

Author Comment

We thank the reviewers for their time, detailed and thoughtful comments and helpful suggestions. We also thank Douglas Day for the time he took to comment on our manuscript and the helpful comments he provided. We provide point-by-point response to the comments below. The reviewer comments are in black and the response are in blue, where italicized text in quotation mark refers to text in the manuscript and revised parts are underlined.

Both reviewers of this manuscript and Douglas Day commented on the purely irreversible vapor wall loss scheme that we employed in the model in the original manuscript. This very good feedback convinced us to implement a detailed two-step reversible/irreversible vapor wall loss scheme into the model. We now use the scheme presented in Huang et al. (2018) with very few alterations. Our implementation of this method is detailed in the revised manuscript, Sect. 2.2. We re-fitted all experimental data with the updated model in the revised manuscript. While the general conclusions of this manuscript are kept intact, some details are not, affecting some of the comments and replies below. We will explain all relevant changes in the response to the referees. The most important difference in the new simulation results compared to previous version is that re-volatilization of vapors (from chamber walls) after raising chamber temperature now leads to a higher gas phase concentration of semi-volatile species and, thus, slightly slower SOA mass loss due to evaporation. In comparison to our previous model fit, this leads to a reduced need of particle-phase oligomerization to describe the experimental data. As we will explain in detail in response to reviewers (response to 4th paragraph of general comments of reviewer 1; response to comment 11 of reviewer 2), a lower oligomer content further improved the model fit to α -pinene pON/OA data, too.

Both reviews also commented on the mechanistic conclusions drawn from this research paper. We agree that the modelling results of this work should not be interpreted as full proof of certain mechanistic features of the chemical system and agree that this could have been misleading in the first submission. We think however that there is a lot of knowledge to be gained from the model by means of exclusion (“X cannot be true if Y is true”) or deduction (“if X were the case, Y would follow”). This manuscript only uses a small training data set from a single experimental campaign as a proof-of-concept and future work with larger training data is expected to be much more conclusive. Thus, in multiple instances, we have toned down the mechanistic conclusions of this manuscript whenever possible as mentioned in the detailed responses and focused on highlighting the methodology. For example, we replaced several instances of “observed” with “suggested by the model” and edited the abstract:

“The results presented here provide new mechanistic insight into the processes leading to formation and evaporation of SOA. Most notably, much of the non-linear behavior of precursor mixtures can be understood by RO₂ fate and reversible oligomerization reactions in the particle phase, but some effects could be accredited to kinetic limitations of mass transport in the particle phase.”

Now reads:

“The results presented here provide new mechanistic insights into the processes leading to formation and evaporation of SOA. Most notably, the model suggests that the observed slow evaporation of SOA could be due to reversible oligomerization reactions in the particle phase. However, the observed non-linear behavior of precursor mixtures points towards a complex interplay of reversible oligomerization and kinetic limitations of mass transport in the particle phase, which is explored in a model sensitivity study.”

Overall, in this work, we introduce a novel approach for interpretation of chamber data with a full kinetic model, using the monoterpene + NO₃ system as an initial test system. To the authors' knowledge, this has never been done in such depth and, while not perfect, constitutes a significant step forward in development of these models and designing laboratory experiments that generate maximal information for the optimization of these models. We see this paper as a first step in the computational, data-driven evaluation of SOA formation with kinetic models. The deliverable in this work is a very comprehensive and adaptable model, applied to a solid set of experimental data. The model can be improved when fed with more information and through feedback of the community.

Author's Response to Referee #1

The authors describe a set of experiments of SOA formation from α -pinene, limonene and mixtures of both by oxidation with NO_3 and their evaluation by model approach. The new experiments link to previous series of experiments of SOA formation with NO_3 as oxidant also performed in the GTEC chamber. SOA is here formed at 5°C and then the chamber is heated in two steps to 25 and 42°C . The mixed experiments the monoterpenes (MT) α -pinene and limonene were oxidized simultaneously and sequentially. The experiments show distinct individual growth and evaporation behavior for limonene and α -pinene. The behavior in the mixtures is different in different ways, in any case the behavior seems not explainable by simple linear combinations of the individual compounds. The model applies a lumped approach to the gas-phase chemistry and is built to take care of organic nitrates in interaction with organics not containing nitrate. The flow of products is distributed to two 6 bin vapor pressure basis sets. In the liquid phase, a scheme for reversible oligomerization is implemented, which leads to non-volatile oligomers. The model is solved by global optimization based on Monte Carlo Genetic Algorithm (MCGA). Searches for global minimum using of the order of $10(!)$ parameters in order to predict essentially the SOA mass and secondly, pON/ON ratio. The pON/ON ratio is derived from AMS data (with some assumptions). Both, SOA mass and pON/ON do not have much detailed structure in time and the increase of temperature led only to smooth variations. I summarize, what I understood: a lumped gas-phase scheme leading to nitrated and non-nitrated products, each product set optimized/mapped onto a 6-bin vapor pressure basis set, a parameterized oligomerization scheme. The combination of experiments and modelling serves to promote the specific type of model approach.

We thank referee #1 very much for their time, detailed analysis and insightful response. Their feedback was very valuable to improve our manuscript. In the following, we will provide point-by-point responses to their comments.

SOA mass and pON/ON were evaluated/interpreted based on the above model approach. The behavior of the individual MT and the deviations in both mixtures are essentially explained in terms of liquid phase reversible oligomerization, dimerization in the gas-phase and possible hindered transport in a viscous liquid phase. Actually, from the onset of the model, solutions are strongly directed towards oligomerization chemistry. The authors openly discuss the limits of their approach.

The referee is correct in their assessment that liquid phase reversible oligomerization, dimerization in the gas phase and hindered transport by the viscous phase are the means in the presented model to explain the behavior beyond lumped gas phase chemistry and volatility basis sets. In this study, we aim to provide a proof of concept example on how the kinetic model can be used to interpret chamber data. We see this work as a multi-step process and want to document our progress in publications when appropriate. Thus, in our initial attempt, we first fitted the data in Fig. 2 without considering mass transport limitations. We show in this proof of concept that oligomerization mechanics explain much of the specific, non-linear features of the experimental data, but alone cannot fully explain the evaporation of monoterpene SOA mixtures. Later, we offer an alternative explanation for slow evaporation by including mass transport limitations in a sensitivity study. This explains the direction of the model towards oligomerization chemistry as solution for the observed experimental behavior. Hence, we think that the fact that reproduction of the experimental data is not perfect and the fact that oligomerization fractions are too high are two sides of the same coin. More measurements (e.g., different chamber conditions), more data (e.g., viscosity etc.), and better exploration of the model parameter space with larger computational

resources will allow for continual development and improvement of the model in the future, to fully constrain and capture all important aerosol properties and characteristics.

I don't share the optimistic view of the authors. Considering the target observations with low leverage and the degree of underdetermination, the reproduction of the target quantities is relatively weak (as also stated by authors at some instances). Especially, pOn/ON is not so well reproduced (Fig. 6c-d).

We agree with the referee that the set of chamber experiments and the kinetic model constitute an underdetermined system. In this work, our main goal is to introduce a novel approach for interpretation of chamber data with a full kinetic model, using the monoterpene + NO₃ system as an initial test system. To the authors' knowledge, this has never been done in such depth in literature and, while not perfect, constitutes a significant step forward in development of these models and designing laboratory experiments that generate maximal information for the optimization of these models. Of course, more and even better designed laboratory experiments would help constraining the data and improve the model. We see this paper as a first step in the computational, data-driven evaluation of SOA formation with kinetic models. The deliverable in this work is a very comprehensive and adaptable model, applied to a solid set of experimental data. The model can be improved when fed with more information and through feedback of the community. To more clearly state the emphasis of this work, we have made the following modifications in the revised manuscript.

In the abstract:

"The methodologies described in this work provide a basis for quantitative analysis of multi-source data from environmental chamber experiments with manageable computational effort."

Now reads:

"The methodologies described in this work provide a basis for quantitative analysis of multi-source data from environmental chamber experiments, but also show that a large data pool is needed to fully resolve uncertainties in model parameters."

