Response to reviewer's comments 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" (acp-2021-1067)

Reviewer #2

The authors kindly thank the reviewer for the careful review of our manuscript, and the quite helpful comments and suggestions. All the comments are addressed below point by point, with our responses in blue, and the corresponding revisions to the manuscript in red. All updates of the original manuscript are marked in the revised version.

In the study by Gao et al., the authors explore the oxidation of b-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 BPC, the influence of nitrogen oxides is examined by the addition of nitrogen dioxide and additional BPC 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 particularly, 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?

Indeed, BCP was subject to rapid wall loss at 213K. However, in the presence of an excess of ozone, BCP was oxidized faster than the wall loss and we could generate a SOA mass load comparable to the other experiments. Due to similar BCP addition times, ozone levels, and SOA mass concentrations we consider it justified to use this experiment for comparison. Furthermore, we discuss the general trend of changes among all five temperatures studied and in this sense the experiment at 213 K is no outlier.

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 oragnics (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 prosed formation of dimers through esterification.

This question is addressed in our response to the general comment 2 of reviewer 1 and we have added the following text to the manuscript.

"Please note that we can't exclude completely that the changing humidity in our experiments has no influence on our results. Nonetheless, we think that the SOA composition we have observed is dominated by gas phase reactions with sufficient water concentrations compared to ambient conditions and that the potential impact of relative humidity on condensed phase reactions was minimized by increasing relative humidity with decreasing temperature (Li and Shiraiwa, 2019; Maclean et al., 2021), maybe except for the lowermost temperature."

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 C4H6O4 and C14H22O4 ,with the former identified in gas-phase SOA in 298K and 313K experiments only (Fig. 5).

Witkowski et al. (2019) identified and reported the main oxidation products from β-caryophyllonic acid ($C_{15}H_{24}O_3$) reacting with OH radicals in the aqueous phase. The main oxidation products they presented included $C_{14}H_{22}O_4$, $C_{15}H_{24}O_5$, $C_{15}H_{26}O_6$, $C_{15}H_{26}O_5$, $C_{14}H_{22}O_6$, $C_9H_{14}O_4$, $C_4H_6O_4$, and $C_5H_8O_4$. As we did not use any OH scavenger in our study, also oxidation products from gas phase reactions of OH radicals with products from BCP oxidation, like β-caryophyllonic acid, were observed. At higher temperatures, β-caryophyllonic acid is present in the gas phase and may partially be oxidized by the OH radicals formed in the first few minutes of the experiments by BCP ozonolysis. However, some of these products can also be formed via BCP reacting with ozone in the presence of OH scavengers (Li et al., 2011; Richters et al., 2016). Thus, $C_4H_6O_4$ can be an indicator of the OH radical related reactions in the gas phase, considering its low molecular weight and hence expected high vapor pressure. From Fig.5, the $C_4H_6O_4$ is more abundant at higher

temperatures (298K, 313K), and it indicates the OH radical related reactions are more substantial which is consistent with our OH yield estimation (to be higher at enhanced temperatures).

On the composition of both gas and particle phase SOA data are presented as normalized signals to total gas or particle CxHyOz(%), respectively, at the given temperature. Whilst this provide 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 contain 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?

We added the absolute signals of all detected gas phase compounds for all five temperatures in the supplement (Fig. S8). Figure R1 shows for the experiment at 213K almost no SOA formation after addition of ozone after the first addition of BCP. The initially added BCP went to the wall very fast and wasn't present for oxidation when ozone was added subsequently 30 min after the end of the first BCP addition. However, when we added BCP for a second time in the presence of ~300 ppb ozone in the chamber we observed substantial SOA formation as the BCP was oxidized before it was lost to the walls. We discuss the results from the experiment at 213K referring to the oxidation products from the ozonolysis of the second addition of BCP.
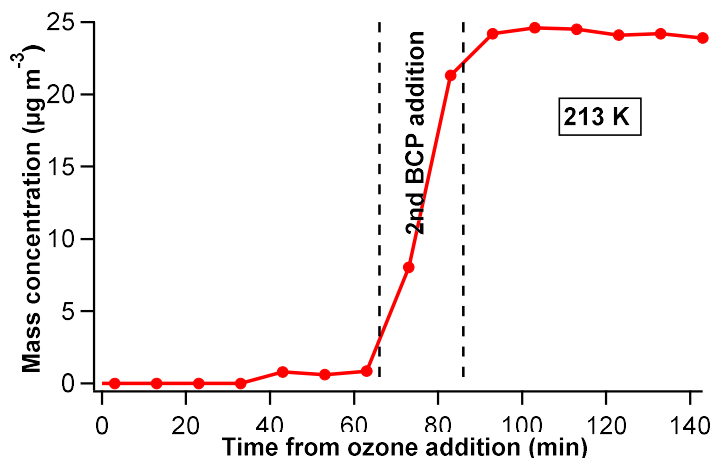
Figure R1. Time evolution of particle mass concentration measured by SMPS in the experiment at 213K.

