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Atmospheric
Chemistry
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Discussions

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

**Anonymous Referee #2**

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General Comments

The authors present some important work on the heterogeneous reactions of Cl and OH with organic aerosols. The authors address an unresolved issue in this field, namely the relationship between laboratory studies of heterogeneous reactions conducted at high reactant conditions and the extrapolation of these results to the real atmosphere in which oxidation occurs at low concentrations for many days. The subject matter and potential impact of the paper is well suited for publication in ACP. However, I have a number of substantial issues (listed in Specific Comments below) with the manuscript that the authors must address before it is suitable for publication ACP.

Specific Comments:

1. It is unclear to me in the manuscript the role of phase (liquid, solid, supercooled liquid) plays in the subsequent interpretation of ozone and chlorine gas absorbing to the surface to either inhibit or enhance the heterogeneous reaction. In particular the authors are vague about the phase of 2-ODA produced in their experiment. The say that squalane and 2-ODA are branched hydrocarbons which may form liquid particles at room temperature, but 2-ODA has a melting temperature of 34-36 degrees C. They later say that the particles are supercooled but no evidence is given. The phase of the particle is likely an important factor in determining the applicability of physical absorption theories. For example, for a liquid particle diffusion of surface O3 and Cl2 into the bulk would be faster than a solid or supercooled liquid aerosol suggesting more sophisticated treatments of their data would be needed. In this respect, comparing liquid particles in Fig. 3 with solid/supercooled particles in Figs. 5 and Fig. 6 could be misleading and would limit the overall breadth of the manuscripts' conclusions about when time and concentration are interchangeable. At the very least the authors should add a paragraph in the conclusion section discussing the role of phase and qualify their conclusions based upon this point.

2. I don't see any error bars on the large flow tube measurements shown in Fig. 2. In fact it seems as if in Fig. 2a the data for the small and large tubes are statistically indistinguishable at low exposures (0-1 x 10ˆ10 molecules per cc) where the initial rate analysis is expected to be most robust. The authors need to justify better the relative size of the error bars (Fig. 3a and b) in the measurements in the small and large flow tubes, since the small flow tube only consists of a single measurement vs. OH exposure. Furthermore, in Fig. 2b, without error bars on the individual measurements in the large flow tube it is difficult to judge the real difference in the raw data despite the large differences in uptake coefficient determined from the data (1.43 vs. 0.87). For example, the authors need to discuss, to satisfy a skeptical reader, why the noise in the large flow tube data at each point is larger than the error bar shown for the single point

measurements in the small flow tube. Given the potential importance of the paper's conclusion, that heterogeneous reactivity can be blocked or enhanced by spectator species previously thought not to participate in the reactions, better justification and description of error analysis in the experimental measurements is needed to better support this conclusion.

3. The authors show only a subset of available literature data in their plot of gamma vs. [OH] and gamma vs. [O3]. They should explicitly show all available data (in Figs. 3 and 5). In particular measurements by Donahue and coworkers,(1-3) Thornton and coworkers,(4) Abbatt and coworkers(5) as well as previous results for their own group.(6-7) Since the experimental conditions (OH and ozone concentrations) in these studies vary to a degree a pattern should emerge which would provide further evidence for or against their hypothesis that absorption either blocks or enhances a heterogeneous reaction. For example, Donahue and coworkers(2) measured an uptake coefficients (with ozone) at low [OH] concentrations and found for hexacosane a value of 1. The same group(3) also measured a range of uptake coefficients (1-10) for C25 to C30 alkanes, hopanes etc. using a HONO and H2O2 precursors. While they attribute gamma > 1 to gas phase oxidation, the smaller uptake coefficients (without ozone) for the less volatile species (e.g. C30) approach 1, which is consistent with their measurements of hexacosane with ozone present. The no ozone measurements of Donahue and coworkers differ from gamma_0 determined in the author's Langmuir analysis (0.56). These results should be reconciled if possible or at least discussed in the current manuscript.

The author's should also try to reconcile their previous measurements of BES + Cl and OH reactions with the current work. For example, in Hearn and Smith(7) the uptake coefficient for OH + BES was measured to be 2.0 at an ozone concentration of 3 x 10ˆ15 molec/cc and a OH concentration of 3 x 10ˆ9 molec/cc. For the Cl + BES(6-7) reaction they report gamma = 1.7-1.8. It seems reasonable to me to plot these previous measurements on Fig. 3 and Fig. 5 and Fig. 6. In addition, the authors

report uptake coefficients for the Cl + 2-ODA reaction (in the absence of O2) of 10, which are much larger than the DOS + Cl reaction measured without oxygen (gamma = 0.9-1.7).(6) If these previous measurements are somehow not relevant to the current manuscript, either due to phase (liquid), molecular structure or experimental conditions some justification is needed in the current manuscript. If these results are relevant then the data should be included in the relevant figures (e.g. Fig. 3, 5, 6).

4. The authors use Br2 to test their hypothesis that physical absorption is playing a role in the uptake coefficient for the Cl + 2 ODA reaction. Without more information I am not at all convinced that the Br2 results are in support of their main conclusions. The authors need to show that Br atoms are not playing a role in the reaction. For example, Moise and Rudich(8) measure an uptake coefficient for Br on an OTS surface of 0.03. One could imagine that if the Br atom concentration is high that this reaction could compete. The authors need to report what the concentration of Br atoms is in their reactor and show that this heterogeneous reaction can be safely neglected and distinguished from the Cl reaction.

In addition, the gas phase Cl + Br2 reaction appears to fast (NIST Kinetics http://kinetics.nist.gov/) so I would expect that the Cl radicals would be greatly suppressed in the experiment. Was this observed? How were the experimental conditions modified to account for this suppression? The authors need to present more details to show that these effects are considered, adequately accounted for and do not impact the main conclusions regarding the Br2 experiment.

In general, the results presented in this paper have real importance for laboratory measurements of atmospheric reactions, however, given the points outlined I am not convinced that the data entirely support the rather strong conclusions presented in the paper.

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