

## Response to the comments of Anonymous Referee #2

### **Referee's Comment:**

The authors report an application of their previously reported K2-SUB and KM-SUB models with some modest model development. A primary conclusion of the paper is that changes in particle diffusivity can be invoked to explain measured changes in condensed phase chemical loss rates. The paper describes the possibility of crust formation and the impacts of this on chemical transformations. The material appears suitable for publication in ACP, but there are a number of concerns that should be addressed prior to publication:

### ***Response:***

We would like to thank the Anonymous Referee #2 for the critical but positive evaluation of our manuscript. The reviewer suggests that our work is well suited for publication in ACP, but raised a number of concerns which are addressed below and taken into consideration in the revised manuscript. The reviewer identified development routes for our present modelling approach and we agree that description of several further aspects of the multi-component system would be desirable. While we agree that the present approach still has limitations, we are keen to point out that it goes far beyond descriptions available in the literature with other modelling approaches: e.g. the experimental data we used to constrain our model was presented by Huff-Hartz et al. (2007) and interpreted by the experimental team by very simply reporting two different rate coefficients for the oleic and palmitoleic acids, one initial and one final coefficient. We are firmly convinced that the development that allowed application of the PRA approach to a complex mixture of reactive aerosol components constitutes a substantial step in kinetic aerosol modelling. We are for the first time in a position to illustrate crust formation in multi-component aerosol mixtures and describe the evolution of diffusivity quantitatively which has -to the best of our knowledge- not been achieved with other models.

### **Referee's Comment:**

i) As the paper is written, it appears that the model considers only volatile and non-volatile components. Given oleic acid is unsaturated at C9, it might be expected that C9 compounds will form as reaction products. Since there is no reference to the evaporation of reaction products, can the authors explain where any fragmentation products go? Ignoring semi-volatile components is clearly a very simplistic approach, and one that could substantially impact on the conclusions. If this is indeed the approach that is taken, a main concern is the dependence of the conclusions on the implicit assumptions in the model construction. The evaporation (and possible recondensation of components, though probably not under experimental conditions where gaseous components would only originate from particles) and resulting evolution of the chemical matrix over the timescales of the experiments need to be considered when interpreting such multiphase chemical processes. At least a thorough discussion of the reasons for making the assumption, its validity and implications of its use should be made.

### ***Response:***

We agree with the reviewer that description of volatilization of products, of semi-volatile species, of hygroscopicity and of condensation and re-condensation would clearly be important steps to accurately de-convolute the various processes dominating aerosol chemistry and physics. Ongoing, but unfinished work at the MPI is aiming to address several of these issues in future studies of simpler systems. We do not believe that our present approach to describe a complex multi-reactive 12-component multi-phase aerosol matrix is 'very simplistic' since it goes far beyond any previous description of ageing-induced

diffusivity evolution which is the focus of the presented work as indicated in the title of the manuscript. In the revised manuscript we now clearly point out that we only address non-volatile and volatile compounds and explicitly explain how the limitations of our approach potentially impact the application to atmospheric aerosols.

*New text added in the revised manuscript (inserted on p. 13014, line 13):*

‘For atmospheric interpretation of the results presented below, it should be noted that the model used in the present study has been optimized to simulate laboratory data for a 12-species organic aerosol matrix in dry conditions (Huff-Hartz et al., 2007). While the 12 components have been chosen to mimic meat-cooking emission profiles containing the key unsaturated compounds commonly used as markers, in particular cholesterol, palmitoleic and oleic acids (Huff-Hartz, et al., 2007 and references therein), real meat cooking emissions are complex mixtures of hundreds of compounds and likely to interact with moisture present in the atmosphere. Particularly in highly humid conditions we would expect considerable deviations between our model results and the behaviour of cooking aerosol in the atmosphere, since hygroscopic growth can impact substantially on chemical ageing and atmospheric lifetimes of aerosols. Product volatilization in the complex 12-component aerosol mixture is also not considered here, mainly because of the lack of experimental data to constrain any modelling attempt. The evaporation and re-condensation of components and the resulting evolution of the chemical matrix may have considerable effects on chemical processes in these multi-species and multi-phase mixtures. While re-condensation is unlikely to be of importance in the experimental conditions where gaseous components originate from particles only, it may be important in complex atmospheric aerosol matrices.’

