

## ***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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We would like to thank Kevin for his helpful comments and suggestions. We address each of his points below:

1. “At least for the Cl<sub>2</sub> case, the authors should consider other explanations for the saturation of the uptake coefficient vs. [Cl<sub>2</sub>] rather than using a physical absorption [sic] 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 Cl<sub>2</sub> plays an important role in propagating the chain reaction. This could also somehow be the case for the O<sub>3</sub> precursor, although it is much more difficult to see a chemical

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explanation, rather than physical adsorption, for the decrease in uptake coefficient with [O<sub>3</sub>].”

We have considered explanations other than a physical adsorption based isotherm for the saturation of the uptake coefficient vs. Cl<sub>2</sub>. We agree that Cl<sub>2</sub> helps to propagate the chain reaction, and, in fact, we interpret the initial increase of uptake with increasing [Cl<sub>2</sub>] (Figure 6) to result from an enhanced chain reaction,  $R + Cl_2 \rightarrow RCl + Cl$ , at the surface of the particle. However, it is not clear how a purely chemical explanation could account for the plateau in the rate at higher [Cl<sub>2</sub>]; why would the radical chain not be enhanced even more at higher [Cl<sub>2</sub>]? Our conclusion is that a physical saturation is responsible.

2. “In our Cl + squalane study [1], 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 are [sic] 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, Cl<sub>2</sub> and O<sub>2</sub>.”

The data in Figure 3(b) result from changing [Cl] by changing [Cl<sub>2</sub>] (i.e. both are changed simultaneously). When we decouple [Cl] from [Cl<sub>2</sub>] and compare the rates of uptake in the small and large flow tubes (Figure 6), we see that the rate is a function of [Cl<sub>2</sub>], not of [Cl]. Despite the fact that [Cl] is ~ 33x higher in the small flow tube than in the large flow tube, the same rate of uptake is measured at approximately the same [Cl<sub>2</sub>].

Our Figure 3(b) is not directly comparable to Figure 10 of Liu et al. [1]. In our figure, the apparent dependence of the uptake on [Cl] actually results from a dependence on [Cl<sub>2</sub>], not [Cl]. In Liu et al.'s figure, [Cl<sub>2</sub>] is held constant and [Cl] is claimed to be varied. However, it is not clear that that figure really demonstrates a dependence on

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[Cl] because the text indicates that it was really the reaction time, not [Cl], that was varied by moving the opaque curtain surrounding the flow tube.

Also, the concentration of O<sub>2</sub> in their measurements was not indicated. We used 20% O<sub>2</sub>. Since the relative and absolute amounts of Cl<sub>2</sub> and O<sub>2</sub> will determine the importance of the competing reactions  $R + Cl_2 \rightarrow RCl + Cl$  vs.  $R + O_2 \rightarrow RO_2$ , the chain propagation could be very different in these two studies. Consequently, it may not be appropriate to compare our Figure 3(b) with Liu et al.'s Figure 10.

3. "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?" This is a very good point, and we will add a statement to the manuscript addressing this issue.

There is no significant loss of the Cl radical between laser pulses and therefore heterogeneous reactions that depend on absolute radical concentrations are not affected by the time decay of radical species between laser shots. A simple calculation shows no significant radical concentration decrease is expected during the 100 ms between laser shots. Acetone (used as a reference for Cl reactions here) concentrations range from  $5 \times 10^{10}$  molecules/cm<sup>3</sup> to  $1.5 \times 10^{11}$  molecules/cm<sup>3</sup>, and the rate constant for acetone + Cl is  $\sim 2 \times 10^{-12}$  cm<sup>3</sup>/molecule/sec.[2]. Thus, in 100 ms, only a 1-3% drop in the Cl concentration is expected. Furthermore, if the acetone depleted the Cl concentration significantly, the observed extent of reaction of the particle species would be different with and without acetone present. Since this was not the case, we conclude that the Cl concentration is not affected greatly by reaction with acetone.

Likewise, Cl recombination ( $Cl + Cl + M \rightarrow Cl_2 + M$ ) is too slow to be of importance.

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With a rate constant of  $\sim 2 \times 10^{-32}$  cm<sup>6</sup>/molecule<sup>2</sup>/sec. [3] and an average [Cl] <  $1 \times 10^{11}$  radicals/cm<sup>3</sup>, we can estimate from the integrated rate law for [Cl] that it drops by only 1% over the 100 msec. between pulses. Significant decay of [Cl] only occurs over this 100 msec time if the initial concentration of Cl ([Cl]<sub>0</sub>) is much larger; for example, if [Cl]<sub>0</sub> =  $1 \times 10^{15}$  radicals/cm<sup>3</sup>, the average [Cl] =  $5 \times 10^{13}$  radicals/cm<sup>3</sup> (over the full 100 msec). Since we used much, much lower average [Cl], we conclude that significant depletion of the [Cl] did not occur between laser pulses.

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

The word "artifact" in the title is chosen to represent the conclusion that we draw from our experiments that the conditions under which and methods by which the rates of reaction are measured influence the measurement.

#### References

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