Reply to review by Anonymous Referee #1

We thank the reviewer for the constructive comments, which we have addressed in a point-by-point fashion below. We have modified the manuscript accordingly.

Kristensen et al. conducted dark ozonolysis of alpha pinene at different temperatures. They found at low temperatures the particle formation rates, particle number and mass concentrations were enhanced. The effects of temperature on particle-phase organic acids and dimer esters were also evaluated. They found the formation of less oxidized dimer esters increased at lower temperatures while the formation of the more oxidized species was suppressed. The link between the dimer ester and HOMs was also discussed. Though the topic of this study is timely and highly demanded in the area of new particle formation, the manuscript is well written, and the results are interesting, I have some major concerns to be addressed before the recommendation of publication. The first major concern is the experiments were conducted at not dry conditions but the effects of RH on results were missing when the authors interpreted the results. The second major concern is the formation pathway of esters proposed by the authors is not fully convincing and other possible formation pathways found by other research groups are not mentioned.

Major comments:

(1) Some statements in the Introduction section are not comprehensive and some related important references are missing, for example: Page 2, Line 50-51, Line 59-61: "higher yields with lower temperatures". This may not be absolutely right, as relative humidity, phase state, and the involved multiphase reactions all affect the SOA mass yields at different temperatures. For instance, von Hessberg et al. (2009) found the oscillatory negative temperature dependence under dry conditions while the positive temperature dependence under humid conditions when examining the SOA yield from the ozonolysis of beta pinene. Pathak et al. (2007) showed that the alpha pinene SOA yields showed a weak dependence on temperature in the 15◦C to 40◦C range, implying that the negative dependence of the partitioning on the temperature is counteracted by a positive dependence of the chemical mechanism (Tillmann et al., 2010). Page 2, Line 58: for organic compound partitioning, besides volatility and total particle mass, particle size and particle phase state also affect the partitioning and the gas-Pa½rticle equilibration timescale significantly (Shiraiwa&Seinfeld,2012; Liu et al., 2016; Li & Shiraiwa, 2019; Zaveri et al., 2014, 2020). Page 2, Line 72: Add Lawler et al. (2018). As far as I know, it is the first paper showing newly formed 20–70 nm particles showed enhancement in alkanoic acids from the perspective of ambient observations.

Reply: We are grateful for the additional information and references provided by the reviewer and we have added this to the manuscript in the following sentences:

Line 64-66: "The extent and timescale to which an organic compound undergoes partitioning is related to its saturation vapor pressure, the available particle mass (Kroll and Seinfeld, 2008) as well as particle size and particle phase (Shiraiwa and Seinfeld, 2012;Li and Shiraiwa, 2019;Zaveri et al., 2014;Zaveri et al., 2020)."

Line 73-79: "In addition to temperature-dependent condensation of oxidation products, temperature-modulated gas and multiphase chemistry has been suggested to influence SOA yields from VOC oxidation. Von Hessberg et al. (2009) observed oscillatory positive temperature dependence under dry conditions and suggested that SOA yields from β-pinene oxidation is governed to a higher degree by the temperature and humidity dependence of the involved chemical reactions than by vapor pressure of the formed oxidation products at different temperatures. Furthermore, Pathak et al. (2007a) observed that α-pinene SOA yields showed a weak dependence on temperature in the 15 °C to 40 °C range, implying that the negative temperature dependence of the partitioning is counteracted by a positive dependence of the chemical reaction mechanism."

Line 86-87: "In relation, Lawler et al. (2018) observed enhanced content of alkanoic acids in newly formed 20–70 nm particles in the Finnish boreal forest."

(2) Experiment section, Page 5, Line 187: As important results of this study are related to dimer esters and organic acids, what are the uncertainties in the estimations of the functional groups within SOA? The authors stated that due to lack of authentic standards,the dimer esters were quantified using DTAA as surrogate standard. What is the effect of using DTAA other than another surrogate, e.g., bis(2-ethylhexyl) sebacate (Ranney & Ziemann, 2016; Claflin et al., 2018)?

Reply: As the majority of the organic acids are identified and quantified using authentic standards, the uncertainties related to the reported data is expected to be low (< 20 %). With respect to dimer ester, a surrogate (DTAA) is used which shows good resemblance to the dimer esters both in chemical structure and UHPLC retention time (as the signal response is affected by eluent composition).

The following sentences has been added to the manuscript (Line 204-206): "The analytical uncertainty is estimated to be < 20 % for carboxylic acids. Due to lack of authentic standards, the dimer esters were quantified using DTAA as surrogate standard. DTAA was chosen due to its structural similarities with that of the dimer esters (dicarboxylic acid with ester functionality) as well as similar UHPLC retention time."

It is difficult to estimate the uncertainties associated with the use of surrogates without available authentic standards for comparison. Using bis(2-ethylhexyl) sebacate is not advisable when quantifying the dimer esters reported in the current manuscript as this compound is structurally and functionally very different from the dimer esters (i.e. contains no acid functionalities) and would thus result in a very different response in the UHPLC-MS system adding to significant uncertainties. With respect to the overall uncertainties related to reproducibility of the performed UHPLC-MS analysis we have added a new figure in SI comparing the UHPLC-MS results of experiments performed at similar conditions. The comparison show < 10 % variation between results from similar experiments. This has been added to the manuscript:

Line 283-284: "From comparison of repeated experiments (Exp. 2.1 - 2.3 and Exp. 3.1 - 3.3) the uncertainties related to the presented UHPLC/ESI-qTOF-MS results are estimated to be less than 10 %, Figure S3)."

