

Response to the comments of Anonymous Referee #2

Referee's Comment:

The authors present a model that couples aerosol surface and bulk chemistry, based on a framework presented earlier by Poschl et al. (2007). This model is then applied to the reaction between ozone and oleic acid - a system that has studied many times in the laboratory. In short the model is used to fit the laboratory experiments from Ziemann et al. (2005), using best estimates of kinetic parameters (such as bulk and surface reaction rates, diffusion coefficients, solubilities, etc.). From this analysis the authors demonstrate that the bulk reaction plays an important role, although the exact contribution of the surface and bulk is not possible due to the uncertainties in the kinetic parameters. The calculations also help constrain the mass accommodation coefficient and demonstrate the sensitivity to this parameter. Suggestions for future laboratory studies also result from the calculations. The paper is clearly written and addresses an important area of atmospheric chemistry. The scientific approach is valid, and the resulting tool (the model) should be especially helpful when applied to multicomponent systems and when surface and bulk reactions are comparable.

As a result, I support this publication after the following comments are adequately addressed:

Response:

We would like to thank the Anonymous Referee #2 for review and positive evaluation of our manuscript. The suggestions for improvement will be implemented upon revision. Detailed responses to the individual comments are given below.

Referee's Comment:

Figures 3 and 4: In Figures 2 and 7 the authors included a plot that compares the experimental data with the calculations (see for example Figures 2a, 7a and 7c). But in others figures this comparison is left out (see for example Figures 3 and 4). I would prefer to see the comparison of the experimental data with the calculations in all the figures. I realize that this information is included in the supplemental data, but it makes for easier reading if it is included in the main text. Since this is more of a personal preference I will leave it to the authors to decide.

Response:

We carefully considered which figures to include in the main manuscript. The comparison with the experimental data is shown for both base cases (Figs 2 and 8) as well as for exclusive surface and bulk reactions (Fig. 7). We consider visualisation of the experiment-model comparison to be most insightful in these cases. The referee's suggestion would mean inclusion of at least 11 further figures in the main manuscript which we do not believe to be useful for the generalist reader (all 138 figures are readily available in the electronic supplement).

Referee's Comment:

Page 26984, line 16-17. The authors suggest that studies covering a longer reaction time would be beneficial. In this case a large fraction of the particles will be oxidized, and the matrix may be very

different from the starting matrix (pure oleic acid). In this case fundamental parameters such as diffusion coefficients, solubilities, etc. may change. Please comment on this point and discuss any possible uncertainty these changes may have on the calculations.

Response:

We are grateful for the referee pointing out this issue which will be discussed in the revised manuscript. The chemical composition of the particle will change increasingly over the course of the reaction. The extent of this deviation from the initial particle composition will indeed become more significant for the longer reaction timescales we propose for future experimental studies to distinguish between surface- and bulk-dominated losses.

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). In line with earlier studies, we expect first-generation products other than nonanal to remain in the particle. Renewal of the surface layer by evaporation is thus unlikely to accelerate the oxidation process substantially. The evaporation of products (in particular nonanal in the present system) 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 and thus on the surface accommodation coefficient can be taken into account by describing $\alpha_{s,0,X}$ as a linear combination of the initial surface accommodation coefficients that would be observed on pure substrates made up by the different surface components Y_p weighted by their fractional surface area $\theta_{ss,Yp}$ (Pöschl et al., 2007; discussed in detail in Shiraiwa et al., 2010a):

$$\alpha_{s,0,X} = \sum_p \alpha_{s,0,X,Yp} \theta_{ss,Yp} \quad (1).$$

In a similar way, the influence of changing chemical composition of the particle bulk on the bulk diffusion coefficient can in principle 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:

$$D_{b,X} = \sum_p D_{b,X,Yp} \Phi_{b,Yp} \quad (2).$$

$\Phi_{b,Yp}$ refers to the fraction of Y_p in the bulk e.g. as mole, mass, or volume fraction. For the base cases presented in this paper, $\alpha_{s,0,X}$ and $D_{b,X}$ are assumed to be constant for simplicity. Bulk diffusion of the liquid phase species (Y : oleic acid) can be corrected in analogy to equation (2) for the gas-phase compound (X : ozone). However, the diffusion of oleic acid is not resolved in K2–SUB to maintain compatibility with resistor model formulations. Bulk diffusion of oleic acid is explicitly included in the KM–SUB model (Shiraiwa et al., 2010a and 2010b) and the adequate corrections for the changing chemical composition in the liquid phase would probably most efficiently be implemented in KM–SUB.

It should be noted – as the referee correctly pointed out – that for long reaction times, the increasing proportion of products in the particle will introduce additional uncertainties in the calculations since branching ratios and molecular properties are less well known in particular for second- and third-generation products. These issues have been clarified in the revised manuscript.

Referee's Comment:

Similar to reviewer 1, I wondered if some of the conclusions in this paper could be obtained with the traditional “resistor” modelling formulations (for example the equations in Worsnop et al. GRL, 2002). I think it would be useful if this was briefly discussed and also highlight in more detail examples where the traditional “resistor” formulations will fail and K2-SUB is needed. This comment doesn't impact my support of this paper.

Regardless, the analysis in this paper is strong and important

Response:

This point has been discussed in detail in the response to referee #1. K2-SUB provides a general set of equations that describe all involved physico-chemical processes. It enables free variation of all relevant parameters (mass transfer and reaction rate coefficients), thus it can describe limiting cases as well as any state in between — depending on investigated reaction systems, conditions and rate parameters. In the approach of Worsnop et al. (2002), different sets of equations have to be applied 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 may be useful for the analysis of laboratory data, but it appears not well suited for efficient modelling of different types of clouds and aerosols under varying atmospheric conditions.

References:

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