We have added the following text to section 2.1:

"During the experiment at 213 K the initially added BCP was lost to the walls, so almost no SOA was formed after the addition of ozone. However, when adding BCP in the presence of ozone, SOA was formed in quantities comparable to the other experiments."

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?

During the experiments, we increased the SOA mass concentrations as to achieve comparable levels among the different experiments. We compared the particle chemical composition for these two additions of BCP and found their mass spectra were similar (before/after the second BCP addition) for all experiments. We have explained this in section 2.1 as follows:

"After depletion of the BCP at a lower ozone level to facilitate the kinetic study we increased the excess of ozone to accelerate the oxidation of remaining double bonds. Yields and chemical compositions are determined and compared for the time period after increasing the ozone level."

Fig 2 indicates that the initial oxidation of the added BCP (65 µg m-3) was performed using a lower ozone concentration (25 ppb) than stated in table 1 (325 ppb). Please clarify.

The first ozone addition of ~25 ppb allowed studying the kinetics of the BCP + ozone reaction. After the BCP was consumed and the particle concentration became stable we increased the ozone concentration to ~300 ppb to accelerate the reaction of the second double bond of the BCP and to make the SOA comparable with others formed at other temperatures. Table 1 states the sum of both ozone additions. We have explained this in the method section as mentioned in the previous comment.

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) ozonlysis or following the second addition of BCP at much higher O3 concentration (300 ppb).

The yields and chemical composition at all temperatures are related to the SOA at higher O_3 concentration (300 ppb), shown as the time period 50-80 min in Fig. 2. We have explained this in the method section as follows:

"Yields and chemical composition are determined and compared for the time period after increasing the ozone level."

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.

We have three additions of BCP in total in Fig. 2. The first BCP addition was done before time zero (addition of ozone) in Fig. 2, and its subsequent decay due to reaction with ozone was detected by PTR-TOF-MS. The second and third BCP addition were at ~76-86 min and ~148-160 min as indicated in Fig. 2. Due to the fast reaction of BCP with the excess of ozone the BCP concentrations did not reach a detectable level. However, as the BCP additions were done using the same device and conditions (e.g., temperature, flowrate), their addition rates can be expected to be very similar.

However, the BCP losses were faster for the second and third BCP addition due to higher ozone levels compared to that for the initial BCP addition.

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?

At the lowest temperature (213K), we couldn't detect any BCP during its addition. We then added ~320 ppb of ozone (time zero) but only observed relatively weak SOA formation (~0.6 µg m^{-3}) after ~40 min, as shown in Figure R1, 66 minutes after ozone addition we added BCP again. The particle concentration increased quickly within several minutes due to the rapid reaction between BCP and ozone. Thus, we conclude that the BCP from the first addition was mainly lost to the wall and had only minor contributions to the SOA formed. Therefore, this experiment can be used for comparison with the other experiments just excluding the initial BCP addition. Potential reactions on the chamber surfaces have no impact on our results because potential reactants and reaction products typically stay adsorbed on the aluminum oxide surface of the wall. We have explained this also in the last General Comment by Reviewer 2 and added the following text to the manuscript:

"During the experiment at 213 K the initially added BCP was lost to the walls, so that almost no SOA was formed after the addition of ozone. However, when adding BCP in the presence of ozone, SOA was formed in quantities comparable to the other 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.

This is indeed an important point. The temperature difference between the simulation chamber and the instruments is a general problem potentially causing biases e.g. due to phase partitioning of oxidation products. To minimize this, we enhanced the sampling flow rates of the instruments, i.e., FIGAERO-iodide-CIMS to shorten the residence times in the sampling tubes, and used thermal insulation materials to reduce the temperature change in the sampling lines, i.e., PTR-TOF-MS. In addition, Huang et al. (2018) has shown for a-pinene SOA for similar sampling procedures at the AIDA chamber that CIMS mass spectra were nearly identical for sampling at different temperatures.

We have explained this by adding the following sentence to the Method section 2.2:

"To avoid potential artifacts, e.g. due to phase partitioning of semi-volatile species in the sampling lines from the chamber to the instruments, the sampling lines were partially insulated and the residence time was below 1-2 seconds."

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.

Particle samples were collected at the stages when the particle concentrations reached stable levels and thus have much lower time resolution than the gas phase data. The red triangles in the middle panel of Fig. 2 show mass concentrations of the particle samples analyzed by FIGAERO-CIMS. The mass spectra, mass loadings, and the signal fractions of specific species were similar for the two particle samples which were collected at the same stage, e.g., for 213K. Thus, the mass spectra shown in the manuscript is the average of the two samples collected at the same stage. We have added the information on the amount of particle samples to section 2.2 as follows:

"We collected 4, 3, 3, 2, 2 particle filter samples for the periods when the particle concentrations reached stable levels in experiments at 213 K, 243 K, 273K, 298K, and 313 K, respectively."

Line240-241: 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).

The time evolution of all other experiments (213K, 243K, 273K, and 313K) are added in the supplement as Figure S4, including the mass concentration and particle number concentration distribution over all the periods. The particle sizes which contribute most to the mass concentration are also added to Table 1 in the manuscript.

