Author comment to anonymous referee #1

Referee comment 1:

The manuscript describes a scheme for classifying the different regimes for heterogeneous reactions and gas uptake on aerosol particles. It extends earlier treatments by some of the authors, seeking to establish a rigorous framework for treating the kinetics of aerosol transformation. In many ways the work represents a logical extension of earlier work. Although I find very little that should be specifically questioned in the manuscript (it all largely seems to follow correctly and presents an incremental development of previous work), there are some areas of the manuscript that are particularly impenetrable for the reader. I also feel there are some more broad ranging questions that the authors should consider in any revised version of the manuscript.

Response:

We thank anonymous referee #1 for his critical but overall positive feedback on our manuscript. He outlines the relevance and significance of our work, but also addresses the problem of unsatisfactory readability and points out that the application to the oleic acid – ozone reaction system leaves the reader with a few unanswered questions. These two aspects of the manuscript were a concern during the writing process and the authors agree that there is still room for improvement in both areas. We will attempt to address the concerns he raises in the points below.

Referee comment 2:

Specifically:

- The manuscript is overly long and full of a large number of acronyms. In many places the reader has to work very hard to disentangle the acronyms for the different limiting cases, different fits, and kinetic symbols. In many cases it feels that the authors are trying to say something fairly straightforward but the manuscript is certainly not written in a straightforward way. This will reduce its impact. I recommend the authors consider reducing the discussion in some places, moving some of the more detailed arguments into more appendices and spelling out the meaning of some of the more significant acronyms throughout, rather than using a complex array of acronyms. It would be helpful to just use the name of the limiting case: even though this may make some sentences longer, it will make them easier to understand.

Response:

The authors agree with the referee and admit that pieces of the manuscript might be hard to disentangle. We appreciate the good and detailed changes that the referee proposes and will try to implement many of them in the revised version of the manuscript. We propose to write out all acronyms once in each section and additionally in a number of other places where this might be helpful. This procedure should improve the readability and still should not crowd the manuscript with repetitions of spelled-out acronyms. In addition to streamlining several points in sections 5 and 6, we will move Sect. 6.4.2 into the appendix since it is discussing a side aspect of the application.

Referee comment 3:

- The significance of the numbers that come out of the fitting to the experimental data for oleic acid is not clear (Table 6). Some of the numbers retrieved are highly variable from measurement to measurement, fit to fit (for example, the value of the accommodation coefficient of ozone on oleic acid surface). The measurements represent a variety of experimental techniques, some resolving size changes and some changes in chemical composition. These are clearly not the same thing and it raises the question of how they can be compared. Further, it is my understanding from the discussion early on in the paper that the model that is being used does not even include the gas-particle partitioning of volatile and semi-volatile products (Page 1003: "As the KM-SUB model does not explicitly treat the products of this reaction, limiting cases were assigned at the point where 50% of the initial reactant Y was consumed using the numerical criteria"). Clearly this leads to ambiguity in how the size and compositional data can be compared. It could also have a significant consequence for the course of secondary chemistry and it is apparent that this is not included in the model with the speciation apparently limited to generic X and Y, ozone and oleic acid.

Response:

Since only one data set was fitted at a time, it is almost impossible to constrain a large number of kinetic input parameters. In particular, the non-limiting parameters will only be constrainable to a certain span of values (e.g. the accommodation coefficient must be larger 1e-4 to not impose its characteristic influence on the system that would be detectable). Finding one common kinetic data set was not possible with the existing choice of data and our existing resources. The numbers that come out of the fitting are meant as possible scenarios and lack any proof of uniqueness. Since this is an area of confusion, we will add a subsection at the end of Sect. 6 that addresses the uniqueness and significance of the individual fits shown in this manuscript. A single (global) fit to multiple experimental data sets would be a marked improvement over these single fits, however, we are of the opinion that this development is a further step in the research process and thus deserves to be treated in a subsequent study that we plan to submit in the near future.

