presence of secondary radical chain reactions leads to conditions in which the radical concentration and time are not interchangeable quantities. In particular, we observed a somewhat complex relationship between the measured effective uptake coefficient and [Cl₂], [O₂] and [Cl] concentrations, which can be explained by chain propagation and termination chemistry. At least for the Cl₂ case, the authors should consider other explanations for the saturation of the uptake coefficient vs. [Cl₂] rather than using a physical absorption based isotherm. The saturation of the uptake coefficient observed in Fig. 6, although appearing to follow a Langmuir type isotherm, could have a chemical explanation since Cl₂ plays an important role in propagating the chain reaction. This could also somehow be the case for the O₃ precursor, although it is much more difficult to see a chemical explanation, rather than physical adsorption, for the decrease in uptake coefficient with [O₃].

In our Cl + squalane study, we also observed that the measured uptake coefficient, as a consequence of secondary chemistry, depends upon the absolute radical concentration in the flow tube. Similar results are shown by the authors in Fig. 3. Our results appear quite different for gamma vs. [Cl], which in our case resembles the results the authors present for their [OH] dependence. It is unclear why there is a discrepancy. One reason may be experimental conditions, since for the Cl system, the uptake coefficient is a sensitive function of Cl, Cl₂ and O₂. For example, given that the uptake coefficient appears to depend upon [Cl] and [OH], I wonder if the authors could comment on the time evolution of the radical concentration after laser photolysis of the precursor. Presumably, right after the laser pulse there is a high radical concentration in the flow tube, which presumably decays before the next pulse arrives. Does the radical concentration between laser pulses decay to zero and what are the potential impacts for a heterogeneous reaction that depends upon absolute radical concentration?

C2682

The word "artifacts" in the title seems like a strange choice, since the authors are reporting a real effect.

1. C.-L. Liu, J. D. Smith, D. L. Che, M. Ahmed, S. R. Leone and K. R. Wilson, The direct observation of secondary radical chain chemistry in the heterogeneous reaction of chlorine atoms with submicron squalane droplets. *Phys. Chem. Chem. Phys.*, 2011, 13, 8993 DOI: 10.1039/c1cp20236g

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