(3) It is nice to show the various relative humidity values in Table 1 but the role of RH in the particle phase state, gas-particle partitioning, multiphase reactions (refer to the papers listed in Major Comment 1) and the concentrations of OH and HO2 radicals is not discussed in the manuscript, which could affect the interpretation of the experimental results. For example, Line 221, would the phase state also play a role (maybe a minor role though) making the maximum SOA mass reached slower at the lower temperature? Would the RH affect the detected concentrations of functional groups (Claflin et al., 2018)

in Sec. 3.3? As the OH scavenger seems not used, would the RH affect the HO2 concentrations and thus the competition with the RO2-RO2 reaction (Claflin et al., 2018; Simon et al., 2020)?

Reply: It is true that RH could affect the growth of SOA particles through changes of the particle viscosity as reported in Zaveri et al (2020) and consequently result in RH-modulated portioning of SVOCs to the particle phase. However, as shown in Table 1, the RH values reported for all experiments are relatively low (<20 %), even at -15 °C, and so are the differences in RH between experiments, thus we do not believe that these differences would have a significant effect. This is supported by Zaveri et al. (2020) stating that "The diffusivity within the aged α-pinene SOA remains appreciably slow even at 80% RH".
However, we have added the following discussion on the particle phase on condensation and evaporation of SVOCs to explain the results from temperature ramping experiments:

Line 370-382 "In contrast, cooling of the formed SOA particles in Exp.1.4 resulted only in a small 0.3 µg m-3 increase in organic acid concentration making up ~ 15 % of the reported 2 µg m-3 increase in SOA mass compared to the constant 20 °C experiment. These results indicates limited gas-to-particle phase condensation of the semi-volatile organic acids upon cooling the SOA. The current findings are in agreement with that of Zhao et al. (2019) who found that during cooling of α-pinene SOA particles the resulting mass growth was largely over predicted by the applied volatility basis set model. As suggested in Zhao et al. (2019) the observed limited condensation of semi-volatiles to SOA particles during cooling is likely attributed to an expected high particle viscosity at the relative low RH conditions of the performed oxidation experiments. Under these conditions, condensed SVOCs are likely confined at the near-particle-surface region thus impeding further partitioning of the gas-phase SVOCs (Renbaum-Wolff et al., 2013). In the current study, this is supported by the relatively small increase in organic acids (Fig. 8) as well as almost negligible increase in particle size (Fig. 7B) observed upon cooling the SOA particles from 20 °C to -15 °C. Also, SVOCs reside near the particle surface, this would indeed explain the effective evaporation of these compounds (i.e. the identified organic acids, Fig. 8) and subsequent reduction in particle size (Fig. 7B) observed in Exp. 1.5."

Furthermore, we have expanded section 3.5 in which the dimer ester formation is discussed to include formation pathways suggested by other research groups including reactions of stabilized Criegee intermediates with oxidation products and RO-RO2 reactions. As suggested by the reviewer the influence of HO2 + RO2 competition is also discussed:

Line 459-469:"The RO2–RO2 reaction is expected to compete with the reactions of RO2 with HO2 radicals. In the absence of an OH-scavenger, the performed oxidation experiments will include the formation of OH-radicals from the gas-phase reaction of α-pinene with O3. The formed OH-radicals reacts readily with O3 yielding HO2-radicals available for RO2-HO2 reactions. As both reactions (O3 + α-pinene and O3 + OH) have a positive temperature dependence, the formation of HO2 and its subsequent reaction with RO2 is expected to increase at the higher reaction temperatures. In Simon et al. (2020) the higher concentration of HO2 leads to an increased competition with the RO2-RO2 self-reaction, which reduced the formation of HOM dimers but increased HOM monomers. In the current study, however, reduction in the concentration of dimer esters due to increased RO2-HO2 competition at higher temperatures is only observed in the case of the low O:C dimer esters. In the case of the higher O:C dimers, it appears that a suppressed competition of HO2 with RO2 at the lower temperatures is less important compared to the reduced availability of more oxidized species for dimer ester formation. "

(4) Figure 9: Is the reaction with RO2 radicals the only termination step? As far as I know, additional termination reactions of CI include their reactions with aldehydes (RC = O), alcohols (ROH), carboxylic acids (ROOH) to form hydroperoxy esters and secondary ozonides and water vapor to form hydroxy hydroperoxides (Claflin et al., 2018; Zeng et al., 2020). Claflin et al. (2018) stated that the only known

gas-phase mechanism for forming esters in their experiments was the reaction of CI with carboxylic acids under dry conditions. Claflin et al. (2018) showed that particle-phase oxidation of carbonyl groups may contribute significantly to the formation of both carboxyl and ester groups in the SOA. Müller et al. (2008) have suggested that the esters they identified by mass spectrometry in SOA formed by α-pinene ozonolysis might be formed by an unknown gas-phase radical mechanism. Could the authors give the reasons why other pathways can be excluded in Fig. 9? As the formation of esters via particle-phase decarboxylation of diacyl peroxides as proposed by Zhang et al. (2015) requires an ionic aerosol matrix such as aqueous ammonium sulfate, could the authors convince the readers the mechanisms proposed by Zhang et al. (2015) indeed happen in their experiments without the presence of inorganic seeds?

