Interactive comment on “Kinetic multi-layer model of aerosol surface and bulk chemistry (KM-SUB): the influence of interfacial transport and bulk diffusion on the oxidation of oleic acid by ozone” by M. Shiraiwa et al.

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Referee General Comment:
This manuscript describes the application of a novel multi-layer model to interpret the oxidation kinetics of oleic acid aerosol. This model represents an extension of a previously published framework for treating gas-particle interactions, referred to as the PRA framework. In particular, the oxidation kinetics of oleic acid (OA) are compared with experimental measurements, considering three plausible limiting scenarios. The observed lifetime of OA is shown to be consistent with either rapid bulk phase chemistry limited by interfacial transport, or slow bulk phase chemistry. The observed lifetime is inconsistent with slow bulk diffusion, as would be expected if OA were embedded in a semi-solid matrix. The manuscript is largely clearly written, although the authors should consider the following comments before the manuscript is accepted for publication.

Response:
We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. The constructive suggestions for improvement are very welcome and will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee Comment 1:
A simple model for treating the surface coverage dependence of the surface accommodation coefficient is considered. It is not clear that assuming simple coverage dependence is a reasonable approximation. How might the surface accommodation coefficient change with chemical composition if the surface varies with oxidation and aging of OA? Indeed, a same comment extends to the treatment of the diffusion constant of ozone (and OA) in the particle - given the variety of low and high molecular weight products that could form, how valid is it to consider that the diffusion constants are independent of time?

Response:
The influence of the changing chemical composition of the quasi-static particle surface on adsorbate surface interactions and thus on the surface accommodation coefficient can be taken into account by describing $\alpha_{s,0,Xi}$ and $\tau_{d,Xi}$ as a linear combination of the initial surface accommodation coefficients $\alpha_{s,0,Xi,Yj}$ and $\tau_{d,Xi,Yj}$ that would be observed on pure substrates made up by the different surface components Yq weighted by their fractional surface area $\theta_{ss,Yq}$ (Pöschl et al. 2007):
\[ \alpha_{s,0,Xi} = \alpha_{s,0,Xi,Yj} \theta_{ss,Yj} \]
\[ \tau_{d,Xi} = \tau_{d,Xi,Yj} \theta_{ss,Yj} \]

In the same way, the influence of the changing chemical composition of the particle bulk on the bulk diffusion coefficient can be taken into account by describing \( D_{b,Xi} \) or \( D_{b,Yj} \) as a linear combination of the initial bulk diffusion coefficients that would be observed in pure bulk \( Yq \):

\[ D_{b,Xi} = D_{b,Xi,Yp} \Phi_{b,Yp} \]
\[ D_{b,Yj} = D_{b,Yj,Yp} \Phi_{b,Yp} \]

The weighting factor \( \Phi_{b,Yp} \) could be the mole, mass, or volume fraction of \( Yp \) in the bulk. (Pöschl et al., 2007).

We will add these discussions in Sect. 2 of the revised manuscript. In the base case simulations, \( \alpha_{s,0,Xi} \) and \( D_{b} \) are assumed to be constant for simplicity.

Referee Comment 2:

It appears that there is no consideration that the products may be volatile as well as involatile. Figure 1 indicates that it is only ozone that is allowed to partition between the gas and condensed phases. As this is unlikely to be true for the experimental measurements, how is this likely to impact on the kinetics modelling? Presumably some contraction of the number of layers must be allowed to occur over time as product is lost from the particle. There is no discussion of how this might be incorporated.

Response:

The main first-generation products from oleic acid ozonolysis are 1-nonanal, which evaporates from the particle, 9-oxononanoic acid, nonanoic acid, and azelaic acid (Rudich et al. 2007; and references therein). In the present study, the evaporation of oxidation products (e.g. 1-nonanal) is not considered. These effects go beyond the scope of the present study, but the gas-particle partitioning of (semi-)volatile species and the effects of chemical transformation on particle size and properties shall be incorporated in follow-up studies. We will clarify this in Sect. 3 of the revised manuscript.

Referee Comment 3:

Given that the model is being applied to a specific system, it would be very helpful to the reader if the equations were formulated first in the general framework, but then also shown explicitly for the components of the OA system.

Response:

Following your suggestion, we will explicitly list the rate equations for the ozone - oleic acid reaction system in Appendix D of the revised manuscript.

Referee Comment 4:

The discussion in the first paragraph at the top of page 290 strictly applies to set the starting surface and bulk concentration of OA. Indeed, it is stated that this is for pure \( Yj \). It is not clear how the changing composition of the particle is accounted for in this treatment of the rate constants for the fluxes between the surface and bulk layers.