We added the following sentence in the introduction:

"We first test the hypothesis whether particle-phase oligomerization in a well-mixed liquid phase can explain the observed behavior. Then, we use the kinetic model to perform a sensitivity analysis on the potential effect of retarded bulk diffusion due to a viscous phase state."

Sect. 4 addresses the issue in detail:

"While there is significance to the general conclusions drawn from the model analysis, the individual model parameters that are returned by the inverse modelling approach must be treated with caution and evaluated in the context of the model and experimental data that are employed. Given the large number of fitting parameters and the limited number of experimental data sets, it cannot be insured that a true and correct global minimum is obtained in this isolated case study. [...] For example, Fig. S5 shows an estimate of the uncertainty in the volatility distributions obtained in this study. The error bars in Fig. S5 are standard deviations of individual re-fits of volatility distributions that all lead to a similar calculation outcome and hence quantify their uniqueness (or lack thereof). Figs. S1, S9, S10, and S11 show sensitivity case studies of very influential model parameters and Table 1 shows a local sensitivity analysis of the remaining input parameters, which gives an impression of their range within a single model fit. However,

the true parameter ranges can be much larger if the model solution space encompasses different kinetic regimes. The uniqueness of the obtained parameter set can be enhanced by inclusion of more experimental data at different conditions or by a priori determination of model parameters such as measurements of volatility distributions, oligomerization degrees or particle viscosities, which will be an imperative task in follow-up studies. However, despite the remaining uncertainties in derived model parameters, the modelling suite presented here constitutes a step forward in the computational, data-driven evaluation of SOA formation with kinetic models.”

Regarding reproduction of pON/OA data: We note that quite a few assumptions were made in obtaining the experimental pON/OA values, namely molecular weight of the nitrated organic molecules and AMS relative ionization efficiency (RIE). Hence, it may not necessarily be a fault of the model that it is not able to produce pON/OA data to 100 %. It could also be somewhat seen as robustness of the kinetic model that not all fluctuations or inaccuracies in the data are rectified by the multi-dimensional model fit. In other words, we do not see evidence for overfitting, which is often a problem of underdetermined systems.

We added the following paragraph to the manuscript:

“The unexpectedly low ON content in the MIX experiment points either towards non-linear effects in chemistry that are not captured by the model or towards uncertainties in the pON/OA measurements. For the latter, there are two major sources of uncertainty. First, a default value of relative ionization efficiency (RIE) of 1.1 is used for AMS nitrate in this study (Canagaratna et al., 2007). This value is typically associated with inorganic nitrate as the RIE of nitrate derived from pON has not yet been experimentally measured to the knowledge of the authors. It is thus not clear how this value depends on chemical composition or if exposure to higher temperature may lead to variation of RIE over the course of an experiment. Second, a constant molecular weight of pON (250 g/mol) is assumed for calculation of pON/OA. However, it is possible that changes in chemical composition result in changes of the average molecular weight during an experiment.”

This is especially concerning, as the observables themselves do not offer much structure to test the quality of the model performance. If one wants to be super-critical, even the structure of the T-behavior of the limonene system (Fig. 2a) and the pON/ON (Fig. 6a) shows systematic deviations, even though the model curves hit the overall behavior quite well. This is more distinct by the step in the α -pinene curve (Fig 3a).

We respectfully disagree that the observables do not offer much structure. The fact that this model is compared to the entire time evolution of signals is large a step forward from just fitting to single points on a SOA yield curve.

- The slow evaporation of organic material is a clear structural element of all experimental data sets that clearly cannot be reconciled without implementing either particle-phase oligomerization or mass-transport limitation (or both).
- The constant pON/OA in the pure limonene system and the triangular time evolution of pON/OA in the α -pinene system (Fig. 5 of revised manuscript) are distinct structural elements for which the model offers an explanation by ascribing different volatility distributions to nitrated and non-nitrated monomeric oxidation products.

We added a simulation to the Supplement (Fig. S7) that signifies how a model run without oligomerization chemistry cannot reproduce the structural elements of the LIM experiment.

“A model fit to the LIM experimental data was attempted without inclusion of particle-phase oligomerization reactions. The model output of this simulation run shows an overall low correlation to the experimental data as it cannot explain the long time to reach peak SOA mass and the slow mass decrease at 42 °C (Fig. S7)”

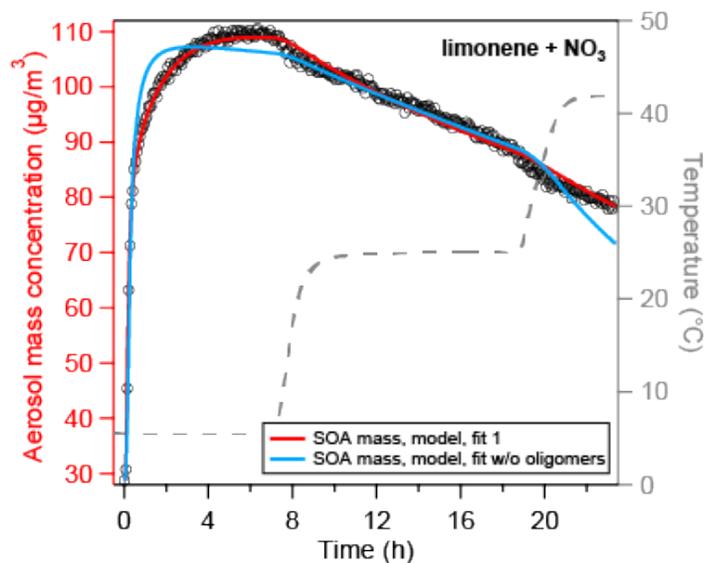


Fig. S7. Comparison of an alternative model optimization run without particle-phase oligomer formation to the best fitting scenario (fit 1) for the LIM experiment. The slow increase of SOA mass (0 – 5 hours) and the slow evaporation at 42 °C (19 – 21 hours) cannot be explained without oligomer formation.

We further expanded the discussion on the consequences of a constant pON/OA of the pure limonene system in Sect. 3.4:

“The fact that pON/OA is rather constant over time thus gives no evidence that decomposition rates of oligomers consisting of nitrated or non-nitrated monomeric building blocks might differ and we use the same oligomer decomposition rate irrespective of nitration state of the product bin. Note that in the absence of oligomerization, a constant pON/OA could only be obtained if nitrated and non-nitrated organics were evenly distributed across the evaporating volatility bins.”

We invite referee #1 to review the new model fits in the revised manuscript. After implementation of reversible vapor wall loss, α -pinene mass can now be reproduced much better (Fig. 4 of revised manuscript) due to re-volatilization of vapors from chamber walls (Fig. S8 in revised Supplement). This enables a fit with low oligomer content that in turn is able to describe the triangular shape of pON/OA evolution for α -pinene SOA as now outlined in Sect. 3.4:

“The temporal evolution of limonene SOA pON/OA was constant, which can be explained with a particle phase mostly consisting of oligomers whose decomposition rates do not differ for nitrated and non-nitrated building blocks. The temporal evolution of α -pinene SOA pON/OA can only be retrieved if the particle phase is predominantly comprised of monomers: sequential evaporation of nitrated and non-nitrated monomers with different vapor pressure leads to modulation of pON/OA.”

We included a discussion on how SOA mass is reproduced by one fit and pON/OA by the other fit for the pure α -pinene SOA experiment in Sect. 3.5.3:

“We have seen in Sects. 3.2.2 and 3.4, that experimental α -pinene SOA mass can only be matched with a model run that ascribes a high oligomer content to α -pinene SOA (fit 2), which is typically not reported in the literature (Romonosky et al., 2017). In return, a high oligomer content cannot describe the time evolution of α -pinene pON/OA properly. Hence if, hypothetically, a semi-solid phase state of α -pinene SOA were to slow down evaporation so that SOA evaporation is reconciled between model and experiment with a particle phase mostly comprised of oligomers, the distinct temporal evolution of pON/OA could still be matched.”

