Reply to the Review (RC3) of “Effect of temperature on the formation of Highly oxygenated Organic Molecules (HOM) from alpha-pinene ozonolysis” by QUÉLÉVER et al.

“This study investigated the effect of temperature on HOMs formation from α-pinene oxidation. Experiments were conducted at three different temperatures (20, 0, and -15°C). It is found that HOMs formation considerably decreases as temperature decreases. It is also claimed that the distributions of HOMs at 20°C and 0°C are very similar, which is conjectured to be due to that the rate-limiting step forming these HOMs occurs before the products become oxygenated enough to be detected by NO3- CIMS. This work investigated the effect of temperature on HOMs formation, which is important to help us further understand the formation mechanism of HOMs. However, there are a number of issues that need to be addressed before the paper can be published.”

We thank the reviewer for the positive feedback and will answer the comments point-by-point below:

Comment 1: **“The major issue involves the comparison of HOMs distribution between 20°C and 0°C. While the authors claim that the distributions are very similar between two temperatures, I beg to differ. Let’s start by looking at Figure 3. By eyeballing, the dominant monomer signal at 20°C ~308 amu, but it was ~325 amu at 0°C. There is also clear difference in the range 350-360 amu between two temperatures.**

Reply to comment 1: In Figure 3, we showed example spectra taken 10 min after α-pinene injection in all the temperature studied, since this was the period when the HOM typically were at their highest. Some precaution should be taken when analyzing those spectra as the chamber might not have been well-mixed yet at this time. This is also the reason for why our main analyses only include periods starting 40 min into the experiments (see also response to reviewer 2). Despite this, we do not find our original conclusion of a rather similar distribution too erroneous; we aimed at emphasizing that all identified compounds considered as HOM are present in the spectra at all the temperatures, and more importantly that there is no clear change in the spectral distribution as a function of oxygen content.

However, after considering the present comment, at the choice to use data 10 min after injection of the VOC may be misleading for a spectral comparison. In Figure R1, we instead plot the spectra averaged between 40 min and 120 min after α-pinene injection. This time period is the one used for figures 5 and 6, and this figure will now replace the original Figure 3 The HOM distribution is also shown in the form of a pie chart, as suggested by the reviewer in a later comment, in Figure R2, where we represented the HOM fraction – larger than 1% - for high loading experiment at 20 °C, 0 °C and -15 °C. From these plots the comparison is not trivial as only the largest HOM contributors are easy to distinguish, and the smaller signals, e.g. dimer species cannot be compared. Hence, we continued our analysis by plotting the HOM signal intensities measured at 0 °C vs those measured at 20 °C in Figure R3. From these figures it becomes clearer that the majority of the HOM signal intensities decreased close to a factor 50 (as depicted by the 1:50 solid line, and with most molecules within the bounds of the 1:25 and 1:100 dashed lines). The most abundant monomer signals are some of the few HOM that show clearly larger discrepancies, but overall, we retain that the spectra can be described as fairly similar. Also, importantly, we cannot isolate any trend related to the oxygen content, which supports our main conclusion: the temperature mostly influences the initial steps of the autoxidation rather than the successive oxygen additions during the HOM formation. Figure R3b was now added to the manuscript as a new Figure 7 in section 3.4.

Comment 2: **"As there are various HOMs formation pathways, it is likely that temperature has different effects on distinct pathways. This brings up one critical issue in the data interpretation - as there are both α-pinene + OH and α-pinene+O3 and the isomerization rates of RO2 from different oxidants are different, I suggest the authors to discuss the temperature effect on two channels separately."**

Reply to comment 2: The reviewer is correct that the isomerization rates of RO2 are different, but not only for the products from the different oxidation pathways, but indeed for every single RO2. For example in the ozone reaction, four different RO2 structures are formed, each having different isomerization rates (Kurtén et al., 2015, JPCA). With the data available to us in this study, we are not able to speculate about how the temperature would affect different RO2 separately. We focus our discussion on the ozone pathway for a few reasons: as mentioned in the methods section 2.2, model simulations estimate oxidation processes to be about 2/3 for ozonolysis and about 1/3 for the OH reaction. Additionally, Jokinen et al. (2015) showed that the HOM yield from OH oxidation is ~10x lower than that of ozonolysis. Therefore, we expect ozonolysis to be the dominant pathway.