Response:

The mass conservation holds not only for pure \( Yj \) but also for non-pure \( Yj \), \( [Y]_{ss} = [Y]_{-2} \) and \( [Y]_{b1} = [Y]_{-3} \) holds only for pure \( Yj \). This assumption is made to estimate \( k_{ss,b,Yj} \) and \( k_{b,s,Xi} \) from the bulk diffusion coefficients \( (D_{b}) \). If the chemical composition of the particle change, the diffusion coefficient may change, which can be incorporated in the model as mentioned in the reply of Referee Comment 1. We will clarify this point in the revised manuscript.

Referee Comment 5:

On a point of clarity, the difference between \( Xp \) and \( Xq \) on page 292 is not clear.

Response:
kBRv,Xp,Xq is the second-order reaction rate between Xp and Xq in the condensed phase bulk of a system with multiple volatile species which can react with each other. In the model system investigated in this study, we consider only a single volatile component (X = O3) and kBRv,Xp,Xq is not used. We will clarify this point in Sect. 2.4 of the revised manuscript.

Referee Comment 6:

The parameters for the model treatments considered are presented in Table 1. It is not clear how these values are arrived at and how feasible they are. Some justification for the choice of these numbers must be given. Given enough parameters in a model, it is always possible to vary the values in such a way that an observation can be reproduced. But the physical significance must be considered and justified.

Response:

We will add the following information in Sect. 3 of the revised manuscript.

The derivation and choice of kinetic parameters were discussed in detail by Pfrang et al. (2009). In view of the uncertainties and limited availability of experimental data we compare three cases covering a range of plausible parameter variations.

In base case 1 (BC1, kinetic limitation by interfacial transport) we assumed fast bulk reaction with a literature-derived rate coefficient of kBR,X,Y = 1.7 x 10^{-15} \text{ cm}^3 \text{ s}^{-1} (equivalent to 10^{6} \text{ L mol}^{-1} \text{ s}^{-1}) (Titov et al., 2005). The surface reaction rate coefficient kSLR,X,Y = 6 x 10^{-12} \text{ cm}^2 \text{ s}^{-1} was adopted from Pfrang et al. (2009). Note that this value is an order of magnitude lower than reported value by other studies (Gonzalez-Labrada et al., 2007; King et al., 2009). Bulk diffusion coefficients were adopted from earlier studies (Db,X = 10^{-5} \text{ cm}^2 \text{ s}^{-1}, Db,Y = 10^{-10} \text{ cm}^2 \text{ s}^{-1}) (Smith et al., 2002; 2003), and the parameters of reversible adsorption were adjusted to match the experimental data of oleic acid decay ($\alpha_{s,0,X} = 4.2 \times 10^{-4}$ and $\tau_{d,X} = 0.01 \text{ s}$).

In base case 2 (BC2, kinetic limitation by bulk reaction) we assumed slow bulk reaction with a rate coefficient $\alpha_{A}$ 30 times lower than in BC1 (kBR,X,Y of 5 x 10^{-17} \text{ cm}^3 \text{ s}^{-1}). The adsorption parameters were re-adjusted to match the experimental data ($\alpha_{s,0,X} = 8.5 \times 10^{-4}$, $\tau_{d,X} = 0.001 \text{ s}$), and all other parameters were kept equal to BC1. Note that in BC1 and BC2 the results can be reproduced with different combinations of $\alpha_{s,0,X}$ and $\tau_{d,X}$, that are closer to prediction of molecular dynamic simulations (e.g. $\alpha_{s,0,X} \approx 10^{-2}$ and $\tau_{d,X} \approx 10^{-9} \text{ s}$; Vieceli et al., 2005; Shiraiwa et al., 2009)). These aspects will be further investigated in follow-up studies.

In base case 3 (BC3, kinetic limitation by bulk diffusion) we assumed slow mass transport in the bulk with diffusion coefficients that are characteristic for amorphous (semi-)solid matrices (Bird et al., 2007; Swallen et al., 2007; Mikhailov et al., 2009) and five orders of magnitude lower than in BC1 and BC2 (Db,X = 10^{-10} \text{ cm}^2 \text{ s}^{-1} and Db,Y = 10^{-15} \text{ cm}^2 \text{ s}^{-1}).

Referee Comment 7:

For the third model treatment, given that bulk diffusion limits the oxidation kinetics, is it not critical that volatilization of products be included, allowing new surface layers to be oxidised repeatedly, rather than by forcing reaction to occur by diffusion only?

Response:

According to earlier studies, the 1-nonanal is the only reaction product that is likely to evaporate, while most products are likely to remain in the particle phase (Vesna et al. 2009). Therefore, surface renewal by evaporation appears unlikely to accelerate the oxidation process substantially. Nevertheless, we intend to investigate such effects in follow-up studies including evaporation and condensation processes in the model.

Reference:


Gonzalez-Labrada, E., Schmidt, R. and DeWolf, C. E.: Kinetic analysis of the ozone...
processing of an unsaturated organic monolayer as a model of an aerosol surface, Physical Chemistry Chemical Physics, 9, 5814-5821, 2007.