And from here on, I have difficulties to understand the purpose of the paper. Is it possible that for fundamental reasons the model does not perform in the mixed cases? I mean, beyond non-linearity, e.g. by betting so strongly on oligomerization? And that the threefold lumping, gas-phase, VBS, liquid phase leads only individual solutions and has not much predictive power.

With this paper, we want to explore with a detailed kinetic model what the mechanistic reason for slow evaporation of SOA can be. The fits in the revised manuscripts now have a better correlation to the mixed precursor cases even in the default run, without considering mass transport limitations. One of the main outcomes of this paper is the fact that some ways of slowing down evaporation is needed to explain the experimental data, beyond just a VBS with very low volatile species. This explained now in more detail in Sect. 3.3.2:

“Fig. S14 shows the time evolution of α -pinene- and limonene-derived oxidation products over time in the MIX and SEQ experiments. More α -pinene than limonene oxidation products evaporate from the particles in these model simulations, as would be expected from the pure precursor experiments. However, the fact that model-experiment correlation in the MIX and SEQ experiments is worse than in the APN and LIM experiments indicates non-linear behavior of the mixed precursor experiments. Because evaporation is overestimated by the model, especially in the SEQ experiment, effects not treated in the current model must lead to a slowing of evaporation speed in the mixed precursor experiments.”

Since it is computationally extremely difficult to treat viscosity correctly in these models, this paper focuses first on oligomerization and tries to make cases for and against oligomerization as the sole cause for our observations. We see this as excellent starting point for future studies to pick up from and finally get a full picture of the interactions of oligomerization chemistry and diffusion limitation in SOA formation and evaporation. We added the following sentence to Sect. 4:

“Since it is computationally difficult to treat the effects of slow mass transport fully in these models, this paper focuses first on oligomerization and tries to make cases for and against oligomerization as the sole cause for our observations.”

However, if so I have a dilemma. One on hand the manuscript presents an interesting approach, is well written and it is interesting to read. It is stimulating and inherently, there is not much to criticize. On the other hand there is a mismatch of – let’s say – interesting hypothesis, derived from the model approach, and their substantiation with observations. For example, the high degree of oligomerization in the limonene case: I don’t see any efforts by the authors to substantiate that interesting prediction by their

experimental data. (In contrast, the work by Faxon et al. does not seem to support a high degree of oligomerization, line 458.)

The referee has a good point about the mismatch of hypothesis and substantiation. The model, at this point in time and with limited experimental data to feed from, gives no clear/full solution for this chemical reaction system. Hence, we reworked many parts of the manuscript and tried to make it very clear that the model result still constitutes a hypothesis unless measurement data of oligomerization rates and viscosity/diffusion are either pre-determined or adequately constrained by model/experiment (cf. Sect. 4).

We think a model is only useful if it is possible to extract more information from the experimental data than one would have without. In our opinion, this model clearly demonstrates how an additional process is needed to describe the non-linear experimental data, and that it is likely oligomerization or slow diffusion. Entangling both, however, is a major accomplishment that we were not able to do in this manuscript “on the fly”.

The model gives a first guess of quantitative parameters as basis of discussion that can be verified, compared and corrected in follow-up studies. We think that this methodology is, while not perfected yet, a clear step forward in analyzing these types of chamber experiments.

Major comments

In general, as a major comment, data are missing to judge the experiments and the model performance. The authors should present at least time series of MT, NO₃ (N₂O₅) and O₃. On top it would be helpful to see a few characteristic oxidation products in comparison to model species. Question: what fraction of MT reacted until the first heating step? (I guess most of MT was reacted).

We included a time series of monoterpenes (which react quickly and fully within ~15 minutes), RO₂ radical sums, N₂O₅, NO₃ and NO₂ for all model simulations in Fig. S12. There is little to no ozone produced in these dark experiments. The model does not include explicit organic species that we could compare characteristic oxidation products to.

It would be also interesting to see model results, e.g. how nitrated and non-nitrated components evolve in time in gas and particulate phase. In general, more plots like Fig. S4.

We agree with this good feedback. Figs. 2 and 3 now show a full time evolution of monomer, oligomer and dimer concentration. We added several plots to the Supplement that highlight different aspects of the model results. Fig. S6 shows the mass concentration of unsaturated compounds (i.e., containing a double bond) in the particle phase. Fig. S8 compares organic mass concentrations on particles with gas phase and chamber wall. Fig. S14 distinguishes oxidation products by precursor origin. Fig. S15 shows a breakdown of products species into non-nitrated, mononitrated and dinitrated species.

A second concern considers wall deposition and heating: given the loss rate of 0.12h⁻¹, about 2/3 of the material in the limonene experiment should have been subject to wall deposition before heating; somewhat less in the case of α-pinene and the mixed experiments. Is it really sure that none of material does come back when the chamber is heated to 25° and 42° and affects the SOA behavior? Is there any experimental prove for that?

The referee raised a good point and in retrospective, our original vapor wall loss scheme was too simple for this kind of model. In our test experiments leading up to the chamber campaign used for this manuscript, we did not see re-partitioning of organic mass to particles when cooling and took this as justification to treat all vapor wall loss irreversibly. Heating to 25 °C and 42 °C, however, causes many semi-volatile molecules to re-volatilize from the chamber wall and significantly slow down volatilization from the particles (cf. new Fig. S8). Hence, we now adopted the two-step reversible + irreversible vapor wall loss scheme from Huang et al. (2018) and re-fitted all model results.

Furthermore, I understand that the SOA mass presented is wall loss corrected (line 155)? How is this considered in the model analysis? Wall loss correction is important for the determination of the mass yield of course. However, the chemistry can only happen in the SOA-particles as they are available in real in the system (or at the walls).

The SOA mass data is particle wall loss corrected and the model is then operated without particle wall loss. This constitutes a simplification, which should hold as long as particle wall loss is much smaller than vapor wall loss. Regarding particle phase chemistry and deposition on walls: since oligomerization is rather quick and oligomers have low volatility, we do not expect much of deposited material to go back into the chamber, but this might be something to consider in future studies.

I don't want to hurt the authors and I don't want to diminish their efforts, but without showing more comparisons of observations and model predictions along the lines above, their approach remains somewhat too speculative. The manuscript as it is now has a taste of "just playing with parameters", - despite the interesting onsets. From these points of view, the paper needs more work and I don't think the manuscript is suited in the current form for publication ACP. I suggest to reject the manuscript, however with the offer that the authors should re-submit an extended version.

The impression of reviewer #1 is understandable when this manuscript is seen as attempt at solving the entire α -pinene / limonene + NO₃ reaction system, which was not achieved in this initial modelling study that focuses on establishment of the model as a tool to interpret chamber data. However, and as outlined in detail above, there is a lot that the model presented in this manuscript is capable of besides "playing with parameters" and already inferred from a very limited set of training data. Together with our more careful presentation of mechanistic conclusions in the revised manuscript, we hope that the reviewer now more clearly sees the benefit of this publication for the Atmospheric Chemistry and Physics community.

Minor:

line 535: I understood, the method is prone to prevent getting stuck in local minima?

Yes, the method as such is much better at this as e.g. a hill-climber algorithm that just runs into the next local minimum. There is still no guarantee that the global minimum is found with a finite amount of sampling time with the MCGA algorithm. However, it would find the global minimum with an infinite amount of sampling time (opposed to hill-climber algorithms). We expand on this issue now in the manuscript:

"Multiple evaluations of MCGA typically give similar results to fit 1, but sometimes get stuck in local minima that are significantly worse. This is a direct consequence of undersampling with MCGA, given the large amount of model input parameters. Typically, about 150000 parameter sets were sampled during a MCGA run, which is not sufficient given the number of input parameters, but marks an upper

achievable range for this study as it takes about three days to complete on an 80 CPU computer cluster.”

In Figure 2. Wouldn't it be natural to show the volatility distribution at the maximum, just before heating?

Good point, Figs. 2 and 3 now show the volatility distribution at peak SOA mass.

Figure 5: Figure title should be "+ NO₃"(?)