Comment 3: **"To continue, the conclusion is drawn mainly based on Figure 6, and the authors noted that there is no clear trend in the yield change for any column. Again, I beg to differ. Take C10H16 column as an example. There is a weak increase in yield ratio (light green → ♉blue) with more oxygen. For C18H28 column, there seems to be a decrease in yield ratio.**

Reply to comment 3: For evaluating the goodness of fit for determining the HOM yields at different temperatures, we implemented a r^2*r^2 information by the size of the squares. In the examples mentioned by the reviewer, $C_{10}H_{16}O_x$ and $C_{18}H_{28}O_y$, ratios involve r^2*r^2 that are below 0.25 which implies a lack of reliable data for isolating a clear trend in our dataset. In addition, even in these columns, the trends pointed out by the reviewer only concern a few of the molecules. In neither case is there a trend line that would contain more than half of the data points in a column, and statistical variability alone will certainly cause apparent trends over a few data points.

Comment 4: "One figure **I suggest to make is a pie chart to show the fraction of each HOM in total HOMs**. By comparing the pie charts between two temperatures, it would be easier to examine the temperature effect on HOMs distribution."

Reply to comment 4: See reply to comment 1 & Figure R2

Comment 5: “Still in Figure 6, why are only five HOM monomers included? There are clearly more HOMs as shown in Figure 3 and Table A2. As a side note, because autoxidation would add two oxygen atoms, it is not proper to present the HOMs formation by +1 oxygen as shown in Figure 6.

Reply to comment 5: In Figure 6, there are 10 HOM-monomers plotted, and these are all the identified closed shell species. Compounds with an odd number of H-atoms are radical species, and their yields cannot be calculated without knowing their reaction rate constants with all other RO2. In the yield calculation for the closed shell HOM species, the CS is the major sink term, but for the radicals this is not the case, and therefore they are not plotted in neither Fig. 5 or 6.

The figure itself does not show any formation mechanisms, only the variety of measured HOM compounds with their specific yield ratio. Therefore, we do not find it improper to present the data this way.

Comment 6: “Lastly, one thing to consider when discussing the temperature effect is the RO2 fate. As the temperature decreases, the RO2+RO2 and RO2+HO2 react rates will also decrease, which increase bimolecular lifetime and enhance the fraction that undergoes isomerization. It would be helpful to quantify the RO2 bimolecular lifetime (Line 435).”

Reply to comment 6: Once the peroxy-radical species is formed, 3 terminations type could occur: (1) bimolecular reaction on the type of RO_2 + RO_2, (2) termination by HO_2 or (3) unimolecular reaction. As shown in Berndt et al. (2018), the reaction rate between RO_2 + RO_2 highly depend on the composition of the species involved in the recombination: every single RO_2 will react at a different rate with another $R'O_2$ (or with HO_2, alternatively) This results in a wide range of reaction rates that can vary by several orders of magnitude. However, bimolecular reactions generally have low energy barriers and thus would not be strongly dependent on temperature, at least if compared to the unimolecular reactions. If this wouldn’t be the case, our measurement should show a big variation in the ratio monomers-to-dimers, which is not the case. While we do agree that it would be interesting to assess the bimolecular lifetimes, our data set does allow such an analysis.

Remarks:

1. How is time-dependent d[HOM]/dt calculated?

We obtained d[HOM]/dt simply from our measured HOM signal, as the change Δ[HOM] between two data points Δt.

2. It would be useful to show the equation to calculate the CS, even included in supplement.

The CS was calculated according to Dal Maso et al., 2005 with refined parameters as mentioned in the method section 2.5. We added the missing reference in the manuscript.

3. Can the authors please describe the sampling lines and inlet? Some discussion of the losses in sampling line and inlet is warranted.

