

Interactive comment on "Dependence of particle nucleation and growth on high molecular weight gas phase products during ozonolysis of α -pinene" by J. Zhao et al.

Anonymous Referee #3

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Gas-phase oxidation products from a-pinene ozonolysis were measured with a CIMS up to a mass-to-charge ratio 700. By correlating gas phase concentration time trends with that of the particle number concentration at different sizes the authors were able to distinguish products contributing to early growth (10-20 nm) and later growth (>20 nm). Some of the mass peaks were attributed to highly oxidized multifunctional organic compounds (HOM) by a comparison with the study of Ehn et al. (2012). The subject of this study is of high relevance to better understand new particle formation and provides some new insight into this topic. The paper is well written and merits publication in ACP. There are a few issues with terminology and interpretation which are outlined

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below and should be considered before publication.

The ozonolysis of a-pinene was done without OH scavenger. Ozone reacts only with compounds with a C-C double bond. Thus, there is only one generation of products produced by ozonolysis. Later generation of products can only be produced by OH radicals formed during the ozonolysis reaction. Adjust the terminology accordingly, eg. Page 10, line 13. This also questions the cleaning procedure of the chamber (Page 8, line 12). Ozone alone reacts only with compounds with a C-C double bond. Without OH radicals this method does not efficiently clean the chamber. Is this the reason for the high background of experiment E1? The criteria given for a clean chamber does not include oxidized organic species. What can you tell about cleanliness with respect to oxidized organic species from PTRMS and CIMS data?

Page 13, line 2: Category II products start to increase with addition of ozone and are therefore not later generation products. Ozonolysis (and OH radical reactions, which also occur to a lesser extent) forms not only products of low volatility, but also of medium and high volatility. My understanding is that category I products are low volatility products which condense first while category II products have a higher volatility and condense later when there is higher particle mass. To distinguish between first and later generation products one would need to perform the experiment with and without OH scavenger. Later generation products will have been formed in the present experimental setup, but the authors do not convincingly demonstrate which products belong to these.

Page 13, line 7: It seems to me that category III products also start to increase with addition of ozone indicating that they are not (only) later generation products. My interpretation is that category III products belong to the volatile fraction of ozonolysis and OH reaction products and may be first and eventually higher generation products. I would also like to see in Figure S6 the time trends of category II and III products.

Page 20, line 22 ff: The authors claim that high m/z peaks belong to high molecular

weight species. Can they confirm that these species are not just clusters (dimmers) of molecules with molecular weights of 200-300 amu.?

The authors mention that the nitrate ion has a high selectivity for ionization. Indeed, it is puzzling that the category I species show the highest concentrations. It is not expected that the species with lowest volatility are the most abundant, higher than the semi-volatile and volatile species. Could you comment on that? This should also be considered for the estimation of growth rates (page 18/19).

Page 5, line 16: Ehn et al. 2011: the reference is 2012. Check also other citations of Ehn et al.

Page 13, line 11: fig 1c not 1b

Page 15, line 2: peak at 308 is not in Table 1

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 9319, 2013.