Yes, absolutely. Corrected.

Author's Response to Referee #2

Summary:

This is an ambitious and creative modeling study with some great ideas. The model optimization methodology seems like a valuable tool to bring to the community.

We thank referee #2 very much for their time, detailed and thoughtful comments and helpful suggestions. Their feedback was very valuable to improve our manuscript. In the following, we will provide point-by-point responses.

The ground-truthing of the model-tuned variables is lacking, however, which is troubling given the huge parameter space that perhaps could have given many different solutions. There are also some experimental choices (same aerosol mass rather than precursor) that could heavily influence the conclusions drawn, so more testing of this model across other variables, e.g. different aerosol mass, same precursor concentration space, would be valuable.

We agree with referee #2. Adding more experiments to the pool of training data will considerably narrow down the uncertainty in conclusions of this paper and is a strong motivation for further studies. For now, we would like to keep this already extensive study within its current scope as a proof-of-principle study establishing the methodology. For comments on aerosol and precursor mass, see points 4 and 31 below.

I'm torn on whether the authors should just be clearer that this is an example of how one can approach these questions and play down the mechanistic conclusions, or whether they really need to do a bit more work to bolster those conclusions before anything should be published.

As outlined in the beginning of this response to referees, we have toned down the mechanistic conclusions of the manuscript when appropriate. We also worked on clarifying what conclusions the model allows (and there are quite a few of them) and which are rather clues into a certain direction.

Major comments:

1) The model has a LOT of tunable parameters. In several places I think you could bolster some of the model-derived parameters by comparison to other literature, e.g., is this degree of temperature dependence reasonable? Does it make sense for oligomerization to be an order of magnitude faster for one terpene than another? Seeking some more literature fixed points to justify elements of this "fully optimized" parameter hyperspace could give more confidence in the conclusions.

We agree with referee #2 that the number of tunable parameters stands in mismatch with the breadth and depth of the training data set. In this study, we aim to provide a proof of concept example on how the kinetic model can be used to interpret chamber data. We show in this proof of concept that oligomerization mechanics explain much of the specific, non-linear features of the experimental data, but alone cannot fully explain the evaporation of monoterpene SOA mixtures. More measurements (e.g., different chamber conditions), more data (e.g., viscosity etc.), and better exploration of the model parameter space with larger computational resources will allow for continual development and improvement of the model in the future, to fully constrain and capture all important aerosol properties and characteristics.

We address this point now extensively in the conclusion section:

“While there is significance to the general conclusions drawn from the model analysis, the individual model parameters that are returned by the inverse modelling approach must be treated with caution and evaluated in the context of the model and experimental data that are employed. Given the large number of fitting parameters and the limited number of experimental data sets, it cannot be insured that a true and correct global minimum is obtained in this isolated case study. [...] For example, Fig. S5 shows an estimate of the uncertainty in the volatility distributions obtained in this study. The error bars in Fig. S5 are standard deviations of individual re-fits of volatility distributions that all lead to a similar calculation outcome and hence quantify their uniqueness (or lack thereof). Figs. S1, S9, S10, and S11 show sensitivity case studies of very influential model parameters and Table 1 shows a local sensitivity analysis of the remaining input parameters, which gives an impression of their range within a single model fit. However, the true parameter ranges can be much larger if the model solution space encompasses different kinetic regimes. The uniqueness of the obtained parameter set can be enhanced by inclusion of more experimental data at different conditions or by a priori determination of model parameters such as measurements of volatility distributions, oligomerization degrees or particle viscosities, which will be an imperative task in follow-up studies. However, despite the remaining uncertainties in derived model parameters, the modelling suite presented here constitutes a step forward in the computational, data-driven evaluation of SOA formation with kinetic models.”

For the comment on T-dependence, please see point 7 below. For the comment on oligomerization rates, please see point 29 below.

2) It seems to me your choices of weight parameters could be highly influential in your conclusions. You mention towards the end some caveats about there existing “extended areas” on the optimization surface with minimal values. Can you pare down the model parameter space by constraining a few to better insure a unique solution that can be trusted to truly be a global minimum?

The referee is right in that the choice of weighting coefficients has an effect on the obtained model fit. As discussed in the response to referee #1 (minor point 2) above and in the response to referee #2’s point 3, 5 and 33 below, it is in general very difficult to obtain a singular fit to the data (multiple days of computation), so it is hard to show the variation by multiple fits. It is important to note, however, that while many fits with different parameter combinations can be found, their overall behavior is often very similar.

Please see also our comments in the next point.

3) Related Q: on line 241-242, you motivate choosing one fit to all the data as “defacto fit”. To address the concerns above, might it not be helpful to at least show a few limiting cases, where some pieces are constrained somehow. Or, show how universal the results by using different weightings w_i and seeing how different the results are?

The revised manuscript shows two “classes” of fits that were obtained from global optimization to show the range of results we typically get from optimization. While fit 2 was a lucky coincidence in that the local minimum that was obtained had a great correlation to the α -pinene SOA mass that was lacking in fit 1, other optimization results we obtained looked very similar to fit 1. Note that both fits behave fairly similar for most of the experimental data set. The fits differ in the way α -pinene SOA formation is described, either using high or low oligomer content. As discussed above, it is in general very difficult to obtain a singular fit to the data (multiple days of computation), so it is hard to show the variation by multiple fits.

Table 1, Fig. S5 and Table S2 are an attempt at showing the variability of parameters. We changed our discussion of the employed fits in Sect. 2:

“In the following sections, only one fit of the model to experimental data will be discussed as de-facto fit as it scored best in our choice of model-experiment correlation estimator.”

Now reads:

“In the following sections, we focus our discussion on one fit of the model to experimental data as it scored best in our choice of model-experiment correlation estimator (“fit 1”, $f = 0.88$ according to Eq. (9)). Multiple evaluations of MCGA typically give similar results to fit 1, but sometimes get stuck in local minima that are significantly worse. This is a direct consequence of undersampling with MCGA, given the large amount of model input parameters. Typically, about 150000 parameter sets were sampled during a MCGA run, which is not sufficient given the number of input parameters, but marks an upper achievable range for this study as it takes about three days to complete on an 80 CPU computer cluster. Among the inferior fits that were obtained, we also found a distinct fit that scores worse overall (“fit 2”, $f = 0.097$), but scores better in some aspects of the data set and will be discussed alongside fit 1.”

It is important to note that we believe that no combination of weighting coefficients would return a fit that consolidates the evaporation behavior of pure and mixed precursor experiments as the model has simply no means of doing so. We added a discussion of this point in Sect. 3.3.2:

“We note that, while peak mass does not coincide between model and experiment for the MIX and SEQ experiment, it is possible to obtain model fits in which this is the case. It is however not possible to match both, the peak mass and the experimentally-observed evaporation pattern. Slight overestimation of peak mass in the fits at hand can hence be seen as a consequence of the optimization algorithm trying to minimize the least squares error when in reality the evaporation pattern could not be reproduced.”

4) While I understand the motivation to run experiments at the same total mass loading, it seems to me that the fact that this means dramatically different terpene precursor concentrations could skew your conclusions. For example, you observe greater dimer formation in α -pinene not because of distinction between those systems’ favored mechanistic routes, but rather simply because the [RO₂] is higher, making that rate faster. Were the [NO₃] also scaled up? I think this could complicate the pictures and possibly lead to unnatural conclusions about preferred product routes across different terpenes. Could you / did you also do a set where the precursor concentrations are the same and the aerosol masses different, and include those experiments in the training dataset for the model?

The referee is right that incorporation of the experiments would be highly valuable. The referee is also correct about dimers being a consequence of precursor concentration. NO₃ was scaled accordingly in the experiments, which should keep the RO₂ + RO₂ channel in check.

For comparing pure precursor experiments, both ways of conducting these experiments seem valuable. Due to limited time and resources, we decided to probe the “same point on the SOA yield curve”, which probes the volatility distributions in the same way and is hence favorable when comparing evaporation rates. Measurements at same precursor concentration would also be valuable. We are planning to use a much larger data set in a more comprehensive follow-up study, but would like to establish the methodology first in the community.

