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***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:

The manuscript under review presents KM-SUB, a benchmark model framework that explicitly treats interfacial and bulk transport as well as chemical reactions at the surface and in the bulk of aerosol particles. It is another paper in a series of recent papers by the authors that apply the modeling framework suggested by Poeschl, Rudich, and Ammann (2007) to different systems, and shows once more how versatile this frame-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



work is. The unique contribution of KM-SUB is that it resolves concentration profiles on the particle surface throughout the bulk of the particle and does not require a-priori assumptions about radial mixing or steady state. The model is applied to the ozonolysis of oleic acid particles, and three scenarios are investigated representing different regimes (kinetic limitation by interfacial transport, kinetic limitation by bulk reaction, kinetic limitation by bulk diffusion). The paper fits well within the scope of ACP, is clearly written and addresses an important topic. I recommend it for publication with some minor modifications.

Response:

We thank Anonymous Referee #2 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:

Kinetic parameters for base cases 1-3: The results of three base cases are instructive, however references for the choice of kinetic parameters are missing and should be added.

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) (Sect. 3). 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 $k_{BR,X,Y} = 1.7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (equivalent to $10^6 \text{ L mol}^{-1} \text{ s}^{-1}$) (Titov et al., 2005). The surface reaction rate coefficient $k_{SLR,X,Y} = 6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ was adopted from Pfrang et al. (2009). Note that this

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

value is an order of magnitude lower than reported value by (Gonzalez-Labrada et al., 2007; King et al., 2009). Bulk diffusion coefficients were adopted from earlier studies ($D_{b,X} = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $D_{b,Y} = 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) (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 ca. 30 times lower than in BC1 ($k_{BR,X,Y}$ of $5 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$). 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 ($D_{b,X} = 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $D_{b,Y} = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$).

Referee Comment 2:

Regarding BC1 and BC2: Both model simulations appear to fit the lab experiment. I assume that one of them is more realistic than the other? Please include a statement that clarifies this.

Response:

Following your comment, we will add the following discussion in Sect. 3.2 of the revised manuscript.

BC1 may be regarded as more realistic, because it uses the only reported value of

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Interactive
Comment

the bulk reaction rate coefficient of ozone with oleic acid, whereas BC2 assumes a ca. 30 times lower value. Nevertheless, both model cases are in good agreement with the available experimental data. Thus, further experiments covering a wider range of reaction times and conditions are needed to elucidate the actual reaction mechanism (see Pfrang et al., 2009).

Referee Comment 3:

Nothing is mentioned regarding the assumption on what species are formed by the oleic acid degradation. Please add some clarification. Could these species react further?

Response:

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

The first-generation products of oleic acid oxidation by ozone are mainly 1-nonanal, 9-oxononanoic acid, nonanoic acid, and azelaic acid (Moise and Rudich, 2002; Katrib et al., 2004; Thornberry and Abbatt, 2004; Vesna et al., 2009). 1-Nonanal is highly volatile and likely to evaporate from the particle (Sage et al., 2009). The other products, however, have higher molecular masses and are more polar, less volatile and likely to remain in the condensed phase (Jimenez et al., 2009). Moreover, they may undergo recombination reactions forming second-generation products of higher molecular mass such as dimers or oligomers in the bulk (Rudich et al., 2007; and references therein). 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.

Referee Comment 4:

Atmospheric implications: What might be a potential impact of having multiple species reacting/adsorbing on the particle? Calculations that include these processes are clearly beyond the scope of this paper, but it would be helpful for modelers who work

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on larger scale models to include a statement if that's possible.

Response:

If there are multiple species adsorbing on the particle in addition to ozone, the competitive adsorption lead to lower surface coverage and lower bulk concentration of ozone, leading to increase of lifetime of oleic acid. We will add this information in Sect. 3.4 of the revised manuscript.

Referee Comment 5:

Page 301, line 1-5: In addition to the possible explanations given by the authors, I am wondering if the existence of oleic acid in aged atmospheric particles can be simply explained by the fact that other species (inorganic and organic) can condense on the particles and coat them, hence shutting off the ozonolysis as described in this paper.

Response:

We agree and will address this possibility in the revised manuscript, which is a special case of slow mass transport because of low diffusivity:

Possible explanations include reduced concentrations of O₃ (and other photo-oxidants) in the particle bulk due to the following effects: (a) chemical reaction with other reactive species, self-reaction or catalytic decomposition; (b) competitive co-adsorption and surface reaction of multiple species such as water vapor and nitrogen oxides; (c) slow mass transport because of low diffusion coefficients in solid or semi-solid phases (crystalline, glassy, rubbery, gel-like or ultra-viscous: Mikhailov et al., 2009). The formation of semi-solid amorphous phases is generally favored by low temperature and low relative humidity, and it can occur in the core of atmospheric particles as well as in coatings formed by condensation of secondary particulate matter. For example, oligomerisation reactions may lead to high molecular mass, low hygroscopicity and low diffusivity of secondary organic coatings, effectively shutting off further ozonolysis and oxidation of oleic acid and other organic compounds in the bulk of coated particles.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Referee Comment 6:

Conclusions: The comparison with K2-SUB is briefly mentioned (“fairly good agreement”). It would be helpful if this comparison was expanded, i.e. for the three scenarios, state more clearly and more quantitatively when high resolution of the bulk is needed and when a simpler two layer approach does just as well.

Response:

The main difference between KM-SUB and K2-SUB is the treatment of diffusion of oleic acid: KM-SUB treats it explicitly whereas K2-SUB does not resolve it and assume radial mixing. In base cases 1 and 2, the modeled number of oleic acid molecules (NY) as well as uptake coefficients of ozone and surface concentrations agrees very well. This is because in the kinetic limitation of interfacial transport (BC1) or bulk reaction (BC2), the diffusion of oleic acid does not play a role. Indeed oleic acid is homogeneous throughout the bulk as shown in Fig 3(b) and 6(b). However, in BC3 of kinetic limitation of bulk diffusion, the simulated decay of oleic acid is faster and the ozone uptake coefficient is higher in K2-SUB compared to KM-SUB, as resolving the diffusion of oleic acid is critical in this case. We will clarify this point in conclusion section by adding below paragraph in conclusions:

Under conditions where the reaction system was kinetically limited by interfacial transport or chemical reaction, the multi-layer model (KM-SUB) was in good agreement with a double-layer model (K2-SUB) using traditional resistor formulations for bulk processes. In case of kinetic limitation by bulk diffusion, however, the K2-SUB model overestimated the rates of gas uptake and oleic acid degradation, because it does not resolve and account for the concentration profile of oleic acid.

Referee Comment 7:

Typos: Page 302, line 2: Verb is missing in this sentence. Caption for figure 10: Should read “loss rate”. Page 313, line 15: Should read “Gäggeler”.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Response:

Following your comments, typos will be corrected.

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Interactive
Comment

Full Screen / Esc

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