Atmos. Chem. Phys. Discuss., 10, C7697–C7700, 2010
www.atmos-chem-phys-discuss.net/10/C7697/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Second-generation products of $\vec{\beta}$-caryophyllene ozonolysis are the dominant contributors to particle mass concentration" *by* Y. J. Li et al.

Anonymous Referee #1

Received and published: 17 September 2010

This study investigates the products formed from the ozonolysis of b-caryophyllene in chamber experiments. Excess ozone is used to facilitate the formation of second-generation products. The particle-phase products are characterized with UPLC-ESI-ToF-MS; 15 products are identified, among them 3 are identified for the first time. 9 out of the 15 products are second-generation products. One of the identified second-generation products has 7 oxygen atoms, the authors suggested that it can contribute to new particle formation based on the estimated saturation vapor pressure.

b-caryophyllene is one of the most well-studied sesquiterpenes and many of the oxidation products have been identified previously. In this work, 3 new products are

identified. While this paper is well-organized and well-written, it seems that the authors could add more materials to this paper to make it more substantial. For instance, including some gas-phase data from the PTR-MS measurements could strengthen their discussion on product volatility. Also, adding some HR-ToF-AMS data could help provide insights into whether the 15 identified products represent substantial fraction of all the particle-phase products etc. (more specific comments below)

I would recommend publication in ACP if the authors can include additional data from other instruments to strengthen their discussions and make this work more comprehensive. Also, the following comments needed to be addressed.

Specific comments:

1. Page 17703, line 15-25. One of the main points the authors made is that this study employs excess ozone while the previous studies are ozone-limited. With this in mind, the readers may expect the products found in this study to be quite different from the previous studies. However, among the 9 second-generation products identified in this study, 6 of them have already been identified in the previous studies even though those studies may not be considered as ozone-rich. The authors should change the wordings of this paragraph so as to avoid sounding misleading.

2. Page 17704, line 21 onwards. The authors should add a table of experimental conditions in the manuscript, such as initial b-caryophyllene concentrations, ozone concentrations etc. It is not clear now how much excess ozone is present in the experiments. Also, do the 50ppb, 100ppb, and 200pb refer to b-caryophyllene concentration or ozone concentration?

3. Page 17708, structures of the products. According to Winterhalter et al. (2009) and Kanawati et al. (2008), secondary ozonide is a major reaction product. In this work, secondary ozonide is not observed (according to Supp. Info). It is true that the presence of water would decrease the formation of secondary ozonide. However, Winterhalter et al. (2009) performed some experiments at RH=36% which is comparable to

the RH of this study (RH=40%), and still observed the formation of secondary ozonide. Do the authors have an explanation for the lack of observation of secondary ozonide in their study?

4. Page 17710, line 8 onwards. The authors should also compare their results to other published data, including Calogirou et al. (1997) and Jaoui et al. (2003), and summarize them in the table.

5. Papge 17711, line 22. (a) By how much does the sum of the surrogate concentrations exceed that measured by the HR-ToF-AMS? This should be stated in the manuscript, otherwise the authors cannot justify that "Overestimates by the UPLC-MS method compared to the AMS method are in agreement are in agreement once these uncertainties are taken into account" and "The comparison therefore suggests that a substantial fraction of the total organic particle mass concentration is represented by the 15 identified products". (b) What are the mass fractions of each of the products identified? Do the mass fraction of each individual product change as a function of the aerosol loading? (c) The HR-ToF-AMS data can probably provide further insights into whether these 15 identified products constitute a majority of the aerosol mass. The H:C and O:C of the 15 identified products are known, and with HR-ToF-AMS the H:C and O:C of the aerosols formed can be determined explicitly. By comparing the H:C and O:C of the 15 products (weighted by their mass fractions) and the H:C and O:C determined by the HR-ToF-AMS, the authors can then comment on whether these 15 identified products represent majority of the particle-phase products. (For reference, in Chhabra et al. (ACP 2010) it has been shown the H:C and O:C calculated from the mass-weighted average of the products agree well with those from HR-ToF-AMS measurements for a-pinene ozonolysis system).

6. Page 17712, product volatilities. In the experimental section, the authors mentioned that a PTR-MS is employed in the experiments. Yet, no PTR-MS data have been presented in this paper (other than measuring the b-caryophyllene concentration). Including gas-phase measurements here could provide further insights to the volatility of

the products and make this paper more substantial. For instance, do the gas-phase data agree well with the vapor pressure calculations (i.e., did the authors observe more of the volatile products in the gas phase?)? Also, did the authors observe any of the second-generation products in the gas phase?

7. Page 17713, discussion about Figure 6. (a) What are the initial b-caryophyllene concentrations for these experiments? (b) How are these mass fractions estimated? Based on the surrogate approach? If so, as stated by the authors the errors should be pretty large (Page 17711). It has been shown that a substantial amount of the aerosol growth from b-caryophyllene ozonolysis is from second-generation products (Ng et al., 2006) and it is reasonable that the second-generation products will be more dominant in experiments with lower loadings based on partition theory, however, I am not sure if the authors can come to this conclusion based on the data in Figure 6 (if the errors from the surrogate approach is included in the error bars, it would make the errors much larger).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 17699, 2010.