Line 251: Did the authors observe new particle formation following the last injection of BCP in all experiments?

As shown in Figures 2 and S4 (supplement), small particles with diameters of 20-40 nm were formed after the last injection of BCP at 298K and 313K. However, at 213-273K, no new particle formation was observed for particles larger of 13 nm following the last addition of BCP.

Line 278-279: What was the reasoning behind not applying OH-scavengers and seed particles to the experiments?

We did not use OH-scavengers in the experiments because we wanted toto study not only the products from ozonolysis but also from OH radical reactions. However, due to the high reactivity of BCP towards ozone, the relative high ozone concentrations, and the relatively low OH radical yields from BCP ozonolysis, we can expect the product distribution being dominated by the ozonolysis reaction. The reason for not using seed particles is that the volatilities of the oxidation products from β-caryophyllene are expected to be low enough to form new particles even without additional pre-existing particle surfaces.

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.

Dimers were found abundantly at 213-243K in the particle phase. However, the gas phase signal of individual dimeric molecules at 213-243K was almost zero and showed no significant change over the experiments, potentially due to the extremely low volatilities at such cold temperatures

for those large molecular-weight species with 28-30 carbon atoms and 5-9 oxygen atoms. We found a slight increase of gas phase signals after the 2nd BCP addition only by summing up all signals of dimers (Figure R2). This may also be an indicator for the dimer formation via esterification from monomers.
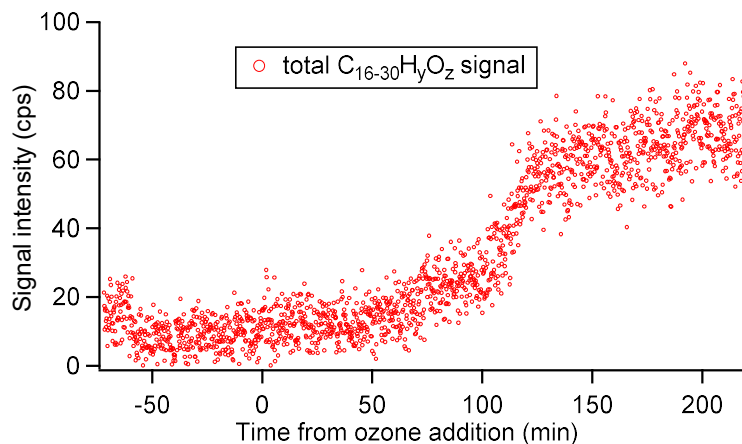
Figure R2. Time evolution of the signal intensity of the sum of all $C_{16-30}H_yO_z$ species.

Line 356-358: Why are the dimeric molecules not observed at temperatures above 273K, despite the presence of the monomeric precursors?

The dimers which were formed at temperatures above 273K were more oxygenated than the dimers formed at 213-243K (cf. Fig. 6), and thus, these two types of dimers should have different monomer precursors. At 213-243K, the dimers are dominated by the lower oxygenated species (DLOC, $C_{28-30}H_yO_{5-8}$), with potential precursors of first-generation oxidation monomeric products, e.g., $C_{15}H_{24}O_3$. However, with the temperature increasing, the β-caryophyllene is oxidized more via the autoxidation pathways, preventing the formation such compounds. Hence, less DLOC dimers were formed. At temperatures above 273K, highly oxygenated monomers, which are expected to have low volatilities, form higher oxygenated dimers (DHOC, $C_{28-30}H_yO_{9-11}$). Between 243-273K there seems to be the tuning point between these two mechanisms and may explain that we find the lowest dimer fraction at 273K (cf. Fig. 8).

Technical corrections

Line 354: Remove punctuation mark after "…vapor pressure"

This was removed.

Reference for Response

Li, Y., and Shiraiwa, M.: Timescales of secondary organic aerosols to reach equilibrium at various temperatures and relative humidities, Atmos. Chem. Phys., 19, 5959-5971, 10.5194/acp-19-5959-2019, 2019.

Li, Y. J., Chen, Q., Guzman, M. I., Chan, C. K., and Martin, S. T.: Second-generation products contribute substantially to the particle-phase organic material produced by β-caryophyllene ozonolysis, Atmos. Chem. Phys., 11, 121-132, 10.5194/acp-11-121-2011, 2011.

Maclean, A. M., Smith, N. R., Li, Y., Huang, Y., Hettiyadura, A. P. S., Crescenzo, G. V., Shiraiwa, M., Laskin, A., Nizkorodov, S. A., and Bertram, A. K.: Humidity-Dependent Viscosity of Secondary Organic Aerosol from Ozonolysis of β-Caryophyllene: Measurements, Predictions, and Implications, ACS Earth and Space Chemistry, 5, 305-318, 10.1021/acsearthspacechem.0c00296, 2021.

Richters, S., Herrmann, H., and Berndt, T.: Different pathways of the formation of highly oxidized multifunctional organic compounds (HOMs) from the gas-phase ozonolysis of β-caryophyllene, Atmos. Chem. Phys., 16, 9831-9845, 10.5194/acp-16-9831-2016, 2016.