Response to the comments of Anonymous Referee #1

Referee's Comment:

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 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.

Response:

We thank the Anonymous Referee #1 for the review and the positive evaluation of the manuscript. The constructive suggestions are very welcome and will be implemented upon revision as indicated below.

An extended discussion of the implications of the longer reaction timescales we proposed in the manuscript is included in the revision:

The chemical composition of the particle will obviously change over the course of the reaction and the extent of the deviation from initial particle composition will become increasingly significant for longer reaction timescales. Dominant initial products from the ozonolysis of oleic acid are known to be nonanal, which is likely to evaporate, as well as 9-oxononanoic, nonanoic, and azelaic acids in the liquid phase (e.g. Rudich et al. 2007; Vesna et al., 2009). We expect first-generation products other than nonanal to remain in the particle phase. Renewal of the surface layer by evaporation is thus unlikely to accelerate the oxidation process substantially. The evaporation of products from particle to gas phase is not considered in the current model, but we are planning to incorporate evaporation and condensation in follow-up studies. The influence of the changing chemical composition of the particle surface on adsorbate–surface interactions i.e. on the surface accommodation coefficient can be taken into account by adjusting $\alpha_{s,0,X}$ (described in the response to referee #2; see also Pöschl et al, 2007 and Shiraiwa et al., 2010). In a similar way, the influence of changing chemical composition of the particle bulk on the bulk diffusion coefficient can be taken into account by describing $D_{b,X}$ as a linear combination of the initial bulk diffusion coefficients that would be observed in pure bulk. For the base cases presented in this paper, $\alpha_{s,0,X}$ and $D_{b,X}$ are assumed to be constant for simplicity. For long reaction times, the increasing proportion of products in the particle will also introduce additional uncertainties in the calculations since branching ratios and molecular properties are less well known in particular for second- and third-generation products.

Referee's Comment:

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

Response:

We thank the Anonymous Referee #1 for the largely positive comments on the manuscript. We understand and appreciate the referee's philosophical question and considerations. Following up on these, we clarified the relations and differences of our approach and that of Worsnop et al. (2002) in the revised manuscript.

K2–SUB provides a general set of equations that describe all physico-chemical processes involved. It enables free variation of all relevant parameters in particular mass transfer and reaction rate coefficients. It thus can describe limiting cases as well as any state in between depending on the investigated reaction systems, conditions and rate parameters.

For instance, K2–SUB allowed us to establish that $\alpha_{s,0,X}$ is the most critical parameter with a highly non-linear impact on chemical losses in both surface and bulk. We can simulate an unlimited number of intermediate cases e.g. to determine that only for $\alpha_{s,0,X} \approx 4 \times 10^{-4} - 10^{-3}$ experimental data could be matched (assuming reasonable reaction rate coefficients and $k_{d,X}$ values similar to those used in Shirawa et al., 2009; however, it should be noted that the experimental data can also be reproduced with other combinations of $\alpha_{s,0,X}$ and $k_{d,X}$, that are closer to predictions from molecular dynamic simulations for related systems; these aspects will be further investigated in follow-up studies). The added flexibility compared to Worsnop et al. (2002)'s approach also facilitates description of Langmuir-Hinshelwood- and Eley-Rideal-type reaction mechanisms. Simulations for various multi-component and multi-phase reaction systems that are more realistic models for atmospheric aerosol can be performed in future, incremental developments of K2–SUB. Such extensions would not be straight forward – if at all possible – for resistor-based models.

In summary, Worsnop et al. (2002) apply different sets of equations for different limiting cases, and it is not clear if and how these equations can be used to describe intermediate states in between the limiting cases. The testing and application of different sets of equations for different limiting cases is useful for the analysis of certain laboratory data, but it appears not to be well suited for efficient modelling of

different types of clouds and aerosols under varying atmospheric conditions. Many experimental and nearly all atmospheric reaction systems do not adhere to ideal limiting-case behaviour tailor-made for traditional resistor model formulations, so that the flexibility added through the K2–SUB development is a significant step in providing a powerful tool to help improving our understanding of interfacial oxidation processes of atmospheric importance.

References:

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