*New text added in the revised manuscript (inserted on p. 13011, line 10):*

‘While there is clear experimental evidence for a retardation of the losses of oleic and palmitoleic acids (Huff-Hartz, et al., 2007), it should be noted that volatilization of reaction products –which is not considered in our approach- might affect the experimental data. The chemical composition of the particle will change during 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 of oleic acid ozonolysis other than nonanal to remain in the particle phase. No data is available on the product volatility or properties for the specific 12-component organic aerosol matrix simulated, so that the evaporation of products from particle to gas phase could not be considered in the current model. However, if crust formation is occurring the loss of volatiles would be restricted to the surface and near-surface bulk, i.e. the amount of volatile molecules relative to the total number of oleic and palmitoleic acid molecules in the particle would be small. 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  $\alpha_{s,0,O_3}$  (see Pöschl et al., 2007, Pfrang et al., 2010 and Shiraiwa et al., 2010). For long reaction times, the increasing proportion of second- and third-generation products in the particle will also introduce additional uncertainties since branching ratios and molecular properties in such complex multi-component and multi-phase matrices are entirely unknown.’

#### **Referee’s Comment:**

ii) Representation of viscosity and diffusion in multicomponent mixtures is highly uncertain; in particular, the lack of miscibility across the full composition range as some components increase dramatically in viscosity may well lead to serious phase heterogeneity and separation into domains of very different compositions and viscosities. The obstruction theory approach taken in the current work is probably as good as is currently available. However, it would have been good to see a more substantial discussion of the sensitivity in the current application to the uncertainties inherent in this approach (e.g. there is no

reason to expect only radial heterogeneity in viscosity; discrete domains analogous to micelle formation by surfactant material in aqueous solutions are equally as possible as complete crusts). It is acknowledged that the supplementary material uses an alternative approach based on an assumed difference in diffusion coefficient of products with respect to reactants. However, there is no discussion of the likelihood of either treatment within the bounds of possible multicomponent particle viscosity and diffusivity.

***Response:***

The referee correctly identified an area of considerable uncertainty in multi-component and multi-phase aerosol matrices and a paragraph has been added to the main text of the manuscript. Alternative descriptions of the diffusivity evolution would certainly be interesting to test (we present two treatments in this paper and compare their relative performance in the supplementary material and in figure S4) and we concur with Referee #2 that the obstruction theory is the most suitable approach at present. An alternative approach, percolation theory, has been applied by Shiraiwa et al. (2011), but constraining parameters required for application of this theory are not available for the multi-component system investigated in the present study. We included a reference to this treatment in the revised manuscript. Resolving self-assembly processes and formation of micelles during oxidative ageing of multi-component aerosols would certainly be very interesting, but -to our knowledge- there is no experimental data (or even qualitative evidence) available to constrain such a modelling approach. If such data will become available we are certainly keen to incorporate this into the modelling framework. This is however not feasible at present.

*New text added in the revised manuscript (inserted on p. 13009, line 14):*

‘While we follow the obstruction theory approach throughout the paper, we tested the sensitivity of our modelling approach on the method used to describe the evolution of diffusivity as detailed in the supplementary material (see Fig. S4). The alternative approach uses a linear combination expression for the time-dependent diffusion coefficients assuming a product diffusivity of  $\frac{1}{4}$  of the initial value (based on a  $M^2$  dependence for dimmer formation). There is a measurable, but not substantial difference between the two approaches. Another alternative approach, percolation theory, has been applied by Shiraiwa et al. (2011), but constraining parameters required for application of this theory are not available for the multi-component system investigated in the present study. We thus used the obstruction theory approach which has been applied in the past (Stroeve, 1975). However, we would like to point out that representation of viscosity and diffusion in multi-component mixtures is highly uncertain: lack of miscibility may lead to phase heterogeneity and separation into domains of very different compositions and viscosities. There is no direct experimental evidence suggesting only radial heterogeneity in viscosity and discrete domains analogous to micelle formation by surfactant material in aqueous solutions may be equally as possible as formation of complete crusts.’

*New text added in the revised manuscript (inserted on p. 13011, line 10):*

‘While there is clear experimental evidence for a retardation of the losses of oleic and palmitoleic acids (Huff-Hartz, et al., 2007), it should be noted that volatilization of reaction products –which is not considered in our approach- might affect the experimental data. The chemical composition of the particle will change during 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 of oleic acid ozonolysis other than nonanal to remain in the particle phase. No data is available on the product volatility or properties for the specific 12-component organic aerosol matrix simulated, so that the evaporation of products from particle to gas phase could not be considered in the current model. However, if crust formation is occurring the loss of volatiles would be restricted to the surface and near-

surface bulk, i.e. the amount of volatile molecules relative to the total number of oleic and palmitoleic acid molecules in the particle would be small. 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  $\alpha_{s,0,O_3}$  (see Pöschl et al., 2007, Pfrang et al., 2010 and Shiraiwa et al., 2010). For long reaction times, the increasing proportion of second- and third-generation products in the particle will also introduce additional uncertainties since branching ratios and molecular properties in such complex multi-component and multi-phase matrices are entirely unknown.’

