

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-1067

Anonymous Referee #1

Referee comment on "Kinetics, SOA yields, and chemical composition of secondary organic aerosol from β -caryophyllene ozonolysis with and without nitrogen oxides between 213 and 313 K" by Linyu Gao et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1067-RC1>, 2022

The authors investigated the SOA formation from the ozonolysis of β -caryophyllene (BCP) at different temperatures in an atmospheric simulation chamber and showed that the SOA particle yields increase with decreasing temperatures. The authors attributed this to the decrease of the vapour pressure of the oxidation products at reduced temperatures and supported this by showing that a larger fraction of products with lower number of oxygen atoms were present at lower temperatures compared to higher, where higher O:C was observed. They also provide, for the first time, reaction rate coefficients for the reaction of BCP with ozone at different temperatures. Furthermore, in each experiment, after the initial amounts of BCP were consumed, additional BCP, ozone and nitrogen dioxide were added to the chamber to form SOA in the presence of nitrate radicals. Advanced mass spectrometry techniques were used to investigate the chemical composition of the gas and particle phase in each experimental setting and showed that the chemical composition had significant temperature dependence.

Overall, I believe that the manuscript falls within the scope of ACP as it provides new information for the SOA formation, composition and kinetics from the oxidation of BCP and importantly, their temperature dependence. I recommend this work for publication after a few major and some minor considerations have been addressed.

General comments:

- The study suggests that the experiments were conducted under representative of the real atmosphere conditions, which might be true for the selected temperature and relative humidity conditions. However, the study uses unrealistically high oxidant and precursor concentrations that could have altered the fate of the radicals. I am therefore wondering how the resulted chemical regime of the experiments could have affected the results presented and their implications to the real atmosphere.
- All the experiments aside from the different temperatures were also conducted under substantially different relative humidity (RH) conditions (13-97%). It was recently shown that the BCP-SOA chemical composition could be considerably affected by the RH levels (e.g., Kundu et al., 2017), therefore how the difference in the RH between the experiments conducted in this study could have affected the reported results? I understand that the authors try to capture the variation of the temperature and RH found in the different layers of the atmosphere. However, I believe that the potential implications of the different RH levels should be included in the interpretation of the results.
- The study compares the SOA yields obtained in this study with values obtained previously in the literature and attributes the observed differences to the potentially different oxidative conditions. Whilst this, at least in part might be true, it may be worthwhile considering the potentially different losses and partitioning of the semi-volatile vapours in the different chambers - even so considering the different materials of the chambers (i.e., Teflon vs Aluminum). Additional discussion should probably be included when interpreting and discussing the SOA yield results.
- In my opinion, a lot more information is required for the operation and data analysis of the FIGARO-CIMS dataset. The authors report a considerably large fraction of products with particularly high molecular weight (>400 Th). It would be helpful for the readers to know the range the mass calibration was conducted, the associated peak assignment errors and thereby, the confidence in the results presented. Furthermore, additional information about the particle-phase background subtraction and sampling strategy would be beneficial.
- I believe that the absorptive partitioning should be considered when discussing and interpreting the results and particularly, the different levels of absorptive mass in each experimental setting. For example, higher SOA yields and lower O:C have been observed at the lower temperature experiments opposed to those conducted at higher temperatures (that exhibited lower yield + higher O:C). Could this behaviour be attributed to the higher levels of absorptive mass present at the higher yield experiments, enabling the partitioning of the less oxygenated (and consequently more volatile species) to the condensed phase, thus decreasing the average O:C? To better understand this, I think that it would be beneficial, at least in the supporting information, to show the time-series of the SOA mass in each experimental setting. This effect could be even more pronounced when the authors compare the ozonolysis experiments with those in the presence of NO₃. The ozonolysis experiments entailed the formation of SOA from the nucleation of the oxidation products, whereas those formed in the presence of NO₃ involve the condensation of the species on the top of those pre-existing particles. Intuitively, the partitioning behaviour of the species in each of these cases could be significantly altered due to the significantly different absorptive mass present and thereby could have affected the reported results and their comparison.
- Further to the above, all the experiments were conducted in the absence of seed particles. Could the potentially different particle number (and thereby surface area) in each experimental setting have affected the partitioning of the species between the particle phase and the chamber walls? What would be the implications on the results? Again, time-series of the particle number/surface area in each experiment might be beneficial.

Specific comments

L57, L87 and L217: As from 2020, IUPAC has released updated values for the reaction rate coefficients for major organic compounds, including BCP that can be found on Cox et al., (2020) and Mellouki et al., (2021). I recommend those values to be used throughout the manuscript, including the calculations performed.

L126: "saturated with its vapour" how this was confirmed?

L140: Why the authors decided to get a slower decay only in the 273K experiments and not the rest? How this could have affected the results?

