Interactive discussion on “Molecular understanding of new-particle formation from alpha-pinene between -50 °C and 25 °C” *by* Simon et al.

We thank the referees for their careful reading of the manuscript and their positive and constructive comments, which are repeated in full below (in black font). Our replies are given in blue font directly after the comments; text that has been added/modified to the manuscript is shown in red font.

Responses to anonymous referee #1

This study investigated low-volatility organics formed during alpha-pinene oxidation in the CLOUD chamber using a nitrate CIMS and a PTR-MS. The paper explores how HOM yields change with temperature as well as how the molecules’ volatilities change with temperature. HOM yields drop with decreasing temperature, however, the yields of ultra low volatility products increase with decreasing temperature (due to the dependence of volatility on temperature). The study also investigates how nucleation of the alpha-pinene oxidation products is impacted by temperature, and it shows that the yield of ultra low volatility products better explains nucleation rates than HOM yields.

Quite frankly, this paper is really great. It’s thorough and novel, and investigates hypotheses that I have heard people suspecting for the past several years. I recommend publication once some minor comments have been addressed.

L95: Haven’t mentioned what autooxidation is yet. **L98:** “HOM” was defined in the abstract, but I don’t see it in the main text. I *think* the standard is to re-define it.

We deleted autoxidation in this sentence as it is not necessary. However, the following sentences will introduce the term autoxidation followed by the definition of HOMs and their volatility distribution accordingly (added to line 94 of the manuscript).

The dominant monoterpene emitted from vegetation (e.g., coniferous trees) is α-pinene, accounting for ~34 % of the total global monoterpene emissions. Most of its oxidation pathways lead to oxidized volatile organic compounds (OVOCs) with a low degree of oxygenation; they are characterized as intermediate-volatility or semi-volatile organic compounds (IVOC, $300 < C^{*}(\mathrm{T}) < 3 \cdot 10^{6}\ \mu\mathrm{g\,m^{-3}}$; and SVOC, $0.3 < C^{*}(\mathrm{T}) < 300\ \mu\mathrm{g\,m^{-3}}$, where $C^{*}(\mathrm{T})$ is the effective saturation concentration, respectively). However, α-pinene has an endocyclic carbon double bond; oxidation of this functionality by ozone can initiate a rapid oxidation process, known as autoxidation (Crounse et al., 2013). Autoxidation proceeds by repeated intramolecular hydrogen shifts (H-shift) of weakly bound hydrogen atoms within peroxy radicals (RO_2). Each H-shift is followed by rapid addition of molecular oxygen (O_2) to form multifunctional peroxy radicals with a high degree of oxygenation, while preserving the radical functionality. Under low NO conditions (Berndt et al., 2018a), these radicals terminate to yield organic products with a high degree of oxygenation and therefore low volatility. Although multifunctional RO_2 radicals formed in autoxidation process are an important intermediate class of compounds in atmospheric chemistry (Rissanen et al., 2015), knowledge about their complex formation mechanisms and kinetics remains far from complete (Ehn et al., 2017).

The autoxidation pathway leads to highly-oxygenated organic molecules (HOMs) with molar yields of several percent (7 % at 20 °C (Ehn et al., 2014); 3.2 % at 5 °C (Kirkby et al., 2016)). This class of oxidation products spans a wide range of volatilities from low-volatility and extremely low volatility towards ultra-low volatility organic compounds (LVOC, $3 \cdot 10^{-5} < C^{*}(\mathrm{T}) < 0.3\ \mu\mathrm{g\ m^{-3}}$; ELVOC, $3 \cdot 10^{-9} < C^{*}(\mathrm{T}) < 3 \cdot 10^{-5}\ \mu\mathrm{g\ m^{-3}}$; and ULVOC, $C^{*}(\mathrm{T}) < 3 \cdot 10^{-9}\ \mu\mathrm{g\ m^{-3}}$, respectively). While the LVOC and ELVOC classes mainly contribute to the growth of embryonic clusters in the atmosphere, the new class ULVOC refers to molecules with sufficiently low saturation vapor pressure that enables them to reach supersaturation and drive pure biogenic nucleation (Donahue et al., 2012; Bianchi et al., 2019; Schervish and Donahue, 2019).

L201: "HVCF" was defined earlier, not "HV". People will be able to figure this out, obviously, but it might slow people down for a moment.

We have changed it to HVCF accordingly.