We added a description of the inlet and the CIMS sampling line in the manuscript in section 2.4: "The instrument sampled air at about 80 cm from the wall of the chamber via a ¾ inch tube directly connected to the CI-APi-TOF, which was located outside the chamber enclosure (~20 °C at all time). The sheath air (taken from a compressed air line) was 30 LPM and the total flow (generated by the house vacuum line) was 40 LPM. The ~1 m long inlet had a flow of 10 LPM caused by the difference between the sheath and total flows. With such a tube length and flow, roughly half of the HOM are expected to be lost to the walls of the inlet lines."

4. It would be useful to show the [SOA] under different temperature. Or a plot to compare the CS between different temperatures.

A much more detailed particle analysis from this campaign will be presented in a separate paper (Kristensen et al., in prep), and therefore we have not included specifics on the aerosol data here. We show below, in Figure R4, a comparison of the condensation sinks at different temperature for reference.

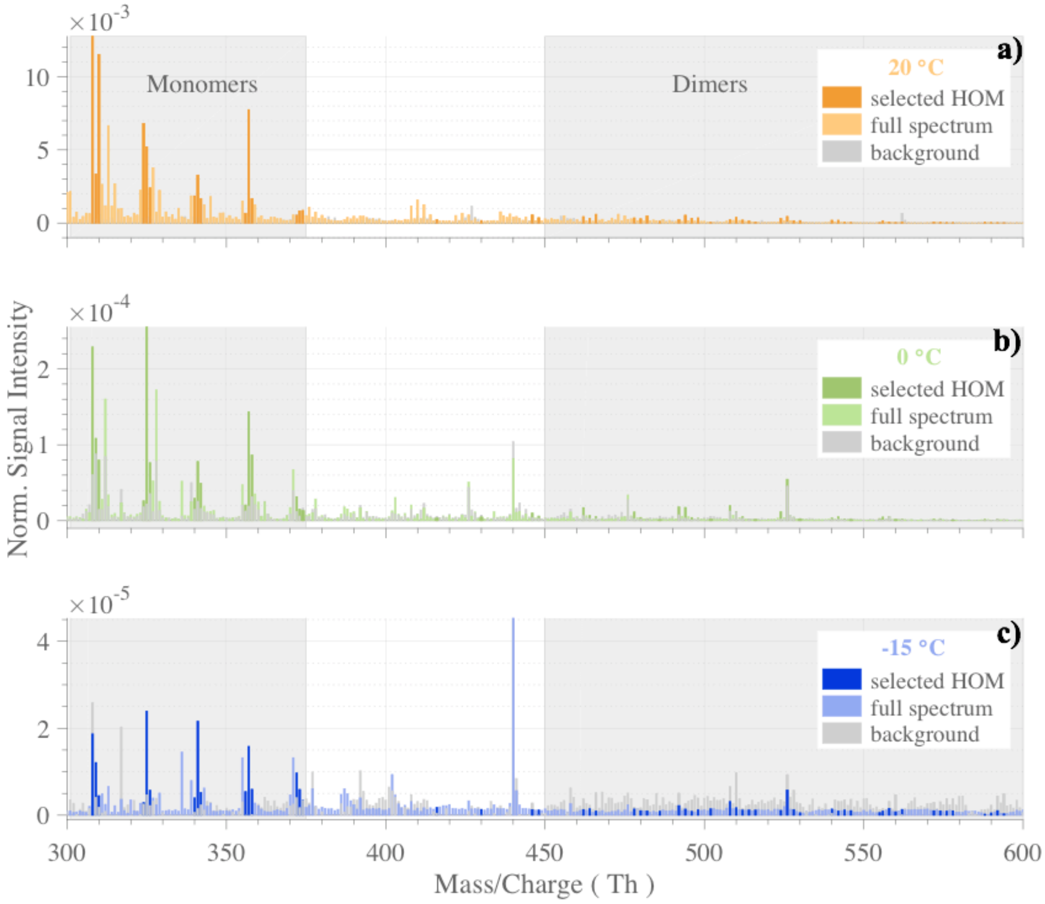

Figure R1 (also new Figure 3 in MS): *Typical HOM mass spectra observed during α-pinene ozonolysis experiments (initial conditions: [α-pinene] = 50 ppb, [O_3] = 100 ppb,) at T = 20 ℃ (panel a) in orange, T = 0 ℃ (panel b) in green, T = -15 ℃ (panel c) in blue. The normalized signals were averaged over 5 minutes during background measurement before VOC injection (gray bars), and from 40 min to 120 min after α-pinene injection (colored bars). Specific masses, selected for representing high-intensity HOM, are highlighted in darker colors. Gray-shaded areas show HOM sub-ranges of monomers and dimers.*