Furthermore, to compare the effect of pure and mixed precursor experiments, we chose experimental conditions that create an about even amount of SOA from both precursors as otherwise the mixed precursor experiments might be simply dominated by limonene SOA.

5) You mention in a few places deriving the aerosol model structure from KM-GAP which is fundamentally a multi-layer model, while I understand that your model is a single well-mixed layer, which is why you couldn't directly probe mass transfer limitations. Are these mentions perhaps relics of an earlier draft of this manuscript that included different modeling? Or am I misunderstanding, and it is something else about the KM-GAP structure than you adopted? Regardless, this is confusing and should be rewritten.

The referee is right, this was confusing. The model is inherently a multi-layer model, but for most calculations in this paper, we ran it with a single bulk layer. The model is inherently capable of simulating mass transfer limitations (as showcased in Fig. 5), but the computational cost is so restrictive that it goes beyond the scope of this paper. We clarified this in Sect. 2.2:

“Note that in this study only a single well-mixed layer is used to describe the aerosol phase.”

Now reads:

“Note that, while the employed model is inherently a multi-layer model, only a single well-mixed layer is used to describe the aerosol phase in the default calculations in this study. Multiple layers were used for the calculations in Sect. 3.5.3 leading to Fig. 6.”

Furthermore, the word “multi-layer” is now avoided in Sect. 4.

6) On the temperature dependences of yield, Paragraph lines 293-301: I think I generally get what you're getting at, but I think the wording is confusing or something may be mixed up. I'll summarize my understanding to help you check whether your correct message is getting through: at higher temperatures, oligomerization is faster, so oligo formation outcompetes semivolatiles repartitioning back to the gas phase and then going to the walls, resulting in larger SOA yields. If this is accurate, the last line (301) looks backwards to me – it should be that the fractional amount that re-evaporates and goes to the wall is smaller, not the fraction that “partitions to the particle phase” is smaller.

We agree with the referee that this paragraph was not formulated clearly enough. We are making two points here and it is important to note that we are talking about the 100 and 1000 $\mu\text{g}/\text{m}^3$ volatility bins. These compounds are to more than 50 % in the gas phase in our experiment.

1. Point 1 is about higher yields at 25 °C compared to 5 °C. The referee understood this correctly: faster oligomer formation at 25 °C outcompetes re-partitioning and subsequent irreversible wall loss, whereas at 5 °C wall loss may dominate.
2. Point 2 is about the observation that oligomer formation at 42 °C is lower than oligomer retention at 42 °C. Even though the oligomer formation rate might be faster, the semi-volatile vapors do not partition into the particle phase in the first place.

We made this distinction clearer in the revised manuscript and expanded this discussion. We re-wrote these paragraphs and moved them to the end of Sect. 3.1.2:

“The results obtained in this study can be compared to and used to interpret results in the previous study by Boyd et al. (2017). In this study, SOA yield at 5 °C is with 130 % significantly lower than the yield of 173”

% reported in Boyd et al. (2017) at 25 °C, which is not in line with equilibrium partitioning theory. A potential explanation could be the temperature dependence of the oligomerization rate coefficient. As the model calculations highlight, condensation of vapors onto the suspended particles stands in competition with loss to the chamber walls, which should not be strongly temperature-dependent. When oligomerization occurs more slowly, oxidation products from higher volatility bins are increasingly lost to the walls before they can be incorporated into the particle oligomer phase. This is confirmed by a sensitivity study that shows a strong influence of oligomer formation rate $k_{form,lim}$ on model output (Fig. S11). In addition to temperature dependence of the rate coefficient itself, the oligomerization turnover might be effectively depressed by a semi-solid phase state at 5 °C as discussed in Sect. 3.5.3.

Another observation in Boyd et al. (2017) was a lower aerosol mass when directly forming limonene SOA at 40 °C compared to first forming limonene SOA at 25 °C and then heating to 40 °C. This observation could also be explained by the successive condensation and oligomerization of semi-volatile vapors suggested by the model in this study. The fraction of chemical species from the higher volatility bins that partitions into the particle phase is much smaller at 40 °C compared to 25 °C. This may prevent the additional slow mass accumulation through oligomerization of semi-volatile oxidation products at 40 °C and result in a lower SOA yield.”

7) Related to the above: what is known about T-dependence of oligomerization rates? Is this amount of SOA yield shift reasonable given anything we know about these rates? Put another way – this model is purely tuned to match your observations, so can we ground-truth the sensibility of this much of a T-dependence?

Please note that the “forward” oligomerization rate was not treated as temperature dependent in the model. We only have T-dependence in the back reaction, so we at least have one handle on the equilibrium oligomer content as temperature increases, while not using too many fitting parameters. We believe to know too little about the T-dependence of equilibrium oligomer content in SOA to make an informed guess on the valid ranges. Kristensen et al. (2017) report a lower ester dimer fraction of SOA formed from α -pinene ozonolysis at 258 K than at 293 K, whereas Huang et al. (2018a) observe the opposite in the same VOC-oxidation system. Nevertheless, we will try to narrow down the range of this parameter in future studies when more experimental constraints are available. Also note that the very high value of $E_{A,decom}$ of 795 kJ/mol for α -pinene given in this study (Table 1) is very poorly constrained due to the small amount of oligomers in the pure α -pinene simulation (fit 1), but we think that the values given for limonene in the range of 100 – 200 kJ/mol might be realistic. A sensitivity study of $E_{A,decom}$ is shown in Fig. S11 in the Supplement showing that it is not too influential in the investigated range.

8) Table 1: so many parameters! Some questions: Don't the k 's and E_A 's on the bottom 4 lines duplicate one another? Why no apin versions of pvap,IM1 & pvap,IM2. And again, I worry that the widely varying c_3 's for apin and limo reflect the kinetics more than the branching ratio, which would be the conclusion one could reach from just looking at this table.

We agree that this model has a lot of flexible parameters and hope we will be able to constrain them better as the model sees more training data. As you can see from our responses here, we tried to reduce the amount of parameters to the absolute minimum for this very first publication of our work. Regarding the specific points:

- The k 's are the rate coefficients and the E_A 's are the activation energies in the Arrhenius equation to account for the temperature-dependence of the decomposition k 's.

- There are no α -pinene versions of $p_{\text{vap,IM1}}$ and $p_{\text{vap,IM2}}$ because α -pinene does not have a second double bond and thus not a potentially stable intermediate. All vapor pressures of α -pinene products are accounted for with the 2x6 volatility bins.

- The branching ratios c_3 and c_4 determine how much nitrated vs. non-nitrated products are produced. Such a mechanistic possibility is needed as an attack of NO_3 to a double bond creates a nitrated product. Depending on the stability of the RO_2/RO radical, the nitrate group is retained or lost. The volatility distributions on the other hand decide about what happens with the nitrated vs. non-nitrated products once produced. Therefore, while these parameters cannot be uniquely determined with a small parameter set, we think that they are in principal orthogonal enough to be distinguished given enough training data.

9) Fig. 5: It looks like the T dep is wrong, because it doesn't capture the slope difference between 25C and 40C for any choice of Db. How did you pick $\Delta(H)$?

Fig. 5 has been replaced in the revised manuscript, but the referee had a good point. Due to the lack of literature values, the $\Delta H = 50 \text{ kJ/mol}$ for diffusion is poorly constrained. For simplification, our sensitivity tests in this manuscript are solely focusing on the diffusion coefficient as a single parameter affecting mass transport rates.

10) Line 315: wouldn't the accommodation coefficient be heavily structure dependent, different for dimers and monomers, for example? Given the difference in gas-phase composition between apin and limo, this could be an important variable.

The referee is right. The mass accommodation coefficient should not only depend on molecular structure of the impinging molecule, but also on phase state of the surface. In the interest of reducing model fit parameters, this was not considered in the current iteration of the model. In the original model calculation, the accommodation coefficient was not a sensitive model parameter since there was no strong competition with the chamber walls. This is corrected in the new version of the model with the implementation of the reversible vapor wall loss terms, but the accommodation coefficient remains fixed to 0.5 for simplicity. A sensitivity study of the influence of the accommodation coefficient is shown in new Fig. S1.