#### **Referee’s Comment:**

iii) There is little description in the methodology section concerning the initial conditions of the model. Indeed, the methodology section is much too brief and unclear. What are the 12 components in the mixed particle? Presumably they include all the reaction products (lumped in some way) of oxidation of the particles as the evolution proceeds. What are the diffusivities of the individual components and how is the diffusivity of the mixture related to the individual components (i.e. what mixing rule is assumed?). Is it assumed that all components are homogeneously mixed throughout the particle (i.e. complete miscibility of all components)? On this note, would all components be expected to be homogeneously mixed throughout the bulk and surface layers and why? What is the RH of the simulations / experiments - how much water would be condensed at equilibrium? Was this equilibrium assumed to pertain at the start of the experiment? In the presence of components ranging in polarity, how would the surface energy contributions in the mixture lead to redistribution of components between the bulk and surface layers? If this study is part of a series of papers and the description of model setup is provided elsewhere in this series, there should be clear reference to where all this information is provided.

#### **Response:**

The methodology of the modelling has been described in detail in Shiraiwa et al. (2010), published open-access in the same journal. Modifications to this model are described in the revised manuscript (we added further details as indicated below). Description of the initial conditions is brief, but all the information has been published in Huff-Hartz et al. (2007) and we are giving reference to this paper. However, since this information is of significant importance for the key messages of our manuscript and Huff-Hartz et al.’s paper is not open-access, we now included a more detailed description.

*New text added in the revised manuscript (inserted on p. 13009, line 16):*

‘Analogous to  $f_{ss}$ , we define the concentration fraction of products in the particle bulk as  $f_b$ . The reaction products are assumed to be (semi-)solid, so that these concentration fractions may be interpreted as degrees of solidification with a value of unity corresponding to complete conversion of reactants into (semi-)solid products.  $f_{ss}$  or  $f_b$  approaching unity thus leads to a shut down of transport due to massively decreasing diffusivity.’

*New text added in the revised manuscript (inserted on p. 13009, line 24):*

‘The 12 components (9.9% unreactive n-alkanes, 14.9% palmitoleic acid, 13.1% oleic acid, 1% nervonic acid, 2.8% cholesterol, 2.0% decanoic acid, 17.7% palmitic acid, 22.4% stearic acid, 1.3% arachidic acid, 2.6% glutaric acid, 6.6% adipic acid, 5.8% suberic acid) have been chosen to mimic meat-cooking emission profiles in dry conditions containing the key unsaturated compounds commonly used as markers, in particular cholesterol, palmitoleic and oleic acids (Huff-Hartz, et al., 2007 and references therein). Product volatilization in the complex 12-component aerosol mixture is not considered here, mainly because of the lack of experimental data to constrain any modelling attempt. Re-condensation of components is unlikely to be of importance in the experimental conditions where gaseous components

originate from the particles only. All components are assumed to be initially homogeneously mixed throughout the particle.'

*New text added in the revised manuscript (inserted on p. 13011, line 10):*

'While there is clear experimental evidence for a retardation of the losses of oleic and palmitoleic acids (Huff-Hartz, et al., 2007), it should be noted that volatilization of reaction products –which is not considered in our approach- might affect the experimental data. The chemical composition of the particle will change during 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 of oleic acid ozonolysis other than nonanal to remain in the particle phase. No data is available on the product volatility or properties for the specific 12-component organic aerosol matrix simulated, so that the evaporation of products from particle to gas phase could not be considered in the current model. However, if crust formation is occurring the loss of volatiles would be restricted to the surface and near-surface bulk, i.e. the amount of volatile molecules relative to the total number of oleic and palmitoleic acid molecules in the particle would be small. 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  $\alpha_{s,0,O_3}$  (see Pöschl et al., 2007, Pfrang et al., 2010 and Shiraiwa et al., 2010). For long reaction times, the increasing proportion of second- and third-generation products in the particle will also introduce additional uncertainties since branching ratios and molecular properties in such complex multi-component and multi-phase matrices are entirely unknown.'

