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Interactive comment on "Elemental composition and clustering of α-pinene oxidation products for different oxidation conditions" *by* A. P. Praplan et al.

Anonymous Referee #3

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This study investigates the similarities and differences in the oxidation products formed from a-pinene ozonolysis and photooxidation. Experiments are conducted in the CLOUD facility at CERN. The negative ions, positive ions, and neutral molecules are measured with APi-ToF in the negative mode, positive mode, and NO3 as ionizing reagent, respectively. The distribution of the clusters, average carbon oxidation state, and the time series of the detected species are presented and discussed. It is found that the products from a-pinene ozonolysis showed a higher oxidation state than those formed in photooxidation.

These novel measurements provide substantial amount of insights into the composition

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of the species formed in these oxidation experiments. The manuscript is generally well-written and will be of interest to the community. However, there are several aspects that weaken the manuscript and should be addressed.

Firstly, the authors need to substantially expand the experimental section. As noted in more details in the specific comments below, the authors need to include a discussion regarding the relative importance of peroxy radical reaction pathways, e.g., RO2+HO2, RO2+NO, in the context of the scavenger used and the NOx levels in the ozonolysis experiment and the photooxidation experiment. This is important as Ehn et al. (2014) showed that the products formed and measured by the CI-APi-TOF in a-pinene ozonolysis experiments are highly dependent on NOx levels. In essence, (just an example), a study comparing products formed from a-pinene ozonolysis in the presence of a large amount of NOx with those formed from photooxidation in the absence of chamber background NOx might have entirely different conclusions compared to the present study.

Secondly, while these measurements are novel, the manuscript is more focused on describing what the similarities/differences are in the oxidation products, rather than why and how. I feel that more discussions on the results are needed regarding what these results mean. I think that the manuscript will be greatly strengthened if the authors can include a discussion on the atmospheric implications of these measurements and results. Based on the data presented in this manuscript and the level of similarities between the oxidation products formed in ozonolysis and photooxidation, it seems like it would be a challenge to apply these results to ambient studies (i.e., it would be challenging to tell whether products detected in ambient measurements are from ozonolysis or photooxidation).

Thirdly, the products formed from the ozonolysis of a-pinene have been measured by the APi-ToF in several previous studies (the authors cited them in the manuscript). The manuscript would benefit from a more thorough discussion in terms of how the results from this study compare to those prior studies.

The more specific comments are listed below.

1. Page 30802, line 14. The authors wrote “two oxidation pathways are known”. The nitrate radical oxidation of a-pinene does not appear to form much SOA (e.g., Hallquist et al., 1999; Griffin et al., 1999; Perraud et al., 2010). However, this is another a-pinene oxidation pathway and should be acknowledged.

2. Page 30804 and page 30805. The experimental section needs clarification and additional information.

a. The authors should provide a general discussion regarding the fate of peroxy radicals, as this will affect the subsequent oxidation products and make it difficult to interpret any similarities/differences in the chemical composition observed in their ozonolysis vs photooxidation experiments.

i. Ozonolysis: what OH scavenger is used? Various scavengers (e.g., CO, cyclohexane, etc) will produce different amount of HO2 (Keywood et al., 2004) and affect the relative importance of the RO2+HO2 channel. What is the background level of NO and NOx? These will inevitably affect the fate of peroxy radicals and subsequent oxidation products in the experiment. For RO2+NO and RO2+HO2 reactions to compete, the mixing ratio of NO only needs to be in the order of ∼40ppt. From figure 2, organic nitrates are also being formed in the ozonolysis experiment. Is this due to background NOx in the chamber?

ii. Ehn et al. (2014, extended data Figure 10) showed that the species measured by CI-APi-ToF in a-pinene ozonolysis is highly dependent on NOx. It is not clear what the NOx concentrations in the ozonolysis experiment in this study are, but the authors should comment and discuss this in the context of the results shown in Ehn et al. (2014). Are the results from this study consistent with the data shown in Ehn et al. (2014)? Please discuss.

iii. In the photooxidation experiment, what is the steady state concentration of NO and

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NO2?

b. It seems that the a-pinene injection scheme is different in the ozonolysis vs photooxidation experiment? In page 30813, it was mentioned that the mixing ratio of a-pinene slowly reaches its equilibrium concentration towards the end of the run, however, for the photooxidation experiment, a-pinene concentration is high at the beginning. How would this affect the suite of products observed? Will the interpretation of the time trends of the products shown in Figures 6-8 be complicated by this

c. Page 30806, line 9. Is the same amount of sulfuric acid added in the ozonolysis vs photooxidation expt the same? Is it added during the experiment? Or, it's already at steady state at the beginning of the experiment?

3. Page 30806, lines 24-26. It is noted that "…based on previous studies, isotopic patterns, and assumptions on chemical reactions, the elemental composition of most compounds could be retrieved". These need to be further elaborated. The corresponding previous studies should be cited. Also, what assumptions on chemical reactions have been made and how are those assumptions justified?

4. Page 30808. In calculating the "average carbon oxidation state", did the authors assume that all the detected ions have the same sensitivity? Please clarify. If the authors did assume all the ions have the same senility, please justify how this is the case. Also, what are the uncertainties in the "average carbon oxidation state" with respect to comment 3?

5. Page 30809, line 22. If the attribution of composition in the negative spectra remains ambiguous (page 30809, line 22), how would this affect the comparison of composition between ozonolysis and photooxidation experiments? I assume this would also bring uncertainties in the calculation of the carbon oxidation state. Please discuss.

6. Page 30812, line 15-20. The authors should provide more insights (from the mechanisms point of view) in terms of why the distribution of clusters in the neutral, positive,

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and negative spectra are more similar for C20 compounds which are independent of their formation pathways.

7. Page 30813, line 11-15. Shilling et al. (2009) has shown that the O:C for SOA is higher in a-pinene ozonolysis experiments with lower a-pinene levels. Also, Ng et al. (2010) showed that the initial products that condense to form SOA have the highest f44 (O:C) in a-pinene ozonolysis. Both studies seem to be consistent with the results shown here and should be added to the citation. Please also include a citation for “the view that most oxidized organic compounds are formed only after long oxidants exposure time”.

8. Figure 6-9. It is not clear to me why some ions decrease faster than others. If I do not understand it wrong, the chamber is operated as CSTR. In this regard, how does one interpret decreasing signals over time – are they reacted away, are they lost to the chamber wall, etc that make them not reaching state steady? Please elaborate and comment on this.

9. This is a more general comment: what is technically defined as ELVOC? With respect to the ELVOC discussed in Ehn et al. (2014), it would seem like pretty much all of the species detected in this manuscript can be considered as ELVOC? 10. Many of the figures are too small to read.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 30799, 2014.