

Interactive comment on “Kinetic modelling of formation and evaporation of SOA from NO₃ oxidation of pure and mixed monoterpenes” by Thomas Berkemeier et al.

Anonymous Referee #2

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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. 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. I'm torn on whether the authors should just be clearer

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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.

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.

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?

3) Related Q: on line 241-242, you motivate choosing one fit to all the data as “de-facto 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?

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 $[RO_2]$ is higher, making that rate faster. Were the $[NO_3]$ 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

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the aerosol masses different, and include those experiments in the training dataset for the model?

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.

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.

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?

8) Table 1: so many parameters! Some questions: Don't the k's and EA'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 c3'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.

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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)?

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.

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

Minor / technical suggestions and edits:

1) Line 23 "could be due to kinetic limitations"

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

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.

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

5) Line 62: "might alter evaporation barrier"

6) Line 65: "kinetic limitations to evaporation (Vaden et al 2011), slowing of particle-phase"

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

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

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

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 se-

quence.”

11) Line 155 “chemical reactions in the gas”

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

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

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.

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

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

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?

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?

19) Line 285: “model runs occupy the”

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.

21) Line 294: “potential explanation”

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

23) Line 319: “falls in between”

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

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

- 26) Line 335: I don't see a temperature plateau in the observations at all.
- 27) Line 344: "57% of monomers, 33% oligomers and 11% gas-phase"
- 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.
- 29) Line 356: structurally, why would it be that apin has an order of magnitude faster oligomerization rate than limonene? Is this reasonable?
- 30) Fig 4: suggest to briefly explain solid & dashed modeled differences in caption
- 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.
- 32) Line 386: "both MIX and SEQ experiments" (spurious commas)
- 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.
- 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?
- 35) In Figure 5 caption: Eq. 5 is not Stokes-Einstein
- 36) Line 530: "state of the product bin"
- 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?
- 38) Line 547: "increase of pON/OA (until the highest temperature"

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

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

41) Line 572: “global SOA burdens.”

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.

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