Reply: We agree with the reviewer that the mechanism proposed by Zhang et al. (2015) is unlikely in the absence of an ionic aerosol matrix. Thus, we have rewritten the discussion of dimer ester formation to include multiple formation pathways suggested by other research groups including reactions of CI with oxidation products with various functionalities. As we cannot exclude other formation pathways (i.e. sCI reactions) Figure 9 has been revised to the possibilities of different reaction pathways.

Section 3.5 (revised): "Gas-phase formation of dimer esters from α-pinene ozonolysis has been suggested to proceed through the reaction of stabilized Criegee Intermediate (sCI) with carboxylic acids resulting in the formation of a class of ester hydroperoxides, α-acyloxyalkyl hydroperoxides (α-AAHPs) (Zhao et al., 2018a;Kristensen et al., 2016). In relation, Claflin et al. (2018) stated that the only known gas-phase mechanism for forming esters in their experiments was the reaction of sCI with carboxylic acids under dry condition. As the reactions of sCI are expected to be temperature-dependent this could explain the lower formation of some of the identified dimer esters (the high O:C dimers) in the current study. Also, as suggested by Kristensen et al. (2017), temperature-modulated condensation of the gas-phase carboxylic acid precursors may also contribute to the observed temperature effects on the formation of dimer esters. As the condensation of the carboxylic acids is vapor pressure dependent it is expected that the less volatile (i.e. more oxidized) species are more effectively depleted from the gas phase at lower temperatures hence hindering their gas-phase reactions with the sCI and reducing formation of the more oxidized dimer esters. Consequently, at the lower temperatures the formation of dimer esters is more likely to proceed through reactions of sCI with the more volatile and less oxidized carboxylic acids species thus potentially explaining the observed increased formation of the low O:C dimer esters in the 0 °C and -15 °C experiments. In addition to the observed temperature dependence of the low O:C dimer esters an increased stability of hydroperoxide-containing species in SOA particles is expected at lower temperatures (Zhao et al., 2018a).

While the formation of α-AAHPs through sCI + carboxylic acids is a plausible mechanism related to many of the dimer esters identified in the current study, this may not be true for all species. In particular, studies on the MW 368 dimer ester (pinonyl-pinyl ester, $C_{19}H_{28}O_7$) and MW 358 (pinyl-diaterpenyl ester, $C_{17}H_{26}O_8$) conclude that the chemical structures of these esters do not include hydroperoxide *functionalities (Beck and Hoffmann, 2016;Kahnt et al., 2018). Consequently, Kahnt et al. (2018) recently suggested an alternative mechanism for the formation of these species involving gas-phase formation and subsequent rearrangement of unstable C19H28O11 HOM species formed from RO2 + R'O → RO3R reaction of an acyl peroxy radical and an alkoxy radical. Specifically, Kahnt et al. (2018) explains that the C19H28O11 HOM species decompose through the loss of oxygen or ketene resulting in the formation of the MW 368 dimer ester (pinonyl-pinyl ester, C19H28O7) and the MW 358 dimer ester (pinyl-diaterpenyl ester, C17H26O8), respectively. Interestingly, in the current study, the particle-phase concentration of the MW 368 dimer ester increases at lower temperatures, while the opposite is seen for the MW 358 dimer esters (Fig. 5), thus indicating significant differences in the mechanism responsible for the formation of these particular dimer esters. In accordance to the mechanism suggested by Kahnt et al. (2018), the different responses to temperature of the two dimer esters could be explained by (1) a temperature modulated formation of the alkoxy radicals related to the 5- and 7-hydroxy-pinonic acid involved in the formation of the two C19H28O11 HOM species decomposing to the MW 368 and MW 358 dimer esters, respectively; or (2) temperature-dependent decomposition and rearrangement of the C19H28O11 HOM species suppressing the more complex decomposition and rearrangement mechanism in which carbon-containing entities (e.g. ketene) is expelled from the HOM.*

However, these explanations are not supported by the temperature ramping experiments performed herein indicating that the formation of the dimer esters is determined by the initial reaction temperature and remains relatively unaffected by heating or cooling. In addition, although accounting for the differences in the temperature response of the MW 368 and MW 358 dimer esters, and to some extent the increased particle concentration of many higher carbon number dimer esters (i.e. C19 species, Fig 6A), a temperature-modulated decomposition does not solely explain the observed decrease in relative yields of dimer esters with higher oxygen number (Fig. 6B). To explain this, the formation and subsequent decomposition of more oxidized HOMs need to be considered as possible precursors for the more oxygen-rich dimer esters.