L171: I think that it would be beneficial for the readers if the authors provide a more detailed description of their error propagation estimates.

L183: What was the relative ionisation efficiency of the AMS and how it was obtained?

L191: where the remaining 0.003m³/min are going? I presume to the exhaust but it would be nice if this was clarified in the revised manuscript.

L204-207: In line with the general comment #4, it is unclear how the background subtraction was conducted. I think that additional information for the data processing would be beneficial.

L231: It is unclear to me how the COSIMA accounts for the losses of semi-volatile vapours. Furthermore, to what extent the interactions of the aluminium walls of the AIDA with the losses of particles and the partitioning of the semi-volatile vapours were considered? Does this have any implications for the reported results?

L246-250: BCP secondary additions are not visible in Fig.2, while the third is not described in the methods section nor related data are shown in table 1. I think that such information should be detailed in the experimental conditions section.

L259: I generally do not support the calculation of the total mass concentrations from the FIGAREO-CIMS assuming maximum sensitivity for all the compounds detected, given that a lot of work has been devoted to illustrate the issue of the differential sensitivity in the instrument along with potential ways to constrain such issues (e.g., Lopez-Hilfiker et al., 2016). Nonetheless, I do see some value in comparing the estimated trends with those derived from the HR-AMS. I would recommend however, definite quantitative statements such as those presented on that sentence to be softened.

L279: Do you have any evidence that the SOA particle yields from the OH oxidation should be higher than the ozonolysis? For other precursors, such as the α -pinene, the SOA yields from the O₃ oxidations have been found to be higher than the OH-initiated oxidation.

L400: How the contribution of the NO₃ oxidation was estimated at different temperatures, given that there are no available BCP reaction rates with temperature? What would be the error in those estimates? Perhaps additional information about the box modelling should be included in the manuscript.

L411: Why the formation of C₁₅H₂₅O₇N indicates that BCP is reacting directly with NO₃ and the formation and not that certain pre-existing O₃-initiated oxidation products are reacting with NO₃? Perhaps a more descriptive approach will benefit the readers.

L421: How the mass of the organic nitrates was calculated from the HR-AMS measurements? It is known that it is challenging to retrieve N-containing species from that instrument (e.g., Farmer et al., 2010), so it would be helpful if more information was provided.

L451: Perhaps adding a reference about the potential thermal instability of N-containing compounds at 313K would be beneficial here. If so, how about their decomposition in the FIGAERO-CIMS?

Technical corrections

L101: "big condensation potential", I think that the authors mean that at lower temperatures the vapour pressure of the components is lower and thereby altering the partitioning behaviour of the species. Probably this sentence needs some rephrasing and appropriate references.

L103: this sentence is a bit difficult to understand, please re-write.

L115: "bottom", I assume of the chamber. Please re-write.

L168: please remove the parenthesis from the contribution of the major ions

L381-386: these are not annotated in any of the figures and are a bit difficult to follow, please re-write.

L390: From figure 2 second addition of BCP appears to be between 150-160 min instead of 180-190 min.

L430: This sentence is not very clear could you please re-write? Also, could this shift be attributed to the different total absorptive mass present enabling the partitioning of the less oxygenated and consequently more volatile species to the particle phase (see also general comment #5)?

L435-436 and L439-440: these sentences are a bit difficult to understand, please re-write.

L457-458: I am not sure if the "BCP ozonolysis in the presence of NO₃ radicals" is the right wording here. If I understand correctly, the BCP oxidation in the last stage of the experiment occurs in the presence of both oxidants.

Fig. S3 I struggle to differentiate the modelled from the measured ozone. Additionally, the reaction rates should have different units?

Please also re-check figure numbering.

References

Cox et al., (2020), Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII – Criegee intermediates. *Atmos. Chem. Phys.*, 20, 13497–13519, <https://doi.org/10.5194/acp-20-13497-2020>

Farmer et al., (2010), Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, *P. Natl. Acad. Sci. USA*, 107, 6670–6675, <https://doi.org/10.1073/pnas.0912340107>

Kundu et al., (2017), Molecular formula composition of β -caryophyllene ozonolysis SOA formed in humid and dry conditions, *Atmospheric Environment*, 154, 2017, 70-81, <https://doi.org/10.1016/j.atmosenv.2016.12.031>.

Lopez-Hilfiker et al., (2016), Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmos. Meas. Tech.*, 9, 1505–1512, <https://doi.org/10.5194/amt-9-1505-2016>

Mellouki et al., (2021), Evaluated kinetic and photochemical data for atmospheric chemistry: volume VIII – gas-phase reactions of organic species with four, or more, carbon atoms ($\geq C_4$). *Atmos. Chem. Phys.*, 21, 4797–4808, <https://doi.org/10.5194/acp-21-4797-2021>