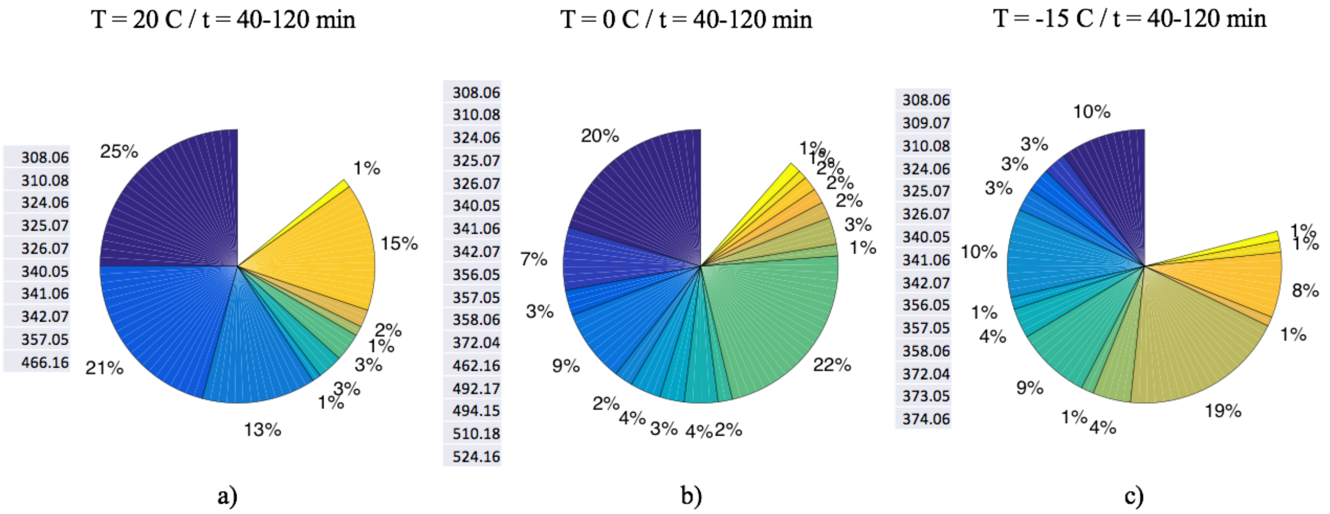

Figure R2: *Evaluation of HOM fraction from 40 min to 120 min after α-pinene injection at 20 ℃ (panel a), 0 ℃ (panel b) and -15 ℃ (panel c). Masse to charge ratios (in Th) are indicated on the left side of each panel where the first compound represents the darkest blue fraction. The 'missing' portion is the sum HOM contributions that are lower than 1 %.*