11) Figure 6: why does the ON content variable seem to be more constrained to the limonene case than α -pinene? Same weights on both precursors, right? Just lower on all ON content?

We assume the referee is referring to $p_{\text{ON/OA}}$ in the pure limonene (LIM) and the pure α -pinene (APN) experiment. Both pure precursor experiments were weighted equally.

In the original model calculations, the complex time dependence of the APN experiment could not be reproduced since both previously presented model fits had high oligomer contents. Since the model does not distinguish between the decomposition rates of nitrated and non-nitrated oligomer building blocks, a strongly varying $p_{\text{ON/OA}}$ could not be realized. With the updated model in the revision of this manuscript, the best fit shows perfect resemblance to the experimental $p_{\text{ON/OA}}$ in the APN experiment. This is due to a low oligomer content. $p_{\text{ON/OA}}$ can easily be modulated in the model by constraining the volatility

distributions of nitrated and non-nitrate oxidation products. This is now explained in the manuscript as follows:

“The best fit model run (solid blue line) captures the ON content very well. As Fig. 3b highlights, the model suggests the higher-volatility monomers to be non-nitrated and the lower-volatility monomers to be nitrated, which causes the distinct trend of pON/OA. The alternative model run (dotted blue line), however, fails to capture the ON time dependence. This is due to the high oligomer content of fit 2 and due to the model not distinguishing between nitrated oligomer and non-nitrated oligomer decomposition rates. Hence, while the oligomer-heavy fit 2 shows a better correlation to a-pinene SOA mass, it fails at describing pON/OA.”

Minor / technical suggestions and edits:

1) Line 23 “could be due to kinetic limitations”

This specific text in the abstract has changed.

2) Line 37 suggest to edit to “results in high yields of various nitrated organic compounds. . .” (since you don’t speciate ONs)

Done.

3) Line 41: “(NO_x = NO + NO₂)”. And suggest to remove the last line of that paragraph, again because not really relevant to this paper.

Done.

4) Line 60 – isn’t this clearly because MCM is (knowingly!) missing a lot of NO₃ chemistry?

The referee is correct. We edited this sentence in the text:

“However, application of MCM to the oxidation of monoterpenes with NO₃ leads to a significant underestimation of particle mass and pON/OA as this mechanism is missing several important chemical reactions, for example, oxidation of the second double bond of limonene is missing completely in MCM (Boyd et al., 2017; Faxon et al., 2018).”

5) Line 62: “might alter evaporation barrier”

We respectfully disagree with the referee and would like to keep the term “evaporation behavior”, describing the behavior of particles regarding mass loss over time.

6) Line 65: “kinetic limitations to evaporation (Vaden et al 2011), slowing of particlephase”

Done.

7) Line 74: “to the best of our knowledge, no model has yet been presented”

Done.

8) Line 93: “can accurately describe the observed formation and evaporation”

Done.

9) Line 133: “in under 4 hours, the chamber enclosure”

Done.

10) Line 139: “SEQ experiment, following peak growth after the first precursor oxidation, a second NO₃/N₂O₅ injection and injection of the second VOC follow in sequence.”

The sentence now reads:

“In case of the SEQ experiment, peak SOA mass after the first precursor oxidation is awaited. Then, a second NO₃/N₂O₅ injection and injection of the second VOC follow in sequence.”

11) Line 155 “chemical reactions in the gas”

Done.

12) Around Eq. 2: add mention of units for [], to help reader make sense of the N_A factor

Added: “(in unit cm⁻³)”

13) Around line 193: motivate why this many volatility bins, and why this odd spacing.

We expanded on the motivation of the chosen volatility bins.

“The six volatility bins employed in this study are chosen to have increased resolution and hence achieve maximum sensitivity around the experimental range of 10 – 100 µg/m³, but still cover a wider range of volatilities.”

Now reads:

“To minimize the number of model parameters, six volatility bins are chosen with higher resolution and around the experimental range (1 – 1000 µg/m³) to achieve high sensitivity. To also cover a wide range of volatilities, a very low volatility and a very high volatility bin are included at the ends of the spectrum”.

14) Around Fig. 1: you mention limonene’s second double bond enabling addition nitrate addition, but I don’t think you ever mention how much of the 2nd double bond oxidizes in your models – is it substantial? Maybe mention here or around your Fig. S1 that shows the limonene scheme.

The 2nd double bond of limonene is mostly oxidized in the model. This is mentioned in the text when discussing model results:

“At peak SOA mass, 33 % of oxidation products still contain a double bond in this model run, all of which are nitrated and present as oligomers.”

There is also a figure in the supplement highlighting this (Fig. S4).

15) Line 198: missing space “publications (Berkmeier”

Done.

16) Line 217: remind us that Z refers to the MT precursor

Added: “of precursor Z”

17) Line 281: big difference in C*s! how are these separated, and how much confidence do you have in these numbers? Really 3 sig figs?

Both C* of mono-unsaturated limonene oxidation products are model fit parameters. The ball park of these numbers was initially constrained using the EVAPORATION vapor pressure estimation tool (Compernelle et al., 2011) on several of the first products that show up in MCM, which all showed vapor pressures around 1e-7 to 1e-5 atm, which corresponds to C* values of 1e3 to 1e5 at 298 K.

The non-nitrated intermediate is almost fully volatile at such high C* and the exact numerical value hence poorly constrained (cf. Table 1). For the nitrated intermediate, we believe that there is significance to the fitted number. Nevertheless, we reduced the significant digits to 2. For clarification, we added the following sentence:

“This means that the non-nitrated intermediate is fully volatile and the non-nitrated intermediate partitions to some extent into the particle phase.”

18) Line 283: why don't you consider oxidation of 2nd double bond in the particle phase? Do you think this won't happen, or it's just a detail not included in this model?

This choice was made to try to minimize model complexity and reduce optimization parameters. We intent to add heterogeneous oxidation chemistry in future studies.

19) Line 285: “model runs occupy the”

Done.

20) Line 290: when you say “peak growth” here it makes me think the maximum slope of the curve, but I think you mean peak mass.

The referee is correct, we changed “peak growth” to “peak (SOA) mass” here and in several other places to prevent confusion of the peak of the mass curve with the point of maximal slope of the mass curve.

21) Line 294: “potential explanation”

Done.

22) Line 305: at what time was this reference decomposition rate range measured?

D'Ambro et al. determined decomposition rates after formation and in the absence of both organic vapors and oxidants.

23) Line 319: “falls in between”

Done.

24) Line 327: “is reached after 3 hours”

Done.

25) Line 328: “SOA yield (25%) is significantly”

Done.

26) Line 335: I don't see a temperature plateau in the observations at all.

Chamber temperature is shown as grey dashed line and shows a distinct plateau (Fig. 3 in the original and revised manuscript).

27) Line 344: "57% of monomers, 33% oligomers and 11% gas-phase"

Done.

28) Lines 353-355: I don't understand this claim about this being a reason for higher yields with O₃ and OH. Those product mixes would be totally different. Suggest to omit this sentence.

Done.

29) Line 356: structurally, why would it be that apin has an order of magnitude faster oligomerization rate than limonene? Is this reasonable?

The referee raised a good point. An order of magnitude higher oligomerization rate of α -pinene does not seem very logical. This is partly because the oligomerization and oligomer decomposition rates can often not be uniquely defined as equilibrium oligomer content is determined by their ratio. On the other hand, this could have been a consequence of not treating phase state: if limonene SOA were more viscous, the apparent oligomerization rate would be much lower than the real rate. We added this thought to Sect. 3.5.3.:

"In addition to temperature-dependence of the rate coefficient itself, the oligomerization rate might also be effectively depressed by a semi-solid phase state at 5 °C (cf. Sect. 3.5.3)."

