"Influence of temperature on the molecular composition of ions and charged clusters during pure biogenic nucleation" by Carla Frege et al.

Anonymous Referee #2

The manuscript describes laboratory experiments in the CERN CLOUD chamber. The authors investigate the molecular composition of positive and negative HOM clusters measured with APi-TOFs at three different temperatures (25◦C, 5◦C and -25◦C). The authors discuss the cluster formation in the positive and negative ion mode, the average oxygen-to-carbon (O:C) ratios focusing on the influence of the changing temperature. They essentially conclude a decrease in the rate of autoxidation with decreasing temperature. The experimental findings are supported by quantum chemical calculations of the binding energies of representative neutral and charged clusters. In general, the paper is well written and presents an interesting topic that is well suited to be published in ACP. The molecular processes of new particle formation, especially if organic molecules are also involved, are not well understood. Therefore, I suggest to publish the manuscript in ACP after considering the following comments.

Page 6, line 167: Impurities from alpha-pinene or chamber background ? Could that be signals from previous experiments (e.g. pinanediol ?)

No, there were no previous experiments with a different molecule. The impurities are most likely from evaporation of α-pinene since their signal increased with the injection of α-pinene to the chamber.

Page 7, line 197: What does "under relatively dry conditions" mean ?

Dry conditions mean basically RH = 0%. This has been clarified. Please also see the plot describing the behavior of the ions as a function of RH in the answer to Referee #1.

Page 10, line 257,258: The ion C20H32O13.NO3- is mentioned two times ?

Thank you for the observation. This has been corrected.

Page 14, line 329: ". . . bands For a . . ." !?

There was a dot missing. This was corrected.

Page: 14, Table 2: The O/C-ratios from the monomers to the dimers are increasing in the positive mode and decreasing in the negative mode. While the decrease could be a result of oxygen loss in the formation of the dimers (in this case covalently bonded dimers (e.g. condensation reactions !?)), the increase in the O/C-ratio is more difficult to explain. One possibility would be the preferred formation from monomers with a rather high O/C-ratio, similar what the authors use as explanation for the tetramer formation, however, I wonder if the authors also included the C10H14OH+ signal in their signal weighted average O/C calculation (looking at figure 4 it seems so). In this case the inclusion of the background signal is of course misleading and should be corrected.

No, the signal of the "contaminant" peaks (i.e. $C_{10}H_{14}OH^+$ and $C_{20}H_{28}O_2H^+$) was not included in the O/C average calculation. We think, as the referee mentions, that the dimers are formed preferentially by the combination of monomers with a high O/C. Because the "contaminant" molecules (with low oxygen content and higher signal) were not included in the calculations, an increase in the O/C ration makes sense under this hypothesis.

Page 14, line 341: The authors often use the expression "cores". I suggest using simply "compounds" or "molecules".

When using the term core we want describe the neutral molecule or molecules contained in the cluster as opposed to the ion that provides the charge. We think it is more convenient than to describe it as the "neutral molecules of the cluster" or the "organic fraction of the cluster", etc. We would like to keep the notation as is.

Page 14, line 345: Again, I have the impression that the authors refer to the background signals mentioned earlier (compounds containing 1 oxygen atom) !? The explanation given on the next page (main oxidation products) is definitely not satisfying (in other words: pinonaldehyde is C10H16O2 and pinonic acid C10H16O3 – a factor of 2-3 higher in oxygen than needed).

We understand that this paragraph could be misunderstood because of the background signal $C_{10}H_{14}OH^+$ and $C_{20}H_{28}O_2H^+$, but those signals were excluded in all calculations. It should be remembered that although the monomer is generalized as molecules containing ten carbon atoms (C_{10}), the band also comprises molecules with slightly less carbon atoms (p.8 l. 208-210). This paragraph also makes reference to those molecules. Signals identified with O/C of 1 are from $C_{10}H_{16}O$ (this could be α-pinene oxide, which has been observed by others), $C_8H_{12}O$, $C_9H_{14}O$, etc. These do not belong to the strong peaks. Monomers with two or more oxygen atoms can be attributed to the main oxidation products, i.e. pinonaldehyde, pinonic acid, etc. We write now:

Ions with O:C ratio less than 0.3 are probably from the main known oxidation products like pinonaldehyde, pinonic acid, etc., but also from minor products like pinene oxide and other compounds that have not been identified so far.