[…], while operating the mixing fans at a high speed and periodically activating the HVCF to remove all charged aerosol particles efficiently.

L242: It's important to give the units for "M_i" here since this is an empirical equation where the units don't match up easily between the right and left-hand sides.

M_i is defined as mass of the molecule i given in g/mol. We have added this information accordingly.

The diffusion coefficients D_i for each $\mathrm{HOM_i}$ are approximated with the expression $D_\mathrm{i}\ [\mathrm{cm^2\ s^{-1}}] = 0.31 \cdot M_\mathrm{i}^{-1/3}$, where M_i [g/mol] is the mass of the molecule.

L266: What does the "3" stand for in PRT3?

A PTR3 is the most advanced version of PTR-MS instruments. The number "3" indicates that the former drift tube has been replaced by a "tripole" consisting of three rods. More details can be found in Breitenlechner et al. (2017).

L347: I think that "negligible" should be "negligibly different".

The sentence has been modified as suggested:

While the additional oxygen in the -OOH group (log *C** = -2.4) has an almost negligible effect in reducing the saturation vapor pressure compared to the -OH group (log *C** = -2.2), neither covalently bound dimers nor the ability of hydroperoxide and peroxy acid functionalities to form intramolecular hydrogen bonds are included in the non-linear terms b_O and b_CO (Donahue et al., 2012; Kurtén et al., 2016)

L367: “under typical conditions” tripped me up here. What does “typical” mean here. Nucleation is not happening in the atmosphere (at an appreciable rate) most of the time.

“Typical” refers to the saturation ratios established in the atmosphere. This is because the “XLVOC” ranges would ideally be defined by gas-phase saturation ratios and not saturation concentrations. However, the saturation ratio depends on the steady-state gas-phase concentration and thus on both the production rate and the loss (condensation) rate. Defining this without getting lost in nuance is problematic, and so we simplified the sentence to “… may effectively nucleate.”

However, ELVOC will condense on any particle of any size with negligible re-evaporation, but may not contribute significantly to nucleation itself, while ULVOC in contrast may efficiently nucleate.

L410: Please give the approximate times of what’s being described in each sentence of the paragraph (right not it only shows up in the first sentence, but it would be useful throughout the paragraph).

We have added the information as suggested to the paragraph.

After the precursors reached a steady-state concentration (13:23 UTC in Fig. 1), the mixing fans were switched from 100 % to 12 % speed, reducing HOM and cluster wall-loss rates by a factor of two to three. Consequently, a new steady-state concentration of α-pinene oxidation product monomers (C_{10}) and dimers (C_{20}) was established on the wall-loss timescale. Due to the increased gas-phase concentration of condensable material, a new-particle formation event was initiated. Molecular clusters started to form and grew into aerosol particles. After the particle formation rate had reached steady state under neutral conditions (J_n), the HVCF inside the chamber was turned off (15:38 – 17:40 UTC in Fig. 1). Due to natural ionization at intensities of ground-level galactic cosmic rays, the ion concentration increased to > 1000 $\mathrm{cm^{-3}}$. Maintaining all other chamber parameters constant, we observed an enhancement of up to two orders of magnitude or more in the nucleation rate of new particles due to ion-induced cluster stabilization (J_gcr) (Kirkby et al., 2016).

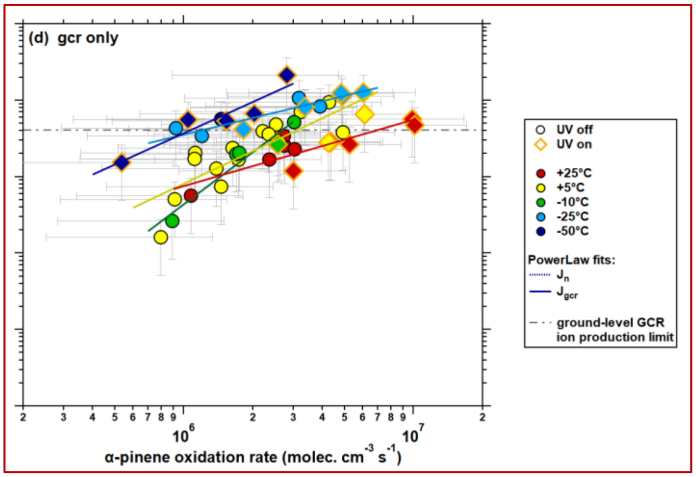
During some stages, the UV light was also turned on to study its effect on the oxidation chemistry by comparing the results with (06:00 – 08:20 UTC in Fig. 1) and without (03:09 – 05:41 UTC in Fig. 1) photochemical reactions under otherwise identical conditions. The particle formation sequence was then repeated at various concentrations of α-pinene and different temperatures over the range of atmospheric interest. In the data analysis, we assume that the particles observed at 1.7 nm mobility diameter are stable against evaporation and serve as a valid proxy for new-particle formation in the chamber.

