

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-1067

Anonymous Referee #2

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-RC2>, 2022

In the study by Gao et al., the authors explore the oxidation of β -caryophyllene (BCP) by dark ozonolysis performed in the AIDA atmospheric simulation chamber with and without the presence of nitrogen oxides at different temperatures. From state-of-the-art analytical techniques, the authors report on the formation and composition of resulting gas- and particle-phase secondary organic aerosol (SOA). Presented results show that temperature effects both SOA yields as well as chemical composition which the authors attribute to temperature-dependent difference in vapour pressure of the BCP oxidation products. Following initial ozonolysis of BCP, the influence of nitrogen oxides is examined by the addition of nitrogen dioxide and additional BCP to the ozone-filled chamber. In the presence of nitrogen oxides, the authors show formation of organonitrates contribution to the SOA with higher contributions of more oxygenated species observed at higher temperatures.

The manuscript provides new and important findings on the temperature-dependent formation of SOA from BCP. The applied analytical techniques are comprehensive including both gas and particle phase characterization of the formed SOA. The manuscript is well written, the results are clearly presented and discussed, and the topic falls within the scope of ACP. I thus recommend this work for publication once the following comments have been addressed.

General comments:

- Discussions on the chemical compositions is mostly based on data from experiment 1a (213K) and 5a (313K). However, in experiment 1a knowledge of the experimental conditions are incomplete from the lack of BCP measurements. In general, the reviewer finds that all experiments vary in their execution and experimental conditions other than temperature. In particular, large variation in BCP concentrations, RH and BCP/Ozone ratios are noted. How do the authors justify comparison between experiments and in particular to exp. 1a?

- Could the author comments on the expected phase-state of the formed SOA particles under the studied conditions? With the large temperature and RH span, the authors should consider this for two at least two reasons; 1) the partitioning of organics (e.g. semi-volatile org and org-Ns species) to the preexisting SOA particles (e.g. Bastelberger, 2017) and 2) particle-bound (surface or bulk) reactions (e.g. Shiraiwa, 2011). With respect to the latter, particle phase-state (solid or liquid) could affect both surface oxidation processes by ozone and OH-radicals but might also affect the proposed formation of dimers through esterification.
- The authors calculate OH-radical yield under the studied conditions and find significantly higher yields at elevated temperatures (5% at 243K vs 15% at 313K). However, due to the fast reaction of ozone with the endocyclic double bond of BCP 91-92% of BCP are calculated to react with ozone under the studied conditions, hence rendering contributions of OH-oxidation of BCP minor. However, considering that the authors attribute formation of higher oxidized compounds to further gas-phase oxidations of first-generation products, it would be worthwhile to discuss the influence of OH-radicals in this regard. In Witkowski (2019), several oxidation products from the OH + β -caryophyllonic acid has been identified including many found in the gas and particle phase of the current study, including $C_4H_6O_4$ and $C_{14}H_{22}O_4$, with the former identified in gas-phase SOA in 298K and 313K experiments only (Fig. 5).
- On the composition of both gas and particle phase SOA data are presented as normalized signals to total gas or particle $C_xH_yO_z(\%)$, respectively, at the given temperature. Whilst this provides a clear picture of the changes to the chemical composition, it fails to report on the differences in concentration of individual species between experiments. For example, in Fig. 5, showing the average CIMS gas phase mass spectra, even at low 213K and 243K gas-phase species seems to be abundant. It would be beneficial to include (in the SI) the absolute signals of the identified compounds, thus to be able to note the differences in abundance of these species between the experiments. As shown in Fig. 5, one might conclude that the gas-phase contains less organic compounds thus undermining the statement of gas-phase oxidation of first generation oxidation products as possible source to more oxidized monomers in particles formed at elevated temperatures. Also, as no BCP could be detected in the gas-phase at 213K due to wall-losses, how do the authors explain the detection of the oxidized species in Fig. 5?

Specific comments:

- The general experimental protocol is unclear and seems to vary between experiments. From Fig.2 and table 1, two ozonolysis experiments without NO₂ (2a and 4a) include more than one addition of BCP. What is the reason for this?
- Fig 2 indicates that the initial oxidation of the added BCP (65 $\mu\text{g m}^{-3}$) was performed using a lower ozone concentration (25 ppb) than stated in table 1 (325 ppb). Please clarify.
- It is not apparent to the reviewer, whether results from yield calculations and chemical analysis relates to SOA formed after the initial (time 0, low ozone, Fig. 2) ozonolysis or following the second addition of BCP at much higher O₃ concentration (300 ppb).
- Despite the typical high time resolution and sensitivity of the PTR-ToF-MS no BCP measurements are reported during the two additions of BCP in Fig. 2. Why is this? If the rate by which BCP is added is the same during the two additions, it would have been useful to see how the loss of BCP changes under the studied conditions.
- Line 126-128: the authors refer to the low vapour pressure and strong wall losses as possible explanation for the lacking BCP measurements at low temperatures. If all BCP

is lost to the chamber walls, from where do the SOA particle mass form? Reactions on the chamber surfaces? if so, how can the authors account for this in their experiments?

- Line 147-148: Do the authors expect any issues from operating all instruments at 296K? This is significantly higher than experimental conditions of 213K and lower than 313K, thus may produce bias in the gas and particle phase measurements from evaporation and condensation of semi-volatile species during sampling.
- Line 191-195: How many particle samples were collected for each experiment and how often were these collected? If multiple samples were collected, showing the evolution of the spectra or specific species (i.e. dimers and trimers) over time could be beneficial.
- Line 240-241: it would be useful if the authors provided similar figures as Fig. 2 (in SI) for all experiments conducted. Also, the authors should state the maximum particle number concentration and particle size (Table 1 og SI).
- Line 251: Did the authors observe new particle formation following the last injection of BCP in all experiments?
- Line 278-279: What was the reasoning behind not applying OH-scavengers and seed particles to the experiments?
- Line 354-355: How do the concentration/relative signal of dimers and monomer change over time? If dimers are formed from esterification of monomers, this could be evident from continuous increase of dimeric compounds after BCP depletion. In SI only time resolved data of monomeric species are shown.
- Line 356-358: Why are the dimeric molecules not observed at temperatures above 273K, despite the presence of the monomeric precursors?

Technical corrections

Line 354: Remove punctuation mark after "...*vapor pressure*"

References

Witkowski B, Al-sharafi M, Gierczak T (2019) Kinetics and products of the aqueous-phase oxidation of β -caryophyllonic acid by hydroxyl radicals, *Atmospheric Environment*, 213, 231-238,

Bastelberger S, Krieger UK, Luo B, & Thomas P (2017) Diffusivity measurements of volatile organics in levitated viscous aerosol particles. *Atmospheric Chemistry and Physics* 17(13):8453-8471

Shiraiwa M, Ammann M, Koop T, & Pöschl U (2011) Gas uptake and chemical aging of semisolid organic aerosol particles. *Proceedings of the National Academy of Sciences* 108(27):11003-11008.