In principal, we would expect that limonene products oligomerize faster as every limonene molecule contains more functional groups that could undergo some sort of condensation or other accretion reaction. This is the case in the new fit 1 presented in the revision of the manuscript, in which limonene products oligomerize at a rate of 17.2 h⁻¹ and α -pinene products oligomerize at a rate of only 0.12 h⁻¹. In fit 2, oligomerization rates for limonene and α -pinene products are very similar at 9.0 h⁻¹ and 7.1 h⁻¹, respectively (Table S2).

30) Fig 4: suggest to briefly explain solid & dashed modeled differences in caption

Good suggestion, the differences in different model runs is now explained in the figure legend of our new iteration of Fig. 4.

31) Around line 381: Isn't this simply because there's higher apin precursor concentration, so the overall kinetics are faster? This seems to be an inappropriate comparison to make since the precursor concentrations were different. Also this made me wonder: were the levels of NO₃ also different across the 2 experiments? Should mention someplace.

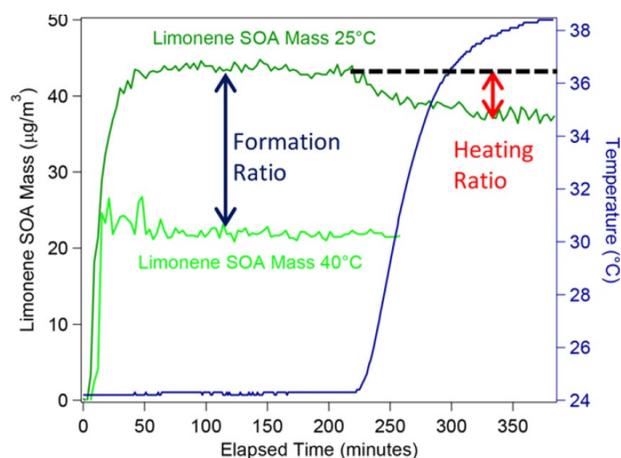
This is an interesting point the referee is making. While the reaction rate of NO₃ with precursor is about 2-times higher for limonene than for α -pinene (according to MCM), the overall reaction flux should be inherently much larger for α -pinene at much higher concentrations. However, the limonene concentration reaches zero 15 minutes after start of the injection period, which is a much shorter time span than the one observed for increase of SOA mass.

We added this point in the manuscript:

“This might be due to slow formation of oligomers, but also simply because the lower amount of limonene precursor and proportionately lower injected NO₃ leads to a longer reaction time. However, the modelled reaction times for α -pinene and limonene to reach 5 % of their initial concentration after precursor injection were both about 15 minutes (cf. Fig. S12), which is a short time frame in comparison to the slow increase of limonene mass.”

Please also see our response to the referee’s point 4, where we justify our choice of doing experiments at constant mass load instead of constant precursor concentrations.

Of note, Boyd et al. (2017) did not see a slow increase of limonene SOA mass at 25 °C and at similar precursor and NO₃ concentrations (the Figure below is taken from Boyd et al).



Regarding NO₃ concentration, input N₂O₅ was always scaled with precursor concentration and used as a 4-fold excess of number of double bonds (i.e. 4-times excess for α -pinene, 8-time excess for limonene). This is mentioned at the end of Sect. 2.1 in the original manuscript:

“An 8-fold excess of N₂O₅ is used for pure limonene experiments, and a 4-fold excess used for pure α -pinene experiments.”

32) Line 386: “both MIX and SEQ experiments” (spurious commas)

Added commas: “... both, MIX and SEQ experiments, ...”

33) Around line 392 is where I started to think the weights are really important here, and wanted to see model runs with different weights.

We fully agree with the referee that a systematic exploration on the effect of data set weights would be very desirable. However, every fit is obtained after multiple days of optimization on an 80 CPU computer cluster, which makes it prohibitive to generate a large quantity of fits. By focusing weights on pure precursor experiments, we make sure that any non-linearity in the mixed precursor experiments is detected as a deviation between model and experiment. We added the following paragraph to Sect. 2.4.

“In this study, pure precursor experiments are each weighted twice as high as the mixed precursor experiments to ensure that any non-linearity in the mixed precursor experiments is detected as a deviation between model and experiment for those experiments. pON/OA data is weighted by a factor of 4 lower

than SOA mass data as the focus of this paper is the formation and evaporation behavior of SOA and more assumptions go into the determination of pON/OA.”

For our justification of the reduced weights of pON/OA, see also the response to point 37.

34) Line 435: is there no RO₂ from the first precursor reaction left? Or possibly some residual limonene that can be oxidized by the next NO₃ injection?

While there is still 20 % of initial N₂O₅ left, there is virtually no α -pinene precursor left at the 2nd N₂O₅ injection. According to the model, α -pinene RO₂ levels are down to about 12 % at the limonene precursor injection and 10 % of their peak concentrations at the second injection of N₂O₅. The overlap should thus be rather small. We added a figure to the supplement that shows concentrations of important gas molecules (Fig. S12).

35) In Figure 5 caption: Eq. 5 is not Stokes-Einstein

Done.

36) Line 530: “state of the product bin”

Done.

37) Lines 534-537: It’s not clear to me why the model doesn’t capture the ON content trends. Unless you’re just saying it’s because you told the model not to try too hard with your low weights? If you weight pON/OA higher does it get the trend?

The referee is correct that it was not possible to perfectly match pON/OA. Especially the magnitude of pON/OA comes out too high in the MIX experiment usually and too low the SEQ experiment, while the shape of the curves is reproduced well overall. While this could be a shortcoming of the model, it could also be uncertainty in the experimental determination of pON/OA. We expanded the discussion in the manuscript:

“The unexpectedly low ON content in the MIX experiment points either towards non-linear effects in chemistry that are not captured by the model or towards uncertainties in the pON/OA measurements. For the latter, there are two major sources of uncertainty. First, a default value of relative ionization efficiency (RIE) of 1.1 is used for AMS nitrate in this study (Canagaratna et al., 2007). This value is typically associated with inorganic nitrate as the RIE of nitrate derived from pON has not yet been experimentally measured to the knowledge of the authors. It is thus not clear how this value depends on chemical composition or if exposure to higher temperature may lead to variation of RIE over the course of an experiment. Second, a constant molecular weight of pON (250 g/mol) is assumed for calculation of pON/OA. However, it is possible that changes in chemical composition result in changes of the average molecular weight during an experiment.”

This inability of getting a good fit caused some problems in the optimization process. At equal weightings, the SOA mass data was fit considerably worse in order to make the pON/OA fit better. Since no assumptions were made in obtaining the SMPS mass data but several assumptions were made when calculating pON/OA from AMS measurement, we picked the 4:1 weighting ratio and obtained good results.

38) Line 547: “increase of pON/OA (until the highest temperature”

Done.

39) Line 560: thermal decomposition of nitrates is not in the model, right? Why not?

Correct. This choice was made to try to minimize model complexity and reduce optimization parameters. We intent to add thermal decomposition of nitrates in future studies.

40) Line 569-570 "These results" . . . is a nonsequitur. Suggest to omit?

Replaced by "The results".

41) Line 572: "global SOA burdens."

Done.

42) Line 573: kinetic multi layer model? I thought it was one well-mixed? See above comments. Also line 580-581 seems to refer to the depth resolution you didn't do here.

Please see response to point 5. The model is inherently a multi-layer model. When testing the effect of a semi-solid phase state on calculation results, which is referenced here, multiple model layers were employed.

Author's Response to Short Comment by Douglas Day

I offer some suggestions to improve the modeling in this study, as a few of the kinetic model input parameters and output results do not appear to be consistent with the state of the science.

We thank Douglas Day for the time he took to comment on our manuscript and the helpful comments he provided. His feedback was very valuable to improve our manuscript; in fact, we significantly overhauled the kinetic model in response to his comments. We will reply to each of the three points he raised separately.

1) Accommodation coefficient.