Figure S3: This was discussed extensively across several paragraphs. I think it would make sense to make this a main-text figure since there are currently 7 main-text figures, which is not overly long for ACP.

We agree that this would improve the general readability and the clarity of the paper. We have moved this figure to the main text accordingly.

Figure 7, panel d. The fit line for -50 C seems to be incorrect.

We have changed the fit line accordingly.



L594: I'm not sure what "avoiding any classification" means here.

This phrase refers to the different HOM definitions in the past as well as the different volatility classes, which are notable influenced by instrumental (*e.g.,* ionization technique) and environmental (*e.g.,* temperature) conditions. As these effects are mentioned in the following sentences, we removed the phrase to avoid confusion.

Figure 7(c) shows the neutral particle formation rates at 1.7 nm (J_{n}) and Fig. 7(d) the galactic cosmic ray particle formation rates ($J_{\mathrm{gcr}} = J_{\mathrm{n}} + J_{\mathrm{iin}}$) as a function of the α-pinene oxidation rate (AP^{T}_{oxrate}). This representation accounts for the change in the oxidation rate of α-pinene with respect to temperature and is independent of the concentration of the oxidation products and their uncertainties in detection by the instrument as well as the HOM definition and the volatility classification.

Figure S5: Make this a main figure too?

We do not consider this necessary because this figure does not contain any information needed to understand the main text and allows comparison to literature to a limited extent only.

L638: "seem" should be "seems"

The sentence has been modified as suggested:

Furthermore, no photochemical reaction (degradation) seems to affect the total HOM yield.

Responses to anonymous referee #2

This manuscript investigates the effect of temperature on the molecular composition of α-pinene oxidation products and new-particle formation rates. As far as I know, this is to date the most systematic study of the temperature dependency of pure organic nucleation and the underlying chemical processes. The manuscript is generally well written. I think it can be accepted for publication after the authors address the following comments and suggestions.

1. Section 3.2: The authors show that the HOM yield decreases by about an order of magnitude from 6.2% to 0.7% from 25 degree C to -50 degree C. However, Quéléver et al. (2019), which is cited in this paper, showed a much stronger temperature dependence of HOM yields. They reported that the HOM yield decreased from 5.2% at 20 degree C to 6.3×10^{-3} % at -15 degree C. What causes this tremendous discrepancy?

Can you add a discussion of the reasons?

This is a good point and we believe that the discrepancy arises from a combination of differences in the experimental and instrumental conditions between the two studies. Before we discuss these differences we first want to point out once more that the yield is calculated from the HOM concentration measured with the nitrate CI-APi-TOF. It is important to note that the HOMs need at least 6 oxygen atoms (Fig. S1); otherwise the nitrate ionization scheme cannot efficiently detect them.

Due to the height of the reaction barrier, the unimolecular reaction (autoxidation) of the RO_2 radicals (H-shift) proceed at much slower rates at low temperatures, while the bimolecular termination of the radicals is much less affected by the temperature (Ziemann and Atkinson, 2012; Frege et al., 2018). Therefore, at cold temperatures, there is a higher chance that an RO_2 radical will be lost before it reaches a high oxygenation and forms a HOM that can be detected by the nitrate CI-APi-TOF. Besides the termination reactions, relevant loss mechanism of RO_2 radicals are wall loss and uptake on particles. Especially under cold conditions it becomes more likely that organic molecules with less than 6 oxygen atoms can condense on pre-existing or newly formed particles, due to their substantially reduced volatility. If this is the case, they will not reach an oxidation level that enables them to be detected by the CI-APi-TOF. In other words, the yield at cold temperatures drops dependent on the condensation sink.

