Atmospheric
Chemistry
and Physics
Discussions

Open Access

ACPD

Interactive
comment

Interactive comment on "Kinetic modelling of formation and evaporation of SOA from NO$_3$ oxidation of pure and mixed monoterpenes" *by* Thomas Berkemeier et al.

Anonymous Referee #1

Received and published: 26 February 2020

The authors describe a set of experiments of SOA formation from a-pinene, limonene and mixtures of both by oxidation with NO3 and their evaluation by model approach. The new experiments link to previous series of experiments of SOA formation with NO3 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) a-pinene and limonene were oxidized simultaneously and sequentially.

The experiments show distinct individual growth and evaporation behavior for limonene and a-pinene. The behavior in the mixtures is different in different ways, in any case

Discussion paper

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.

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.

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).

Printer-friendly version

Discussion paper

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 a-pinene curve (Fig 3a). 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-liearity, e.g. by betting so strongly on oligomerization? And that the three-fold lumping, gas-phase, VBS, liquid phase leads only individual solutions and has not much predictive power.

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.)

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).

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.

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 a-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?

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).

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.

Minor:

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

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

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

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-55, 2020.