A detailed study on the formation of HOMs during the ACCHA campaign is presented by Quéléver et al. (2019). Here, significantly lower (by orders of magnitude) HOM gas-phase concentrations are observed in -15 °C experiments compared to 20 °C experiments. As the HOMs form through autoxidation of RO2, low temperatures and thus decreased autoxidation is expected to result in lower formation of HOMs, with reduced formation of the more oxygenated species. Interestingly, however, Quéléver et al. (2019) observed no correlation between the degree of oxidation (i.e. O:C-ratio) of the identified HOMs and the magnitude by which the formation of these was reduced at lower temperatures. This is in contrast to the observed temperature effects on the formation of the identified dimer esters presented in the current study (Fig. 7), and thus rule out the formation and decomposition of more oxidized HOMs as mechanism for the formation of more oxygen-rich dimer esters. In Quéléver et al. (2019), one possible interpretation of the observed temperature effect on HOMs is that the rate-limiting step in the autoxidation chain takes *place already in the first steps of autoxidation. This is supported by the observed decreased concentration of dimer esters with a higher number of oxygen atoms, which also indicates that the formation of the identified dimer esters could proceeds through reaction of products from RO2 autoxidation. The involved oxidation state of these products may vary depending on the degree of autoxidation undertaken by the RO2 radical as well as the radical termination of these including unimolecular processes leading to loss of OH or HO2 or bimolecular reactions with NO, HO2 or other RO2 resulting in the formation of ROOR dimers. As the autoxidation as well as the bimolecular reactions of peroxy radicals are temperature-dependent, these processes may provide explanation for the observed response to temperature of the different dimer esters. Claflin et al. (2018) showed that the autoxidation and radical termination reactions of the Criegee Intermediate RO2 radicals may results in a plethora of different products covering a range of oxidation states and functionalities; including multifunctional RO2 radicals, hydroperoxide, carbonyl, alcohol, carboxylic and peroxycarboxylic acid, dialkyl and diacyl peroxides. Of these, carbonyls, alcohols and carboxylic acids reacts readily with sCI resulting in dimeric compounds such as secondary ozonides, α-alkoxyalkyl hydroperoxides (AAAHs), and α-AAHP, respectively (Chhantyal-Pun et al., 2018;McGillen et al., 2017;Khan et al., 2018;Claflin et al., 2018). In addition, gas-phase RO2–RO2 reactions have been proposed as conceivable mechanism for the formation of dimers from α-pinene ozonolysis (Claflin et al., 2018;Zhao et al., 2018b). Here, RO2 produced from the isomerization or decomposition of Criegee Intermediates are suggested to participate in RO2-RO2 reactions resulting in dialkyl or diacyl peroxides. The formation of dimer esters through reactions of RO2 is supported by an observed decrease in dimer esters concentrations at higher levels of NOx in ambient air measurement in Hyytiälä, Finland (Kristensen et al., 2016) and supports the formation proposed by several studies (Ehn et al., 2014;Berndt et al., 2018;Zhao et al., 2018b) involving RO2 cross-reactions as likely route of gaseous dimer formation. The RO2–RO2 reaction is expected to compete with the reactions of RO2 with HO2 radicals. In the absence of an OH-scavenger, the performed oxidation experiments will include the formation of OH-radicals from the gas-phase reaction of α-pinene with O3. The formed OH-radicals reacts readily with O3 yielding HO2-radicals available for RO2-HO2 reactions. As both reactions (O3 + α-pinene and O3 + OH) have a positive temperature dependence, the formation of HO2 and its subsequent reaction with RO2 is expected to increase at the higher reaction temperatures. In Simon et al. (2020) the higher concentration of HO2 leads to an increased competition with the RO2-RO2 self-reaction, which reduced the formation of HOM dimers but increased HOM monomers. However, in the current study, reduction in the concentration of dimer esters due to increased RO2-HO2 competition at higher temperatures is only observed in the case of the low O:C dimer esters. In the case of the higher O:C dimers, it appears that a suppressed competition of HO2 with RO2 at the lower temperatures is less important compared to the reduced availability of more oxidized species for dimer ester formation. We propose that, although different in chemical structures and O:C-ratios, dimer esters and HOMs may be linked via their formation mechanisms, both involving RO2 autoxidation. The particle-phase dimer esters* *and the gas-phase HOMs may merely represent two different fates of the RO2 radicals. If conditions are favorable and efficient autoxidation takes place, this will result in the formation of HOMs, which by the definition recommended by Bianchi et al. (2019) in this case means any molecule with 6 or more oxygen atoms that has undergone autoxidation. On the other hand, dimer esters could be the product of RO2 cross reactions or reactions of sCI with the autoxidation termination products with O:C ratios influenced by the number of potential autoxidation steps undertaken by the involved RO2 species prior to reaction or termination (Fig. 9). Whether the formation of dimer esters proceeds through ROOR dimer formation from RO2-RO2 cross reactions or through monomeric compounds reacting with sCI is yet to be determined.*

Lastly, thermodynamics need to be considered as a possible explanation for the observed temperature responses of the high and low O:C dimer esters. As reported in Kristensen et al. (2017), the identified dimer esters span across a wide range of volatilities. Here, many of the low O:C dimer esters may be sufficiently volatile to allow considerable fractions to exist in the gas phase at high temperature. Consequently, the increased particle-phase concentration observed at the lower temperatures may solely be attributed to enhanced gas-to-particle phase partitioning of these species. Supporting this, Mohr et al. (2017) identified dimeric monoterpene oxidation products (C16–20HyO6–9) in both particle and gas phases in ambient air measurements in the boreal forest in Finland."

Minor comments:

(1) P2, Line 55: Cite a review paper (e.g., Nizkorodov et al., 2011; Noziere et al., 2015) after "...peroxides and peroxy-acids".

Reply: The suggested papers are now cited as suggested.

(2) P5, Line 163: Does the temperature gradually and continuously change or the system stay for some time at each temperature? In Figure S1, for the panel for Exp. 1.5, move "Temp" closer to the temperature line instead of the RH line.

Reply: The temperature changes gradually and continuously as evident from Figure S1 (Exp. 1.4 and 1.5). This is now stated in the sentence (Line 178-180): "In both experiments the gradual and continuous temperature ramping was initiated approximately 40 min after the injection of α-pinene, hence before the SOA formation plateaued."

Reply: Figure S1 (Exp. 1.5) has been changed as suggested.

(3) Was OH scavenger used in the experiments?

Reply: No. This is now clarified in the manuscript. The following sentence has been added (Line 186): "All experiments were performed without the addition of an OH-scavenger to the chamber."