Quéléver et al. (2019) use a 5 m³ Teflon bag chamber (AURA) in a batch mode without internal mixing, while this study was performed in a 26 m³ electropolished stainless-steel chamber (CLOUD) in a continuous flow mode with turbulent mixing induced by the mixing fans. Therefore, the chamber wall loss is almost comparable: ~ 10^{-3} s^{-1} in the AURA chamber; ~ $2.3\cdot10^{-3}$ s^{-1} in CLOUD. However, Quéléver et al. (2019) use a substantial higher α-pinene precursor concentration by more than a factor of 10 compared with CLOUD. This results in a much higher condensation sink for RO_2 radicals and HOMs to particles in the ACCHA experiments (~ $1\cdot10^{-1}$ s^{-1}) compared to the CLOUD chamber experiments (~ $2.3\cdot10^{-3}$ s^{-1}) at cold temperature. Also, the lack of internal mixing can lead to much higher condensation loss in a so-called reaction plume than derived by the particle measurements and leads to a much higher variance, see Dada et al. (2020). Therefore, the HOM yield variation with temperature can differ significantly with the conditions inside the experiment chamber.

Another difference between the two studies is the design of the sampling probe. At CLOUD a core sampling system was used, which was not deployed by Quéléver et al. (2019) and results in higher sampling line losses. While some of the HOM might be volatile enough not to be lost in the sampling line at warm temperatures, the same/similar HOM might stick more efficient to the sampling line at cold temperature. This effect can also cause a bias towards lower determined yields at cold temperatures.

We added this information in the main text to line 239,

A fraction of 8.5 standard liters per minute (slm) of the total flow in the inlet line (40 slm) is sampled from its center. This set-up minimizes the section length to 30 cm that transports the sample to the instrument at the smaller flow rate, reducing the sampling loss rate of HOMs to less than 30 %.

and to line 393, to draw the reader's attention to this crucial characteristic.

Note that the condensation sink in the CLOUD chamber is lower than in other chamber experiments, where similar experiments have been conducted.

Moreover, we added a direct discussion to line 477,

However, Quéléver et al. (2019) reports a much stronger temperature dependence of the HOM yields with decreasing temperature, which may result from a combination of differences in the experimental and instrumental conditions between the two studies. It is important to note that the HOMs require at least 6 oxygen atoms (Fig. S1); otherwise, the nitrate ionization scheme cannot fully detect them. The unimolecular reaction of the RO_2 radicals proceed at much slower rates at low temperatures, due to the height of the reaction barrier, while the bimolecular termination of the radicals is much less affected by the temperature (Ziemann and Atkinson, 2012; Frege et al., 2018). Therefore, at low temperatures, there is a higher chance that an RO_2 radical will be lost before it reaches a high oxygenation and forms a HOM that can be detected by the nitrate CI-APi-TOF. Besides the termination reactions, relevant loss mechanism of RO_2 radicals are wall loss and uptake on particles. Especially under cold conditions, it becomes more likely that organic molecules with less than 6 oxygen atoms can condense on pre-existing or newly formed particles due to their reduced volatility and can thereby increase the condensation sink compared to high temperatures. As a result, the HOM yield drops significantly depending on the condensation sink, which tends to result in lower determined yields, especially at low temperatures.

2. Figure 6: The authors mentioned that “the highest and lowest bin are overflow bins”. How do you treat the yields in the volatility bins outside the range of this figure? Specifically, did you add the yields in all volatility bins < -11 to the bin of -11, or did you simply neglect these bins with the lowest volatility? I suggest that the author add some inserts or some more panels to illustrate the volatility distribution of ULVOC at even lower volatility bins. I speculate that at -50 degree C the volatility distribution of ULVOC could extend to a bin much lower than -12. This may help to explain why the NPF rates at -50 degree C are significantly larger than those at warmer temperatures even for the same ULVOC concentration (Fig. 7b).

The concentrations in the bins of lower volatilities C* < -11 are added to the last bin shown in the figure. Therefore, no condensable material in lower bins is neglected. However, in the revised version of Fig. 6 we have added more information about the ULVOC range. Since the detection efficiency of the nitrate CI-APi-TOF (LOD ≤ $5\cdot10^4$ molecules$\cdot$cm^{-3}) is below the minimum concentration shown on the y-axes of the figure, there are also non-zero bins corresponding to lower volatility that cannot be seen. However, the cumulative sum takes these bins into account and is therefore slightly larger than the first visible bin with the lowest volatility shown in the figure.

Also, why does PTR3 detect many ELVOC compounds under -10 degree C, but much fewer (or even none) under -25 degree C and -50 degree C?