The analyzed data sets are all based on compositional information and not on size changes: Ziemann (2005) and Hearn et al. (2005) used mass-spectrometric techniques and Lee et al. (2007) utilized Raman spectroscopy for determination of the changes in particle composition. From this standpoint the techniques should be fairly comparable within experimental errors. The referee is correct in pointing out that the model we employed neglects gas-particle partitioning, but we believe this is the correct thing to do for the following reasons:

1. *No size data was reported by the experimental efforts. While full treatment of evaporation is desirable, it would introduce more kinetic parameters which must be fit. These can hardly be constrained without including size dependent data to the fitting process.*
2. *Evaporation of oleic acid is rather negligible due to its low vapor pressure and short experimental timescale of seconds (Ziemann,2005; Hearn et al., 2005). Some of the reaction products (e.g., nonanal) are known to be semi-volatile and their evaporation may cause shrink of the particle; Shiraiwa et al., 2012 have applied KM-GAP to the Ziemann 2005 data and have shown that the particle would shrink with the radius decreasing from 200 to 187 nm in 30 s. This aspect is certainly subject to further studies, but for now our view on the reaction system is meant to be rather coarse, trying to detect the overall kinetic regime and not making highly quantitative predictions.*

The referee is correct that secondary chemistry has not been included in the analysis yet, which is consistent with earlier work (Shiraiwa et al. (2010), Shiraiwa et al. (2012)). The degree to which this influences the analysis is unknown to the authors and beyond the scope of this manuscript.

Referee comment 4:

- Although the authors do go to great length to address the sensitivity of the model fitting to the various model parameters, I am still left wondering how unique the fits are, particularly when the measurements at only a handful of points are compared to simulations in which the sensitivities to many parameters are explored. On pages 1017, the authors state: "This example demonstrates the breadth of possible behaviors for cases that do not fall into a distinct limiting case but rather exhibit regime behavior." This indeed seems to be the main conclusion but is this a surprise? Maybe I am misunderstanding the method used by the authors to fit the oleic acid but they seem to have exclusively focussed on the sensitivity of fitting the data after 10% of the reaction has occurred (i.e. at one specific point during the reaction). On page 1016 they state: "Sensitivity coefficients are given at 10% reaction course as this will reduce the potential influence of reaction products and avoids the initial, highly transient behavior which is expected as the surface and first bulk layers come into equilibrium with the gas phase.“ Although their rationale is clear, how is limiting their sensitivity analysis to only one region of time consistent with the recognition that different regimes exist and, presumably, their expectation that the model should be capable of separating out the interplay of different kinetic parameters when different regimes are active?

Response:

In our manuscript, sensitivity analysis was used as a tool to confirm the assignment of a limiting case that has been made based on the decision criteria outlined in chapter 2. The premise is the following: When a kinetic parameter is actually limiting the reaction, then a small alteration of the parameter inside the model (as done in a sensitivity analysis) should affect reaction speed. We chose to only include the information from the sensitivity analyses for one point in reaction course for simplicity reasons. In fact, the kinetic regime is of course likely to change over time (see section 3.5 of submitted manuscript), but this was not our focus when doing a sensitivity analysis to confirm limiting case assignments made using the parameters described in chapter 2. We will add a statement to section 6.5 to make clear that sensitivity analysis has only been used as an auxiliary tool to confirm that model behavior obeys the limiting case to which it was assigned, and has not been used as part of the fitting process itself.

Referee comment 5:

- It is not clear what conclusions on the oleic acid system are being reached. How do their conclusions about the limiting cases compare with the conclusions reported by the authors of the original papers? A truly unique outworking of the model framework would be if it was used to fit all of the data from all of the measurements made in one global fit. I do not believe the authors have done this – the fits in Table 6 appear to be independent for each experiment.

Response:

We want to stress that this manuscript (and in particular its application to oleic acid – ozone reaction system) should not be seen as an attempt to gain new mechanistic insights into this system. Our aim was to (i) showcase the way our classification systems works and (ii) demonstrate that fits to several previously reported independent data sets may be assigned a relatively small set of different kinetic behaviors.
All fits performed for this study were performed using one data set at a time and no common fit has yet been obtained. It was not our intention to judge between these fits at this point of research and we thus left the different outcomes of our fits to several data sets stand with very little comment purposely. Our preliminary attempts to generate a global fit to multiple experimental data sets by combining single fits did not yield a unique, satisfactory solution. A truly global fit will require significantly more computational resources and presents several unique challenges; we continue to work on this project and are in the early stages of a manuscript on this topic.

References:

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