

## Response to the comments of Anonymous Referee #1

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

This manuscript presents a logical development of recent work by the authors in simulating the time dependence of heterogeneous chemistry in well-defined systems of atmospheric relevance studied through controlled laboratory measurements of aging. The unique focus of this manuscript is the influence of decreasing diffusivities of reactants within a particle on the lifetime and timescale for chemical transformations to occur. In particular, the reaction of oleic acid with ozone is considered, where the particle consists of a mixture of components and for which a decrease in diffusivity over time is explored following the formation of oligomers. In some ways, the manuscript feels fairly incremental, considering a coupling of the diffusivity to composition while neglecting key processes such as the volatilization of products and the partitioning of water to the particle as the chemical makeup changes. The impact of the manuscript would be much more significant if the heterogeneous aging were coupled to these two processes. The authors should address the following comments before the manuscript is accepted for final publication.

### ***Response:***

We thank the Anonymous Referee #1 for the critical but positive evaluation of our manuscript. The reviewer indicates that our research is well suited for publication in ACP, but raised a number of points 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 highly 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 'increment' in kinetic aerosol model development. 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. Description of volatilization of products, of semi-volatile species, of hygroscopicity and of condensation and re-condensation are clearly further and very 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.

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

(1) The authors consider the implications of this work for atmospheric aerosol. My concern is that this section is compromised to a great extent by the neglect of volatilization and hygroscopicity. The loss of volatile products and the absorption of water would both lead to changes in particle composition and changes in diffusivity. The authors should discuss the limits of their model more clearly, defining the conditions under which the model predictions may be considered to be accurate and relevant to the atmosphere, and highlighting the potential impact of considering the loss of volatiles and hygroscopic growth on the chemical ageing.

### ***Response:***

We added a new paragraph in the ‘Atmospheric implications’ section reflecting the reviewer’s valid comment and discussing in more detail how the limitations of the present modelling approach impact on the atmospheric interpretation of the presented results. We explicitly define which conditions lead to larger deviations between our model results and the behaviour of cooking aerosol in the atmosphere. We specifically discuss how product volatilization and hygroscopic growth impact on the chemical ageing of 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.’

**Referee’s Comment:**

(2) On page 13011, final line, the authors refer to a parameter that defines the degree of solidification. This parameter must be defined clearly in the main body of the manuscript and limiting values discussed, particularly describing how this is related to the change in diffusivity and the formation of a ‘crust’.

**Response:**

We added a paragraph more clearly defining the degree of solidification in the main text of the manuscript. We also discuss the limiting values and the relation of the degree of solidification to crust formation and changes in diffusivity.

*New text added in the revised manuscript (inserted on p. 13011, line 29):*

‘The concentration fractions of products in the quasi-static surface layer,  $f_{ss}$ , and in the particle bulk,  $f_b$ , are illustrated in Figs 3 (b) and 6, respectively. Since the products are assumed to be (semi-)solid, we interpret these fractions as degrees of solidification with a value of unity corresponding to a complete conversion of reactants into products.  $f_{ss}$  approaching unity thus corresponds to the formation of a surface crust which would effectively shut down transport into the particle core due to the massively decreased diffusivity in the quasi-static surface layer.’

**Referee’s Comment:**

(3) I am concerned that the authors may be over interpreting experimental data. In Figures 1(a) and (b), the interpretation of the experimental data appears to rely on the accuracy of two data points alone, the longest time points in both figures. How reliable are these measurements? What level of accuracy can really be achieved in inferring the decreasing diffusivity from these measurements, a few orders of

magnitude? This is particularly important given that the model does not consider the evolving composition through loss of volatiles that is undoubtedly happening in the actual measurement.

***Response:***

The referee correctly points out that the chemical composition of the particle will 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. This is discussed in more detail in the revised manuscript. 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 previous experimental studies on oleic acid ozonolysis, we expect first-generation products other than nonanal to remain in the particle phase. However, no data is available on the product volatility for the complex organic aerosol matrix simulated. The evaporation of products from particle to gas phase could thus not be considered in the current model. 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 of simpler systems. 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 products in the particle will introduce additional uncertainties in the calculations due to the absence of experimental data on branching ratios and molecular properties in particular for second- and third-generation products.

The reduced reactivity reported by Huff-Hartz et al. (2007) is clearly visible in the last 2 (out of 7) measurements. Since we did not carry out the experimental work we cannot comment on the experimental accuracy and rely on the uncertainties quoted by Huff-Hartz et al., a highly experienced group with substantial expertise in experimental aerosol studies. Given those uncertainties the last two points give clear evidence of a retardation of the oxidative loss both for oleic and for palmitoleic acids. We have no reason to believe that Huff-Hartz et al.'s uncertainties are incorrect and have strong confidence in the experimental work presented by this reputable team. The initial and final rate coefficients discussed by Huff-Hartz et al. also illustrate that the retardation has been considered by the experimental team to be a real effect clearly outside the experimental error limits. It is true that at long reaction times it is possible that loss of volatiles affects the experimental data and we added a comment to this end in the revised manuscript. 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 thus limiting the impact of the assumptions made in our approach. Values for diffusivity were varied within what we believe is a reasonable range (see Shiraiwa et al., 2011 for a detailed discussion; several references to this paper are given in the manuscript).

*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  $\alpha_{s,O_3}$  (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.’

## References:

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