This effect can very likely be attributed to different sampling lines that were used for the PTR3. During the CLOUD12 campaign (+25 °C; -25 °C) a longer inlet line with some bends was used, while a straight sampling line was applied during CLOUD13 (+5; -10; -50 °C). The straight line lead to lower sampling line losses for HOMs and ELVOCs. At temperatures above -10 °C, the PTR3 cannot detect ELVOCs, since only HOMs with an O/C > 0.9 belong to this volatility class and the PTR3 ionization scheme is not suitable to detect these (Fig. S1). The ELVOCs detected at -10 °C and below are close to the LOD of the PTR3 instrument ($8\cdot10^5$ molecules$\cdot$cm^{-3}). Moreover, the overall α-pinene reaction rate at -10 °C ($3.1\cdot10^6$ molec.$\cdot$cm$^{-3}\cdot$s^{-1}) is slightly higher compared to -25 °C ($2.3\cdot10^6$ molec.$\cdot$cm$^{-3}\cdot$s^{-1}) or -50 °C ($2\cdot10^6$ molec.$\cdot$cm$^{-3}\cdot$s^{-1}), which leads to a higher ELVOC yield and concentrations above the detection limit of the instrument. Since the ELVOC range at -10 °C is completely covered by the CI-APi-TOF within its uncertainties, we do not expect any significant change to the cumulative sum at -25 °C, while at -50 °C the PTR3 shows higher concentrations of ELVOCs than the CI-APi-TOF.

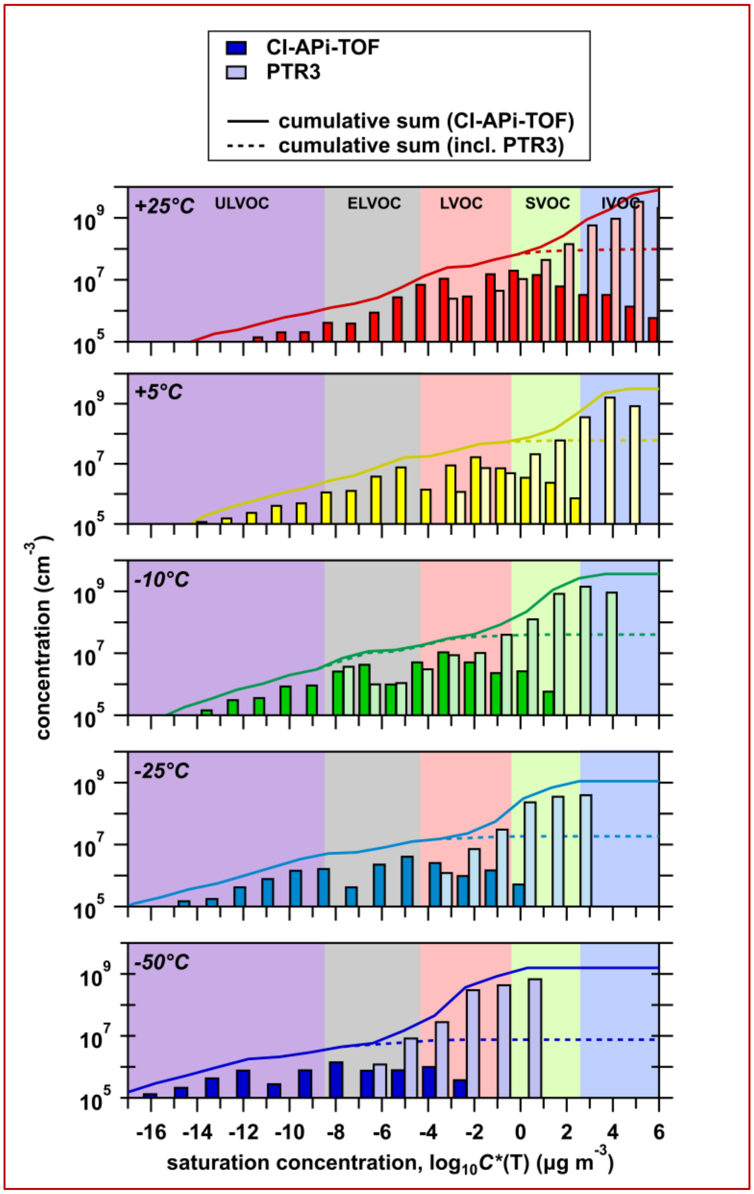


Figure 6: Volatility distribution of the measured oxidation products for five representative temperatures.