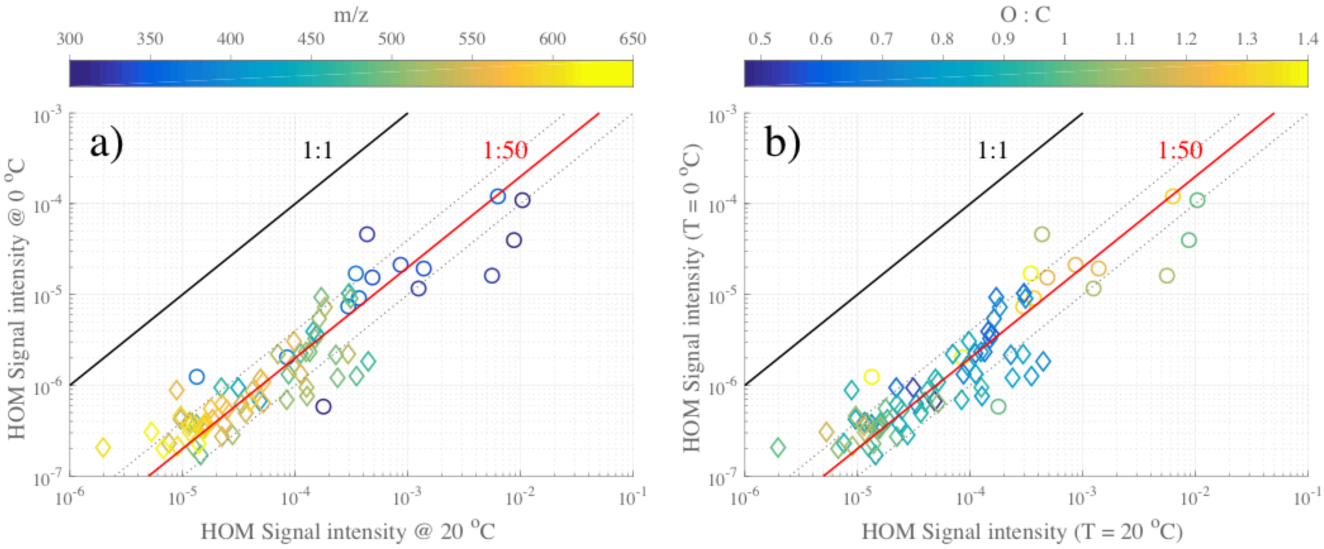

Figure R3: *Scatter plot on the HOM normalized signal intensity at 0 ℃ and at 20 ℃. The data points are colored by the mass-to-charge ratio (panel a) or by oxygen-to-carbon ratio (panel b) with distinction between monomer – circle markers - and dimer compounds – diamond markers. Guide lines were added as indicators: 1:1 line – in black, 1:50 line – in red ,1:25 and 1:100 lines - in dotted grey.* ***Figure R3b) was added to the manuscript as Figure 7.***

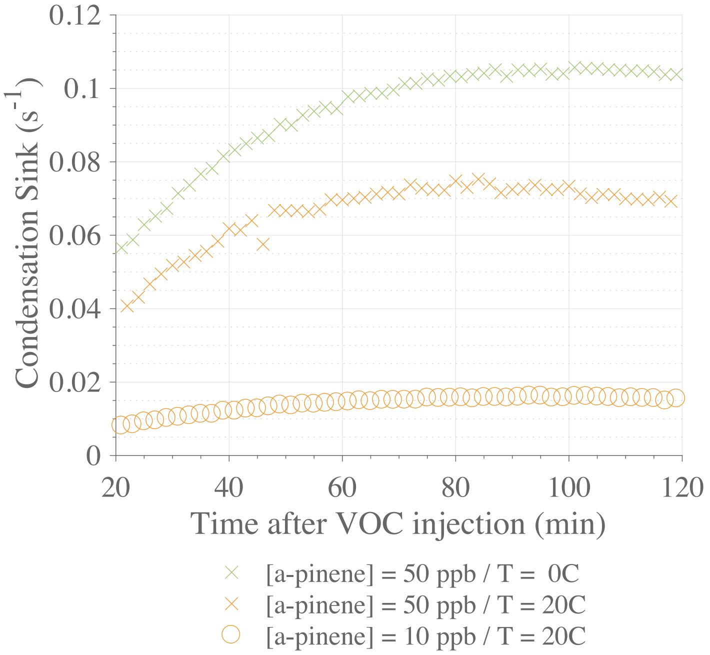

Figure R4: *Calculated condensation sinks over some ACCHA runs. Data shown from 20 min to 120 min after α-pinene injection for experiments performed at 50 ppb at 0 ℃ (16-Jan-2017) - green crosses, and 20 ℃ (12-Jan-2017) – red crosses, and at 10 ppb at 20 ℃ (12-Dec-2016) – red circles.*

References:

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