(4) Reference list: P19, Line 547: The title of Jensen et al. (2020) is Temperature and VOC concentration as controlling factors for chemical composition of alpha-pinene derived secondary organic aerosol:

https://www.atmos-chem-phys-discuss.net/acp-2020-100/. P21, Line 613-614: Peräkylä et al. has been published in ACP.

Reply: This has been corrected.

Reply to review by Anonymous Referee #2

We thank the reviewer for the constructive comments, which we have addressed in a point-by-point fashion below. We have modified the manuscript accordingly.

General comments: This work by Kristensen et al. studied ïA¸a¸-pinene SOA formation and composition at different temperatures (20ï´ C˘rC, 0ï´ C˘rC, and -15ï´ C˘rC) in a chamber facility. This study examined organic acids and dimer esters in the SOA composition through off-line LC-MS analysis. These chemicals were estimated to account for substantial fractions (15 – 30% and 4 – 11%, respectively) of total SOA mass. Dimers with lower O:C ratios (< 0.4) were found to increase at lower temperatures. In temperature ramping experiments, SOA mass and composition were found to be governed mostly by initial temperatures. Overall, the manuscript is well written and demonstrates new findings regarding temperature effects on ïA¸a¸-pinene SOA composition on the molecular level, especially at very low temperatures. But a few major concerns need to be addressed before this manuscript can be considered publishing.

Specific comments:

1. This manuscript has several companion papers published, as mentioned in the Introduction. If comparisons will be made with these papers, I suggest adding a section in the Results that briefly describes the main findings of these companion studies relevant to this work would be helpful.

Reply: As the comparison with companion papers are very limited in the manuscript confining only to a short reference to the findings by Quéléver et al. (2019) in section 3.5 we do not believe that further descriptions of the findings of the companion papers are needed – especially considering the length of the manuscript in its current form.

2. Line 167 – 169. The influence of injection flow rate was not motivated clearly. Why did the authors think changing injection flow rate could affect the experiments? Without clear motivation, this part should be removed.

Reply: This has been removed as suggested by the reviewer.

3. What is the scientific basis that made the authors to use O:C ratios of 0.4 as the threshold? What if one chooses 0.5? Instead of using an arbitrary value, showing histogram as a function of O:C ratios (by 0.1 increment) might be better.

Reply: The value of 0.4 is derived from Figure 6 and is the O:C value above which all dimer esters show a decrease in concentration at -15°C compared to 20 °C. Unfortunately, this is not clearly stated in the manuscript. We have thus added a figure to the SI (Figure S5) showing dimer ester yields at -15°C relative to 20 °C (yield @ -15°C / yield @ 20°C) as a function of O:C-ratios and added a line showing how the 0.4 value (actually 0.38) is derived.

The following sentence has been added (Line 333-335): "Accordingly, the dimer esters are grouped based on their O:C ratios, with the more oxidized dimer esters having an O:C > 0.4; the O:C value above which all dimer esters show decreased concentration at the lower -15 °C compared to 20 °C (Figure S4)."

4. Line 290 – 297. The authors observed different results compared to Kourtchev et al. (2016). The explanation should be explained to some extent. For example, whether the higher SOA mass loading under higher VOC lead to condensation of SVOC, which as a result lower oligomer fraction, as a competing process with the mechanism presented by Kourtchev et al. (2016).

Reply: The comparison with Kourtchev et al. (2016) has been removed as the finding by Kourtchev et al. (2016) relates to the number of oligomeric compounds and not their concentrations, thus a direct comparison is not valid. However, we have added the following relating to Kourtchev et al. (2016):

Line 320-324: "In relation, Kourtchev et al. (2016) observed a positive relationship between temperature and oligomer fraction in aerosol samples collected at Hyytiälä in summer 2011 and 2014 but ascribed this to differences in the VOC emissions. However, the current study, indicates that temperature alone may influence the formation of dimeric compounds thus supporting to the ambient observation in Kourtchev et al. (2016)."

5. As direct comparisons were made for the LCMS measured organic acids and dimer esters between different temperature conditions, one would expect that the quantified concentrations are reproducible and the relative abundance between different conditions are reproducible as well. In the current form of the manuscript, the reproducibility or uncertainty range was not discussed and should be addressed in the revised manuscript (e.g., error bars on Figures 5 and 6 representative of reproducibility).

Reply: We agree with the reviewer in that the evidence of the reproducibility of the performed LCMS analysis is lacking in the current form of the manuscript. To remedy this, we have added a new figure in the SI comparing the LCMS results of experiments performed at similar conditions. The comparison shows < 10 % variation between LCMS results from similar experiments. This has been added to the manuscript:

Line 283-284: "From comparison of repeated experiments (Exp. 2.1 - 2.3 and Exp. 3.1 - 3.3) the uncertainties related to the presented UHPLC/ESI-qTOF-MS results are estimated to be less than 10 %, Figure S3)."

6. Line 312 – 317. The authors argue that higher O:C dimers are formed through RO2- RO2 reactions, followed by diacyl peroxide decomposition; while lower O:C dimers could be diacyl peroxides. However, it is not necessary that diacyl peroxides have lower O:C ratios than their decomposition products (loss of CO2). This argument needs to be better justified.

Reply: We agree with the reviewer and have removed the argument in question.