The mass concentration and volatility distributions of HOMs shown here are at the same α-pinene oxidation rates $(2-3\cdot10^6\ \mathrm{molecule\cdot cm^{-3}\ \cdot s^{-1}})$ and run conditions as data shown in Fig. 4. The summed HOM concentration of each volatility bin is divided into the nitrate CI-APi-TOF (dark color) and the PTR3 instrument (light color), respectively. Each volatility bin is defined at 300K, shifted and widened according to their corresponding temperature. The solid lines for each temperature represent the cumulative sum of the volatility bins of both instruments towards higher volatility, while the dashed line represents the nitrate CI-APi-TOF only. HOMs detected by the nitrate CI-APi-TOF (LOD ≤ $5\cdot10^4$ molecules·cm^{-3}) below $1\cdot10^5$ molecules·cm^{-3} are added to the cumulative sum. This results in slightly higher concentrations of the cumulative sums when compared with the first visible bin. The color bands in the background indicate the volatility regimes as in Donahue et al. (2012) and Schervish and Donahue (2019).

3. Section 3.5, Line 588-589: The NPF rates under ion-free conditions still have a large spread. Particularly, the NPF rates at -50 degree C are still significantly larger than warmer temperatures. I guess the ULVOC distribution I mentioned in my last comment might be a possible reason.

We agree with the referee that Fig. 7b indicates a larger spread for neutral (ion-free) compared with GCR conditions. The reason for this difference could be related to the variability of the volatilities within the ULVOC class. Under GCR conditions, it seems, that the ion stabilizes the nucleating cluster efficiently. Therefore, the cluster growth does not depend strongly on the exact volatility of an added ULVOC molecule.

Under ion-free condition, nucleating clusters in the pure biogenic new-particle formation are generally less stable against evaporation. Therefore, the probability that a cluster grows, due to an arriving molecule is strongly dependent on its volatility compared to the GCR case. Conceptually, the evaporation rate of a cluster containing two different ULVOC monomers will be related to the average volatility of those two monomers. We consider the ULVOC range to be the volatility range where it is increasingly likely that a cluster will grow, not evaporate, and thus nucleate. However, we estimate that the nucleation rate will still likely be a function of volatility within the ULVOC (and partially the ELVOC) range. Additionally, the bin assignment is uncertain by one bin (a factor of 10 in volatility). For the GCR case it is also possible that the stabilizing effect of an ion essentially shifts the relevant volatility range by some number of bins (*e.g.*, the kinetic nucleation rate at a ULVOC concentration of $1 \cdot 10^6$ molecules$\cdot$cm^{-3} would be approximately 300/s). However, the ion effect is not considered in the VBS model (*i.e.*, we do not shift the bins due to the presence of ions), which could result in a greater uncertainty (larger spread) at warm temperature, while this effect is less apparent at colder temperatures. This means that the same ULVOC concentration can nucleate less in warmer temperatures and in the absence of ions compared to GCR conditions.

One additional point to consider is that the nucleation rates under neutral conditions, especially at warmer temperatures, are low, so the data are close to the lower detection limit of the measurable formation rates in the chamber (see Dada et al. (2020) for more information about uncertainties in calculating the nucleation rates). Also, the effect of temperature on the operation of condensation particle counters including the particle size magnifier is poorly quantified (Wimmer et al., 2015). This could explain at least some of the scatter in the data under ion-free conditions.

In conclusion, the volatility distribution within the ULVOC class matters especially for the neutral conditions. Ideally, all lines of the nucleation rates for the different temperatures would coincide into a single line in Fig. 7b. Nevertheless, compared with panel a (total HOM concentration) the use of ULVOC concentration in panel b indicates that ULVOC is a much better description of the nucleating species than total HOMs. However, as the referee points out, even within the ULVOC class the exact volatilities can matter.

We have added the information to section 3.5; starting at line 587:

The evaporation rate of a cluster containing two ULVOCs will conceptually be related to the average volatility of those two molecules. Due to the sufficiently low saturation vapor pressure, we consider the ULVOC range to be the volatility range where it is increasingly likely that a cluster will grow, not evaporate, and thus nucleate. This is consistent with the result shown in Fig. 7(b) as it unifies the new-particle formation rates at all temperatures and shows that the ULVOC concentration provides a better proxy compared to the total HOM concentration. Ideally, all lines of the nucleation rates for the different temperatures would coincide into a single line in Fig. 7b. However, the nucleation rate will still likely be a function of volatility within the ULVOC (and partially the ELVOC) range.

