

Response to the comments of Anonymous Referee #1

The authors have addressed many if not most of the issues I raised in my original review - but unfortunately the revision has introduced a number of new problematic issues. The overall readability of the manuscript is unfortunately still in places quite poor - especially the discussion of reaction mechanisms is extremely confused and confusing. (The introduction, in contrast, is substantially improved - thank you for that!) Substantial copy-editing, by someone who also understands the chemistry, is still needed before this can be published.

Response: We thank the reviewer for the positive evaluation to our last revision and the critical comments to the reaction mechanism discussion. Our point-by-point responses are shown in blue color as below.

Some major issues:

E.g. Line 239: "addition of oxygen atoms to the intermediate alkoxy radicals", this seems to imply some sort of $RO + O_3$ reactions going on, that would certainly be a major discovery for atmospheric science, but I see no evidence anywhere for anything like this. O_3 will attack the double bonds, but after that it plays no direct role in the oxidation - the repeated claims to the contrary would need much stronger evidence to be taken seriously. The observed $[O_3]$ dependent changes are very likely related to more indirect effects, including the effect of O_3 on NO_x and RO_2 levels (and thus the fate of RO_2), the production of OH (this is correctly identified in the manuscript), and of course for limonene the probability of both double bonds being attacked (also correctly identified, though discussed in a confusing manner). The discussion on how $[O_3]$ affects the reaction mechanisms (in this section and elsewhere) must be thoroughly amended to reflect what is actually known about atmospheric oxidation.

Response: Thank you. To elucidate the term "oxygen-increasing-reactions (OIR)" clearly, we changed the sentence "addition of oxygen atoms to the intermediate alkoxy radicals" to "producing new alkyl radicals through O_2 addition to an existing alkyl radical \rightarrow reaction between RO_2 radicals \rightarrow isomerization of the alkoxy radicals" (L240-241). We agree with that O_3 can influence the RO_2 level and have added this point in Line 239. However, NO_x is not used in this study. Thus, we do not suggest that indirect effect of O_3 on NO_x level plays an important role in the observed $[O_3]$ dependent changes.

E.g. on line 267, the statement "accelerated autoxidation by higher concentrations of ozone" seems to convey (though I note this may just be a language issue rather than a chemistry issue) a profound ignorance about what autoxidation actually is: it is oxidation driven solely by O_2 , where (by definition) no further oxidants are needed. Or in other words, O_3 only STARTS the autoxidation process, the $[O_3]$ concentration can by definition not accelerate (or decelerate) it. (Any effects must, as said above, be indirect, and relate e.g. to the fate of RO_2 as controlled by the concentrations of NO, other RO_2 , etc).

Response: Agree. We have changed the "indicating their faster conversion to high oxygen-containing organic molecules via accelerated autoxidation by higher concentrations of ozone" to

"indicating the preferred formation of high oxygen-containing organic molecules at higher concentrations of ozone, which may be associated with the indirectly accelerated autoxidation via O₃-augmented RO₂ levels etc. " (L269-270).

Line 279: "oxidative fragmentation by OH", while OH certainly plays a big role here, this is a bit confusing: isn't it rather the O₃ - oxidation which tends to drive fragmentation? Or does this refer to fragmentation via acing-type reactions, i.e. after attacks by more than one oxidant (e.g. an initial O₃ attack, and then OH oxidation of the subsequent products)? Please clarify.

Response: Thanks. We have clarified this sentence by changing it to "fragmentation of first-generation products and condensing compounds (Hallquist et al., 2009; Kroll et al., 2007; Zhao et al., 2015) " (L283-284).

-Line 292: "generate OH via hydroperoxide channel", this is wrong or at least misleading, OH is generated in the Criegee step (common to BOTH channels shown in e.g. their figure 10). Also, while ozonolysis of the exocyclic bond will certainly make more sCI, also the sCI will typically form OH as even the thermal reaction is quite quick (bimolecular reactions of sCIs CAN happen, but are usually not the major sink). Thus this overall discussion is somewhat confused and misleading.