7. Section 3.4. After temperature ramping to 20 ï´ CˇrC or -15ï´ CˇrC, the SOA mass do not merge to the level in constant 20 ï´ CˇrC or -15ï´ CˇrC. The similar temperature effects have been studied in prior studies (Warren et al. 2009; Zhao et al., 2019). Zhao et al. (2019) provided some possible explanations for this behavior. The molecular results here, are likely better quantified and thus are in better position to explore more on the mechanistic explanation. However, it is missing from this section in the current form, except that the authors claimed the initial temperatures play a bigger role in final SOA mass.

Reply: We agree with the reviewer and have added a discussion on the results from temperature ramping:

Line 370-382 "In contrast, cooling of the formed SOA particles in Exp.1.4 resulted only in a small 0.3 µg m-3 increase in organic acid concentration making up ~ 15 % of the reported 2 µg m-3 increase in SOA mass compared to the constant 20 °C experiment. These results indicates limited gas-to-particle phase condensation of the semi-volatile organic acids upon cooling the SOA. The current findings are in agreement with that of Zhao et al. (2019) who found that during cooling of α-pinene SOA particles the resulting mass growth was largely over predicted by the applied volatility basis set model. As suggested in Zhao et al. (2019) the observed limited condensation of semi-volatiles to SOA particles during cooling is likely attributed to an expected high particle viscosity at the relative low RH conditions of the performed oxidation experiments. Under these conditions, condensed SVOCs are likely confined at the near-particle-surface region thus impeding further partitioning of the gas-phase SVOCs (Renbaum-Wolff et al., 2013).

In the current study, this is supported by the relatively small increase in organic acids (Fig. 8) as well as almost negligible increase in particle size (Fig. 7B) observed upon cooling the SOA particles from 20 °C to -15 °C. Also, SVOCs reside near the particle surface, this would indeed explain the effective evaporation of these compounds (i.e. the identified organic acids, Fig. 8) and subsequent reduction in particle size (Fig. 7B) observed in Exp. 1.5."

8. From the title, it appears linking HOMs with organic acids and dimer esters is a key subject for this study. However, the manuscript discussed very little on this connection (only Section 3.5). The results of the referred companion study using NO3-CIMS should be discussed more extensively. Further, it is true that at lower temperature, HOM formation via RO2 autoxidation is limited, bimolecular RO2 reaction is expected to increase. But this does not necessarily mean that RO2-RO2 dimer formation is going to be enhanced. How about RO2 + HO2 and RO2 + RO2 which lead to monomeric products? These two reactions are both temperature dependent and are likely more important than RO2 autoxidation (5-10%) and RO2+RO2 to ROOR (5 – 10%). Thus, the temperature effects on RO2 + HO2 and RO2 + RO2 could more likely govern the changes in RO2 autoxidation and dimer formation. It is a four-factor relationship, but only the two less dominant pathways are discussed. In addition, as pointed by the authors, RO2 + RO2 might only explain some of the dimer esters.

Reply: We agree with the reviewer that the title may be misleading as the discussion on HOMs in relation to organic acids and dimers is relatively brief in the manuscript. We have thus changed the manuscript title to capture the content in a more accurate manner: "The Aarhus Chamber Campaign on Highly Oxidized Multifunctional Organic Molecules and Aerosols (ACCHA): Particle Formation, Organic acids, and Dimer Esters from Alpha-Pinene Ozonolysis at Different Temperatures

In relation, we have expanded the section (now section 3.5) in which the dimer ester formation is discussed to include formation pathways suggested by other research groups including reactions of stabilized Criegee intermediates with oxidation products and RO-RO2 reactions. Also, as suggested by the reviewer the influence of HO2 + RO2 competition is also discussed.

Technical comments:

1. Line41. Add "(SOA)"followed by "secondary organic aerosol". With this change, the "secondary organic aerosol" at Line 45 could be removed.

Reply: This has been changed as suggested by the reviewer

2. Line 43 – 46. ïA˛ a˛ -pinene is also dominant OA source at other locations. For example, Zhang et al. 2018, 115, 2038, PNAS and Lee and Thornton et al., 2020, ACS Earth and Space Chem. (in press) show monoterpene SOA are the largest sources of PM in the southeastern US.

Reply: The following sentence has been added (line 49-50):"In addition, (Lee et al., 2020;Zhang et al., 2018) show that monoterpene SOA are the largest sources of particulate matter in the southeastern US."

3. Line 49. A new study (Zhao et al., 2019, 3, 2549, ACS Earth and Space Chem.) performed similar temperature-ramping experiments with compositional analysis like this work and should be added in this list and perhaps later discussion (Section 3.4).

Reply: A reference to the work by Zhao et al., 2019 has been added to the list.

4. Line 130 – 146. Are the suite of online instrumentation situated in the cold room as well? It should be provided and if not, potential influence caused by temperature variation should be discussed.

Reply: The following sentences has been added
Line 143-144: "Additional instrumentations are situated in air-conditioned (constant 20 °C) laboratory directly outside the cold room."
Line 158-160: "SMPS and PSM measurements were performed as close as possible to the cold room trough insulated tubing extending ~ 40 and ~ 10 cm from the cold room, respectively, thus minimizing residence time and potential influences caused by temperature variations."

5. Line 150 – 154. Two sentences have repeated texts. Please reword.

Reply: This has been corrected

6. Line 161. This sentence should clarify if the temperature ramping started before or after SOA formation reached plateau.

Reply: The sentence now reads (Line 178-180) : "In both experiments the temperature ramping was initiated approximately 40 min after the injection of α-pinene, hence before the SOA mass formation plateaued"

7. Section 2.1. Slight RH variations between different temperature conditions are shown in Table 1, but should also be mentioned (one sentence) in the description.