And to line 593:

Thus, we estimate that the bin assignment is uncertain by about one bin (a factor of 10 in volatility). Further, the stabilizing effect of ions is not considered in the VBS model. Under ion-free condition, the pure biogenic nucleating clusters are generally less stable against evaporation. It is possible that the stabilizing effect of an ion essentially shifts the relevant volatility range by some number of bins and results in a larger uncertainty at warm temperatures, while this effect is less apparent at colder temperatures in absence of any ions for the same ULVOC concentration. The probability that a cluster grows under ion-free conditions, due to an arriving molecule, is strongly dependent on its volatility compared to GCR conditions. Therefore, the exact volatility distribution can also be important within the ULVOC class, especially for the neutral conditions.

And to line 600:

In addition to the poorly quantified effect of temperature on the operation of condensation particle counters, including the PSM (Wimmer et al., 2015), another point to consider is that the new-particle formation rates under ion-free conditions, especially at warmer temperatures, are low. Due to very low particle concentrations in the chamber, the data are close to the lower detection limit of the measurable formation rates. Both factors lead to a higher uncertainty in the nucleation rate calculation (Dada et al., 2020).

4. Figure 7: In panels a and c, as temperature decreases, the nucleation rates remain roughly unchanged from 25 degree C though 5 degree C to -10 degree C, but increase sharply at lower temperatures. Any reasons?

Please see also the reply to the previous question. The sharp increase of up to two orders of magnitude in nucleation rate at temperatures lower than -10 °C only applies to neutral conditions (Fig. 7c), while under GCR conditions (Fig. 7d), the increase is much smaller (less than 1 order of magnitude). However, it should be noted that the nucleation rate under GCR conditions is also limited by the ion pair production rate in the CLOUD chamber (dark gray dash-dotted line in Fig. 7). At low temperatures, the neutral and GCR nucleation rates are almost the same, while the difference between the two conditions increases sharply with temperature, which is much easier to recognize from Fig. 7a. This reflects the increased stability of the neutral clusters against evaporation without any stabilizing agent (*e.g.,* ions) at low temperatures and the strong sensitivity of the pure biogenic nucleation to environmental conditions and the concentration of ions (Kirkby et al., 2016).

The non-linear behavior of the nucleation rates with temperature can be explained by the increased concentration of LVOCs at lower temperatures (Fig. 6). Due to the strong reduction in volatility, also first-order oxidation products (OVOCs) may enhance nucleation and certainly will take part in the initial growth of nucleation cluster at much smaller cluster sizes, while their oxidation rate is much less affected by the temperature compared to the autoxidation rate of HOMs.

We also have added this discussion to section 3.5; starting at line 600:

While there is no significant change in the new-particle formation rate from +25 °C to -10 °C, a sharp increase of up to two orders of magnitude in J_n occurs at lower temperatures. This non-linear behavior of the nucleation rates with decreasing temperature can be explained by the increased stability of the neutral clusters against evaporation without any stabilizing agent (*e.g.,* ions), along with the strong temperature shift of the volatility classes. At low temperatures, more products fall in the ULVOC range and the increased concentration of LVOCs may enhance nucleation and certainly growth (Fig. 6). Due to the strong reduction in volatility, also first-order oxidation products (OVOCs) will take part in the initial growth of nucleating clusters at much smaller cluster sizes, while their oxidation rate is much less affected by the temperature compared to the autoxidation rate.

And to line 606:

This comparison shows that the neutral HOM clusters are relatively unstable and, especially at high temperatures, have significant evaporation rates, which demonstrates the strong sensitivity of the pure biogenic nucleation to environmental conditions and the concentration of ions (Kirkby et al., 2016).

5. As the author mentioned, this study covers a wide temperature range from ground level (25 degree C) to the upper-free troposphere (-50 degree C). However, the experiments are all conducted at a constant pressure of 5 hPa larger than surface pressure while the pressures in the real atmosphere can decrease from about 1000 hPa to about 100 hPa along with the temperature decrease. Will the pressure change significantly affect the temperature dependency of NPF rates? I would appreciate some discussions because this will affect how these results should be interpreted in the context of the real atmosphere.