In the model description (Sect. 2.2), it is stated that an accommodation coefficient (α) of 0.1 for organic species was assumed for this study and references the paper Julin et al. (2013), which is a molecular dynamics simulation study of water vapor accommodation coefficients (and reports α of unity). Recent isothermal chamber (Krechmer et al., 2017; Liu et al., 2019) and flow reactor (Palm et al., 2016) studies, as well as molecular dynamics simulations (Julin et al., 2014) of accommodations coefficients for SOA-forming organic compounds into organic aerosols show values near unity for a wide range of compound functionalities, structures and volatility, as well as organic aerosol types. Therefore, I suggest that the authors use a more-relevant α value of unity (or near unity) for the modeling presented here. While other studies have shown lower values of α for organic molecules (e.g., references included in Fig. 3 in Liu et al. (2019)), those methods tended to be less direct, in many cases involve substantial heating, and/or contain limited information about the volatility of the compounds changing phase state, as compared to the Krechmer et al. (2017) and Liu et al. (2019) studies. If the authors feel that a range of α values should be considered for these modeling studies, then an approach that tests the sensitivity to the different values (including $\alpha=1$) could be implemented.

We agree that the chosen accommodation coefficient (α_s) of 0.1 underrepresents the values typically found for larger organic molecules on liquid organic surfaces (Julin et al., 2013). A recent paper by von Domaros et al. (2020) showed that the bulk accommodation coefficient for ozonolysis products of squalene on squalene ranges roughly from 0.1 and 1 and is closer to 1 for the larger molecules. We would like to raise two points justifying our choice and clarifying the impact of α_s on calculation outcome.

- (1) In our experiments, SOA formation occurred at 5 °C and phase state of particles might differ from phase state at room temperature, which in turn could cause α_s to be less than unity.
- (2) The results presented in the initial submission were insensitive to α_s in the range ~0.005-1 because vapor wall loss was slow and irreversible. The results presented in the revised manuscript are more sensitive to α as vapor wall loss had a fast and reversible as well as a slow irreversible component (see our response to point 2 below). We now used an accommodation coefficient of 0.5 in all model calculations and added a sensitivity study to the Supplement (Fig. S1). The sensitivity study shows that the effect of α_s is negligible between numerical values of 0.5 to 1, but gains importance at values lower than 0.5.

2) Irreversible loss of gas products to chamber walls.

It appears that reaction product gases are assumed to be irreversibly lost to the Teflon chamber walls (Sect. 3.1.2, lines 295, 304, 315). This aspect is only mentioned in the results sections, and not earlier in the model description, so it is not clear why the authors made this assumption. However, several studies

over the past decade have shown that gases partition reversibly to and from Teflon chamber walls, with a strong dependence on compound volatility (e.g., Matsunaga and Ziemann, 2010; Yeh and Ziemann, 2014, 2015; Zhang et al., 2015; Krechmer et al., 2016).

The volatility basis sets shown in this manuscript in Figs 2 and 3 show that a substantial fraction of compounds that participate in aerosol formation are at $c^* = 10, 100, 1000 \mu\text{g}/\text{m}^3$. Figure 4 in Krechmer et al. (2016) summarizes measured values of F_p (fraction of compound in gas-phase vs wall+gas) vs compound volatility, and shows that for $c^* = 10-1000$, large fractions, up to 20-100% (that are not in the aerosol) remain in the gas-phase. Therefore, I suggest that the authors consider implementing a more realistic parameterization of the gas-wall interactions based on current literature, or otherwise demonstrate that the assumption does not significantly affect their results.

We followed this suggestion and implemented the two-step vapor wall loss approach described in Huang et al. (2018b) into our model. Please find an extensive description on this approach in Sect. 2.2 of the revised manuscript. While this did not have a major impact on the quality of the model fit or the conclusions drawn, it had a significant impact on the obtained model parameters such as volatility distributions.

3) Gas-to-wall loss rate.

In Sect. 3.1.2 (lines 313-322), it is stated that a loss coefficient of gas-phase molecules to the chamber wall was determined to be equivalent to a loss timescale of 3.0×10^4 seconds (8.3 hours). This is an output of the modeling, it appears. The authors state that it falls in the range of values in the literature, citing the studies by Ziemann and colleagues (Yeh and Ziemann, 2015; Krechmer et al., 2016) who measured values of 1×10^3 s (0.27 hours) and those done in the CalTech chamber (3×10^4 to 5×10^5 s; 8.3-140 hours). However, a more recent experimental and modeling study by the CalTech group (Huang et al., 2018) concluded that the timescale relevant to the bulk equilibrium of gases with the surface layer of the chamber walls is rapid (1×10^3 s), in accordance with the Ziemann and colleagues studies — while the long time constants measured by the earlier CalTech studies, such as in Zhang et al. (2015), were more likely due to slower inner layer diffusion processes in the Teflon film (as the experimental timescales in those earlier CalTech studies were too slow to capture the fast bulk partitioning to the surface layer of the chamber walls). Such diffusion through the bulk Teflon is very slow and has little effect on typical chamber experiments. Additionally, another group has reported gas-to-wall rates similar to Ziemann and colleagues for a similar sized chamber (10 m³), as described in Ye et al. (2016) who reported a timescale of 0.26 hours (rate coefficient: $3.8 \pm 0.3 \text{ h}^{-1}$), as did Ziemann and colleagues in a somewhat larger chamber (20 m³) reported in Liu et al (2019) (rate coeff: $1.0 \times 10^{-3} \pm 20\% \text{ s}^{-1} \Rightarrow$ timescale 0.26 hours). Therefore it would be expected that for this experiment, where temperatures are changed relatively rapidly, effects of gas-wall partitioning on the bulk SOA measured would be dominated by the fast time ~ 10 -minute time constant. Therefore, it is concerning that the model results support a timescale that is 30 times slower for that process — and suggests that there is at least one other aspect of the modeling, related to some kinetic framework or input, that is very inconsistent with the system being modeled. I suggest that the authors constrain the wall loss timescale to be consistent with the literature, in order to improve the model representation of these experiments.

Please see our response to the previous point. Vapor wall loss is now fully implemented according to Huang et al. (2018b). By including the reversible wall loss terms, the fitted irreversible vapor wall loss

coefficient in this study is now very much in line with previous observations by other groups. Please see the new discussion in Sect. 3.1.2:

“The irreversible loss rate of wall-adsorbed molecules into the chamber wall is determined to be $I_{w,i} = 1.2 \times 10^{-4} \text{ s}^{-1}$, which is within the range of values reported as re-evaluation of literature data in Fig. 5 of Huang et al. (2018). Fig. S8 shows the distribution of organic molecules between wall, particle and gas phase in the model for all experiments conducted in this study. The dependence of model output on $I_{w,i}$ is explored in Fig. S9, indicating that the model output simulating the LIM experiment is more sensitive to changes in $I_{w,i}$ than the simulation of the APN experiment described below, which can be attributed to the slow uptake and oligomerization process of semi-volatile molecules that stands in competition with irreversible wall loss.”

Generally, as the manuscript is presented, it is difficult to predict (beyond some qualitative speculation) what the effects of these inputs / assumptions / and outputs have on or indicate about the main results presented for this study. Therefore, it would be very useful if sensitivity studies were conducted to help understand the dependencies and assess the robustness of the results presented (i.e. oligomerization rate constants and their contributions to the SOA, effects of particle diffusivity, volatility basis sets and organic nitrate evolution vs time).

We added the following sensitivity analyses to the Supplement:

Fig. S1 – Sensitivity runs of model fit 1 on the influence of the accommodation coefficient α_s on (a) the LIM experiment and (b) the APN experiment.

Fig. S9 – Sensitivity runs of model fit 1 on the influence of the irreversible wall loss coefficient $I_{w,i}$ on (a) the LIM experiment and (b) the APN experiment.

Fig. S10 - Sensitivity runs of model fit 1 on the influence of the effective enthalpy of vaporization ΔH_{vap} on (a) the LIM experiment and (b) the APN experiment.

Fig. S11 – Sensitivity runs of model fit 1 on the influence of (a) the activation energy of oligomer decomposition $E_{A,\text{decom},\text{lim}}$ and (b) the oligomer formation rate $k_{\text{form},\text{lim}}$ on the model simulation of the LIM experiment.

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