#### **Referee's Comment:**

minor: comments such as "representative of atmospheric cooking aerosols" should be avoided, since the system under investigation is a very much simpler analogue of such particles. On the same subject, the work of Allan et al., 2010 definitely did not show that oleic acid was one of the most prominent reactive components of cooking aerosols (p13005). Similarity of AMS spectra cannot be used to infer molecular composition. The language in the current paper should not oversell the representativeness of the study. Individual unsaturated acids or mixtures of a few components are convenient model systems for study rather than representative of the majority of the mass of real atmospheric particles, whether well-established in the literature or otherwise.

#### **Response:**

We followed the argumentation and formulations used in Huff-Hartz et al. (2007) using the 12 component mix as a proxy for cooking aerosol. We did not intend to oversell our study, which we consider an exploratory case study. To avoid the negative impression and misunderstanding reflected in the referee's comment, we are happy to change the wording of our manuscript and clarify this aspect.

*New text added in the revised manuscript (inserted on p. 13014, line 13):*

'For atmospheric interpretation of the results presented below, it should be noted that the model used in the present study has been optimized to simulate laboratory data for a 12-species organic aerosol matrix in dry conditions (Huff-Hartz et al., 2007). While the 12 components have been chosen to mimic meat-cooking emission profiles containing the key unsaturated compounds commonly used as markers, in particular cholesterol, palmitoleic and oleic acids (Huff-Hartz, et al., 2007 and references therein), real meat cooking emissions are complex mixtures of hundreds of compounds and likely to interact with moisture present in the atmosphere. Particularly in highly humid conditions we would expect considerable deviations between our model results and the behaviour of cooking aerosol in the

atmosphere, since hygroscopic growth can impact substantially on chemical ageing and atmospheric lifetimes of aerosols. Product volatilization in the complex 12-component aerosol mixture is also not considered here, mainly because of the lack of experimental data to constrain any modelling attempt. The evaporation and re-condensation of components and the resulting evolution of the chemical matrix may have considerable effects on chemical processes in these multi-species and multi-phase mixtures. While re-condensation is unlikely to be of importance in the experimental conditions where gaseous components originate from particles only, it may be important in complex atmospheric aerosol matrices.’

*Text replacement throughout the revised manuscript:*

‘representative of atmospheric cooking aerosols’ has been replaced by ‘approximating atmospheric cooking aerosols’.

*Text replacement in the revised manuscript:*

‘One of its most prominent reactive components is oleic acid (Allan et al., 2010)’ has been replaced by ‘The aerosol-mass spectrometer spectra of one of its most prominent reactive components have strong similarity to oleic acid (Allan et al., 2010).’

#### **Referee’s Comment:**

technical: the dotted lines are only dotted at very high magnification and should be represented differently

#### **Response:**

We are grateful for this observation and have amended the dotted lines in the relevant figures.

#### **References:**

Huff Hartz, K. E. H., Weitkamp, E. A., Sage, A. M., Donahue, N. M. and Robinson, A. L.: Laboratory measurements of the oxidation kinetics of organic aerosol mixtures using a relative rate constants approach, *J. Geophys. Res.-Atmos.*, 112, D04204, 10.1029/2006jd007526, 2007.

Pfrang, C., Shiraiwa, M. and Pöschl, U.: Coupling aerosol surface and bulk chemistry with a kinetic double layer model (K2-SUB): an exemplary study of the oxidation of oleic acid by ozone, *Atmos. Chem. Phys.*, 10, 4357-4557, 2010.

Pöschl, U., Rudich, Y. and Ammann, M., Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions - Part 1: General equations, parameters, and terminology, *Atmospheric Chemistry and Physics*, 7, 5989–6023, 2007.

Rudich, Y., Donahue, N. M. and Mentel, T. F.: Aging of organic aerosol: Bridging the gap between laboratory and field studies, *Annual Review of Physical Chemistry*, 58, 321-352, 2007.

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Shiraiwa, M., Ammann, M., Koop, T. and Pöschl, U.: Gas uptake and chemical aging of semi-solid organic aerosol particles, *Proceedings of the National Academy of Sciences*, 108(27), 11003-11008, 2011.

Vesna, O., Sax, M., Kalberer, M., Gaschen, A., Ammann, M., Product study of oleic acid ozonolysis as function of humidity, *Atmospheric Environment*, 43, 3662–3669, 2009.