Response: Thank you. We removed the " via hydroperoxide channel" to avoid confusion.

Line 376, "Alternatively": this is not an "alternative", this is the mechanistic detailed explanation for exactly the same channel that the authors have just discussed. Again, this discussion is very confused, and seems to be repeating essentially similar things many times, without realising that they are talking about the same thing.

Response: Thanks. We improved this part as follows (L378-384):

"The accretion products formed from self-combination or cross-reaction of RO₂ radicals has been proposed to be generally important in producing higher-functionalized RO₂ radicals, HOM dimers, and SOA via the following pathways (Berndt et al., 2018b; Bianchi et al., 2019; Kahnt et al., 2018; Ehn et al., 2014; Berndt et al., 2018a; Tomaz et al., 2021) :



Where the RO \cdots O₂ \cdots R'O means a cage structure intermediate formed from the asymmetric cleavage of tetroxide and eventually converts to ROOR' (Lee et al., 2016)".

Line 383: The Shi et al reference is unfortunately very unlikely to explain anything here, at least not in the gas phase: the rate coefficients corresponding to the energetics shown in that paper for

the RO₂ + alkene reactions are far too slow to yield any products (in the gas phase) at any reasonable concentrations (as can easily be verified e.g. using simple transition state theory as an upper limit to the rates). Note: the RO₂ + alkene energetics in that paper are likely more-or-less correct, it's just the conclusions that are not compatible even with their own numbers. And the single-reference methods employed therein cannot even begin to describe the actual RO₂ + R'O₂ reaction mechanism, so for those their barriers are of course completely off (actual multireference calculations, cited even by themselves, show that they are compatible with atmospheric observations). RO₂ + alkene might be playing a role in the liquid phase (along with a number of other better-known condensation reactions), but certainly not in the gas phase.

Response: Thanks. We have removed the discussions on reaction of RO₂ with alkene to avoid misleading.

Selected minor issues:

-use of the word "saturated" in the abstract: this is an extremely unfortunate word choice, as "saturation" can mean several different things even in this exact context (from the number of double bonds to the vapor pressure, to the levelling off that the authors apparently refer to). Please formulate more clearly what is meant here (presumably the levelling of with respect to the ozone concentration, or something similar). I realise that the authors may have picked the term "saturate" from my original comment - I apologise for that!

Response: Thank you. We changed "saturate" to "exhibit higher yield" (L20-21).

-Line 67: "bear" new particles - bear is not needed here ("undergo" is a decent verb also for NPF).

Response: Thanks. We have removed the "bear" to avoid redundancy (L68).

-Line 76: "redox functionalities": this doesn't mean anything. Reformulate

Response: Thank you. We have deleted this term to avoid confusion (L77).

-Line 242: "redox activity of SOA": meaningless

Response: We have changed "redox activity" to "the oxidative potentials" (L244).

-Line 249: "non-condensation reaction": what is meant by this?

Response: Thanks. We clarified this term by changing it to "non-condensation reactions that dominated by hemi-acetal reactions followed by hydroperoxide and Criegee radical reactions might play an important role in the limonene SOA formation" (L251).

-Line 254: "formula number of assignable organic molecules": I don't understand what is meant by this.

Response: We changed the term "assignable" to "identified" for clarification (L256).

Line 373, "oxidation degree of RO₂ termination": what is meant by this?

Response: We changed this sentence to "reflecting the higher oxidation degree of HOMs in β -pinene SOA than limonene SOA-associated HOMs" for clarification (L375-376).

Response to the comments of Anonymous Referee #2

The authors have addressed most of my comments with few exceptions detailed below. I recommend publishing the manuscript after addressing these minor comments.

Response: We thank the reviewer for the positive evaluation to our last revision. Our point-by-point responses are shown in blue color as below.

1. Initial comment #1, it is worth adding a note that the peak intensity is not directly translatable to abundance/concentration.

Response: Thanks. We have added "It is noted that peak intensity of MS spectrum is not directly translatable to abundance or concentration" in L173-174.