The following sentence has been added (Line 180-182) "Note that small variations in RH (< 25 %) are observed in between all conducted experiments arising from heating or cooling of the dry chamber air (Table 1)."

The Aarhus Chamber Campaign on Highly Oxygenated Organic Molecules and Aerosols (ACCHA): Particle Formation, Organic acids, and Dimer Esters from Alpha-Pinene Ozonolysis at Different Temperatures

~~The Aarhus Chamber Campaign on Highly Oxidized Multifunctional Organic Molecules and Aerosols (ACCHA): Particle Formation and Detailed Chemical Composition at Different Temperatures~~

K. Kristensen[1], L. N. Jensen[2], L. L. J. Quéléver[3], S. Christiansen[2], B. Rosati[2,4], J. Elm[2], R. Teiwes[4], H. B. Pedersen[4], M. Glasius[2], M. Ehn[3], M. Bilde[2]

[1]Department of Engineering, Aarhus University, 8000 Aarhus C, Denmark
[2]Department of Chemistry and iClimate, Aarhus University, 8000 Aarhus C, Denmark
[3]Institute for Atmospheric and Earth System Research – INAR / Physics, P.O. Box 64, FI-00014, University of Helsinki, Finland
[4]Department of Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark

Correspondence to: Kasper Kristensen (kasper.kristensen@eng.au.dk) and Merete Bilde (bilde@chem.au.dk)

Abstract

Little is known about the effects of low temperatures on the formation of secondary organic aerosol (SOA)~~SOA~~ from α-pinene. In the current work, ozone-initiated oxidation of α-pinene at initial concentrations of 10 and 50 ppb, respectively, is performed at temperatures of 20, 0 and -15 °C in the Aarhus University Research on Aerosol (AURA) smog chamber during the Aarhus Chamber Campaign on highly oxidized multifunctional organic molecules and Aerosol (ACCHA). Here, we show how temperature influences the formation and chemical composition of α-pinene-derived SOA with a specific focus on the formation of organic acids and dimer esters. With respect to particle formation, results show significant increase in both particle formation rates, particle number concentrations and particle mass concentrations at lower temperatures. In particular, the number concentrations of sub-10 nm particles were significantly ~~enhanced~~ increased at the lower 0 and -15 °C temperatures. Temperatures also affect chemical composition of the formed SOA. Here, detailed off-line chemical analyses show organic acids contributing from 15 to 30 % by mass, with highest contributions observed at the lower temperatures indicative of enhanced condensation of these semi-volatile species. In comparison, a total of 30 identified dimer esters were seen to contribute between 4 – 11 % to SOA mass. No significant differences in the chemical composition (i.e. organic acids and dimer esters) of the α-pinene-derived SOA particles are observed between experiments performed at 10 and 50 ppb initial α-pinene concentrations, thus suggesting a higher influence of reaction temperature compared to that of α-pinene loading on the SOA chemical composition. Interestingly, the effect of temperature on the formation of dimer esters differs between the individual species. The formation of less oxidized ~~(oxygen-to-carbon ratio (O:C) < 0.4)~~ dimer esters (oxygen-to-carbon ratio (O:C) < 0.4) is shown to increase at lower temperatures while the formation of the more oxidized ~~(O:C > 0.4)~~ species (O:C > 0.4) is suppressed, consequently resulting in temperature-modulated composition of the α-pinene derived SOA. Temperature ramping experiments exposing α-pinene-derived SOA to changing temperatures (heating and cooling) reveal that the chemical composition of the SOA with

respect to dimer esters is governed almost solely by the temperature during the initial oxidization and insusceptible to subsequent changes in temperature. Similarly, the resulting SOA mass concentrations were found to be more influenced by the initial α-pinene oxidation temperatures, thus suggesting that the formation conditions to a large extent govern the type of SOA formed, rather than the conditions to which the SOA is later exposed.

For the first time, we discuss the relation between the identified dimer ester and the highly oxidized multifunctional organic molecules (HOMs) measured by Chemical Ionization Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-TOF) during ACCHA experiments. We propose that, although very different in chemical structures and O:C-ratios, dimer esters and HOMs may be linked through the mechanism of RO_2 autoxidation, and that dimer esters and HOMs merely represent two different fates of the RO_2 radicals.

1. Introduction

The oxidation of volatile organic compounds (VOC) constitutes an important source of secondary organic aerosol in the atmosphere. Due to its atmospheric reactivity and its high estimated global emission rate of ~30 Tg/yr (Sindelarova et al., 2014), the atmospheric oxidation of the biogenic VOC α-pinene has been widely studied. The boreal forests are considered abundant sources of α-pinene with varying but sizeable emissions occurring all year around (Hakola et al., 2003;Hakola et al., 2009;Noe et al., 2012). For this reason, the oxidation of α-pinene and subsequent formation of secondary organic aerosol (SOA) is expected to occur at conditions with a wide range of VOC concentrations and atmospheric temperatures.

A number of smog chamber studies have investigated the effect of α-pinene concentration and reaction temperature on the formation of SOA from α-pinene oxidation (Svendby et al., 2008;Pathak et al., 2007;Tillmann et al., 2010;Warren et al., 2009;Kourtchev et al., 2016b;Kristensen et al., 2017;Zhao et al., 2019). Most of the published studies, however, focus on SOA mass yield (defined as mass of SOA formed per mass of reacted VOC) and reports higher yields with increasing VOC concentrations and lower temperatures. The effect of subzero temperatures, on gas phase oxidation products, nucleation, particle growth and particle chemical composition, remains a largely unexplored area (Huang et al., 2018;Stolzenburg et al., 2018).

