

# ***Interactive comment on* “Coupling aerosol surface and bulk chemistry with a kinetic double layer model (K2-SUB): oxidation of oleic acid by ozone” by C. Pfrang et al.**

## **Anonymous Referee #1**

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This paper describes an extension of the detailed kinetic flux modeling approach described by Poschl, et al 2007 to study the competition between surface and bulk reactions in regulating the loss rate of oleic acid in particles exposed to ozone. The modeling approach is well described and the authors compared the model predictions to a set of experimental results. The authors also performed several sensitivity studies in order to examine the importance of specific parameters such as the mass accommodation coefficient, Henry’s law constant for ozone in organic liquids, and the liquid phase diffusion coefficient.

The paper over all is well written and the arguments and assumptions made are largely

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appropriate. Of course, one of the major issues with the reductionist approach taken in this modeling study is that poorly constrained or unknown chemical or physical parameters must be specified. I think the authors did a commendable job in this regard.

The conclusions are inline with the results, but I do have trouble discerning just how significant an advance these conclusions represent in terms of our understanding of gas-particle interactions. They do provide a clear indication that the competition between surface and bulk reactions is significant and difficult to separate especially for liquid phase particles where reactant diffusion is relatively rapid. They also provide some quantitative limits on the surface reaction rate constant, and provide a clear suggestion for future experimental studies: measure the decay in particulate oleic acid at a constant ozone flux as a function of time for longer than 30 seconds. These conclusions are useful to the community and thus this paper warrants publication.

My criticisms of the paper are more philosophical than scientific. One question that stays in my mind is to what extent does this more detailed model really reveal new insights? One could argue that from earlier papers examining the functional dependence of the oleic acid loss under different limiting cases (e.g. fast surface reaction, no surface reaction w/slow bulk reaction, etc), we could infer that teasing out surface from bulk reactivity could be challenging, that there was a strong dependence on the choice of  $\alpha$ , and that the loss rate would likely be sensitive to the chosen solubility. In other words, could this paper not have been written based solely on a careful and comprehensive application of the various equations in say Worsnop, et al (GRL 2002)?

I readily acknowledge in Worsnop, et al (GRL 2002) various processes were decoupled in order to arrive at analytical formulas describing the decay of oleic acid under certain limiting conditions. By explicitly solving (numerically) the coupled kinetic equations, the authors clearly provide a more rigorous treatment and ability to assess "transition regions" between the various limiting cases. However, the sensitivity studies in this paper come across to me as studies of the various limiting cases. A few words or a figure comparing predictions from the closest relevant limiting case in Worsnop et

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al to that predicted by the K2-SUB might be helpful for better elucidating the added understanding gleaned from K2-SUB.

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