2. Initial comment #7, for a C₉-compound, if it contains 6 oxygen atoms, it would be classified as non-HOM (O/C<0.7), which is slightly different from the common classification of HOM definition (Bianchi, Kurten et al. 2019). While it is totally fine to have a different definition, I suggest noting the difference so that readers can better follow.

Response: Thank you. We clarified this point in the line 212-213: "It is noted that the current definition of HOMs is different from previous studies and does not count in HOM trimmers or other HOMs with higher oligomerization degrees, which is warranty to be explored in follow up studies".

3. Initial comment #11, even though the double bond equivalents of β -pinene SOA are high, they may contain only rings and C=O and do not necessarily contain C=C double bonds. As the C=C of β -pinene react with ozone in the first step, how are "new" C=C bonds formed? In another word, what is the potential chemical mechanism behind "the conversion of less oxidized organic molecules into high oxygen-containing organic molecules" promoted by excessive ozone?

Response: We agree with that high double bond equivalents of β -pinene SOA does not means high C=C abundance. We suggest that oxygen-increasing-reactions play important role in the conversion of less oxidized organic molecules into high oxygen-containing organic molecules. To clarify our discussion point, we have revised the initial lines 228-229 as follows: "indicating the preferred formation of high oxygen-containing organic molecules at higher concentrations of ozone, which may be associated with the indirectly accelerated autoxidation via O₃-augmented RO₂ levels etc." (L269-270).

Reference

- Berndt, T., Mentler, B., Scholz, W., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion product formation from ozonolysis and OH radical reaction of α -pinene: Mechanistic insight and the influence of isoprene and ethylene, *Environ. Sci. Technol.*, 52, 11069-11077, <https://doi.org/10.1021/acs.est.8b02210>, 2018a.
- Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion product formation from self- and cross-reactions of RO₂ radicals in the atmosphere, *Angew. Chem. Int. Ed.*, 57, 3820-3824, <https://doi.org/10.1002/anie.201710989>, 2018b.
- Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crouse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly oxygenated organic molecules (HOM) from gas-phase autoxidation involving peroxy radicals: A key contributor to atmospheric aerosol, *Chem. Rev.*, 119, 3472-3509, <https://doi.org/10.1021/acs.chemrev.8b00395>, 2019.
- Ehn, M., Thornton, J. A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Maso, M. D., Berndt, T., Petaja, T., Wahner, A., Kerminen, V. M., Kulmala, M., Worsnop, D. R., Wildt, J., and Mentel, T. F.: A large source of low-volatility secondary organic aerosol, *Nature*, 506, 476-479, <https://doi.org/10.1038/nature13032>, 2014.
- Kahnt, A., Vermeylen, R., Iinuma, Y., Safi Shalamzari, M., Maenhaut, W., and Claeys, M.: High-molecular-weight esters in α -pinene ozonolysis secondary organic aerosol: structural characterization and mechanistic proposal for their formation from highly oxygenated molecules, *Atmos. Chem. Phys.*, 18, 8453-8467, <https://doi.org/10.5194/acp-18-8453-2018>, 2018.
- Lee, R., Gryn'ova, G., Ingold, K. U., and Coote, M. L.: Why are sec-alkylperoxyl bimolecular self-reactions orders of magnitude faster than the analogous reactions of tert-alkylperoxyls? The unanticipated role of CH hydrogen bond donation, *Phys. Chem. Chem. Phys.*, 18, 23673-23679, <https://doi.org/10.1039/c6cp04670c>, 2016.
- Tomaz, S., Wang, D., Zabalegui, N., Li, D., Lamkaddam, H., Bachmeier, F., Vogel, A., Monge, M. E., Perrier, S., Baltensperger, U., George, C., Rissanen, M., Ehn, M., El Haddad, I., and Riva, M.: Structures and reactivity of peroxy radicals and dimeric products revealed by online tandem mass spectrometry, *Nat. Commun.*, 12, 300, <https://doi.org/10.1038/s41467-020-20532-2>, 2021.