This is an excellent question that has been brought up for decades by the community. While we would like to carry out experiments at reduced pressure, the practical challenge of operating the CLOUD chamber at reduced pressure has prevented us from doing so.

From the physical perspective, there are two points to consider that emerge from lower pressures (and densities): (a) the reduced molecule/cluster collision rate at 100 hPa compared to 1000 hPa and consequently (b) the reduced possibility to release the enthalpy of condensation (latent heat) of nanocluster by condensational growth and phase change reactions to the bath gas (Wedekind et al., 2008; Yang et al., 2019), which can lead to a reduced cluster stability.

The reaction rate to form nucleation clusters and particles depends on the collision rate between gaseous molecules and thus on their concentration in the air. Unlike volume mixing ratios, the total concentration is independent of the total pressure. Since our figures show nucleation rates as a function of total concentration, not volume mixing ratio, the effect on the collision rate of the condensable molecules is removed and should yield the same rate even under reduced pressure. However, the HOM concentration (*e.g.,* $1\cdot10^{7}$ molecules$\cdot$cm^{-3}) at ground pressure (~1000 hPa) is reduced linearly by a factor of 10 proportional to the pressure in the upper troposphere (~100 hPa) (*i.e.,* $1\cdot10^{6}$ molecules$\cdot$cm^{-3}).

Concerning the reduced cluster stability due to the reduced possibility to release the enthalpy of condensation; the size and number of heavy atoms in the nucleating clusters with two ULVOCs (mainly 20 carbon and several oxygen atoms) very likely allow for the efficient distribution of the additional energy of the cluster formation in form of vibrational and rotational excitation within the cluster. Based on considerations of simple unimolecular reaction theory (Rice-Ramsperger-Kassel-Marcus (RRKM) theory) the cluster formation rates should be well into the high-pressure limiting regime even at 100 hPa in the upper troposphere and so we do not anticipate a strong pressure dependence throughout the troposphere for biogenic nucleation involving HOMs.

In addition, if the reviewer is asking about change in nucleation rates due to increase in altitude, we think that other factors need to be considered as well, such as increased ionization capacity, decreased absolute humidity, decreased sinks and decreased availability of condensable gases for particle growth. Furthermore, also some chemical oxidation reactions are pressure dependent, but compared to their temperature dependence this is only a minor influence. Moreover, we believe that most of the HOMs are likely produced in the vicinity of their precursor sources, due to their high reactivity with oxidants, and then transported to higher altitudes by convective updrafts (Williamson et al., 2019) or are produced by second-generation chemistry. However, this is more or less speculative and needs to be examined more closely in the future.

This information is also added to section 3.5; starting at line 597:

Moreover, the representation of the nucleation rates as a function of the total concentrations, not volume mixing ratios, removes the influence of the pressure effects on the molecule/cluster collision rates at different atmospheric altitudes.

And to line 611:

While our experiments were carried out at ground-level pressure (~970 hPa), we expect that our concentration-based new-particle formation rates also apply to the upper troposphere within their uncertainties. The size and number of heavy atoms in the nucleating clusters containing two ULVOCs allow for the efficient distribution of the cluster formation energy in the form of vibrational and rotational excitation within the cluster. Therefore, we do not anticipate a strong pressure dependence throughout the troposphere for biogenic nucleation involving HOMs.

However, there might be other factors affecting the new-particle formation in the upper troposphere. These include the increased ionization capacity, the absolute humidity, the coagulation sink and the availability of condensable gases for particle growth. Also, some chemical reactions are pressure dependent, but compared to their temperature dependence this is mostly a minor effect. Moreover, we believe that most of the HOMs are likely produced in the vicinity of their precursor sources, due to their high reactivity with oxidants, and then transported to higher altitudes by convective updrafts (Williamson et al., 2019) or are produced by second-generation chemistry. However, this is speculative and needs to be investigated in future studies.

6. Line 477-479: This argument can be moved to the next section.

We agree that this sentence is a good introduction for the following section. We have moved the sentence as suggested.

7. Line 511: What are "other chemical systems"? Please clarify

We agree this formulation is indistinct. The phrase should indicate other condensable gases from organic sources, but also inorganic sources, such as sulfuric acid.

Consequently, the nucleation and initial growth rate may be limited for each individual HOM. Therefore, further support from other condensable gases, such as sulfuric acid and ammonia may be required to grow these clusters to larger sizes before they are lost to walls or pre-existing particles.

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