Once emitted to the atmosphere, α-pinene is oxidized through reactions with atmospheric oxidants such as ozone (O_3), hydroxyl ($OH^{\cdot}$) and nitrate ($NO_3^{\cdot}$) radicals. These reactions have been shown to result in numerous oxidation products with various chemical functionalities, including alcohols, aldehydes, ketones, carboxylic acids, peroxides and peroxy-acids(Nizkorodov et al., 2011;Noziere et al., 2015). As a result of their lower volatilities, many α-pinene derived oxidation products (e.g. carboxylic acids) partition to already existing particles in the atmosphere contributing to particle growth and increased SOA mass. The extent to which an organic compound undergoes partitioning is related to its saturation vapor pressure and to the available particle mass (Kroll and Seinfeld, 2008) as well as particle size and particle phase (Shiraiwa and Seinfeld, 2012;Li and Shiraiwa, 2019;Zaveri et al., 2014;Zaveri et al., 2020). Due to the temperature dependence of the saturation vapor pressures of organic oxidation products, higher SOA mass yields from increased condensation of organics are observed at lower temperatures (Pathak et al., 2007;Saathoff et al., 2009;Warren et al., 2009;Svendby et al., 2008).

The saturation vapor pressure of a given organic species is closely related to its chemical structure. Depending on their specific molecular structure and the amount of strong hydrogen bond donor-acceptor groups, the products of α-pinene oxidation may undergo condensation or, if sufficiently low volatile, nucleation, with the latter resulting in new particle formation (Kulmala et al., 2013;Riccobono et al., 2014). In addition to temperature-dependent condensation of oxidation products, temperature-modulated gas and multiphase chemistry has been suggested to influence SOA yields from VOC oxidation. Von Hessberg et al. (2009) observed oscillatory positive temperature dependence under dry conditions and suggested that SOA yields from β-pinene oxidation is governed to a higher degree by the temperature and humidity dependence of the involved chemical reactions than by vapor pressure of the formed oxidation products at different temperatures. Furthermore, Pathak et al. (2007a) observed that α-pinene SOA yields showed a weak dependence on temperature in the 15 °C to 40 °C range, implying that the negative temperature dependence of the partitioning is counteracted by a positive dependence of the chemical reaction mechanism. Multiple studies report on new particle formation arising from the oxidation of α-pinene and suggest the formation of so-called extremely low volatile organic compounds (ELVOC, Donahue et al. (2012b)) capable of gas-to-particle conversion (Bonn and Moorgat, 2002;Lee and Kamens, 2005;Gao et al., 2010;Tolocka et al., 2006;Claeys et al., 2009;Ehn et al., 2014;Metzger et al., 2010;Kirkby et al., 2016;Bianchi et al., 2019). Although the chemical composition of α-pinene SOA has been extensively studied, uncertainty still remains regarding the chemical structure and functional groups of the compounds responsible for nucleation. Recent quantum chemical results indicate that multi carboxylic acids with three or more acid moieties are some of the most likely compounds to participate in new particle formation (Elm et al., 2017; Elm et al., 2019). In relation, Lawler et al. (2018) observed enhanced content of alkanoic acids in newly formed 20 –70 nm particles in the Finnish boreal forest.

Recently, highly oxidized multifunctional organic molecules (HOMs) have been identified in α-pinene oxidation studies (Bianchi et al., 2019;Ehn et al., 2014;Jokinen et al., 2014;Rissanen et al., 2015). Formed via a gas-phase autoxidation mechanism (Crounse et al., 2013) involving intramolecular hydrogen abstraction by peroxy-radicals, HOMs represent a class of organic compounds which can promptly reach high degrees of oxygenation (Ehn et al., 2017). Oxygen-to-carbon (O:C) ratios exceeding unity have been reported for monomeric compounds (Mutzel et al., 2015;Ehn et al., 2014). The high O:C ratios are attributed to multiple hydroperoxide functionalities and the compounds have been perceived as likely candidates for nucleation and initial particle growth owing to their low volatilities (Tröstl et al., 2016;Kirkby et al., 2016). However, computational studies have shown that HOMs originating from α-pinene autoxidation can have surprisingly high vapor pressures considering their O:C ratios, and it is mainly the dimeric compounds that are likely to be classified as ELVOC (Kurtén et al., 2016;Peräkylä et al., 2020~~19~~).

High molecular weight (MW > 300 Da) dimer esters formed from oxidation of α-pinene have been identified in laboratory-generated and ambient air SOA (Hoffmann et al., 1998;Tolocka et al., 2004;Gao et al., 2004;Yasmeen et al., 2010;Witkowski and Gierczak, 2014;Kourtchev et al., 2015;Zhang et al., 2015;Kristensen et al., 2013;Kristensen et al., 2014;Kristensen et al., 2016;Kristensen et al., 2017;Mohr et al., 2017). Several mechanisms for the formation of dimer esters have been proposed, including gas-phase mechanisms such as clustering of carboxylic acids (Hoffmann et al., 1998;Claeys et al., 2009;DePalma et al., 2013) and reactions involving reactive intermediates such as stabilized Criegee intermediates (SCI) and RO_2 species (Kristensen et al., 2016;Zhang et al., 2015;Berndt et al., 2016;Witkowski and Gierczak, 2014;Zhao et al., 2015;Kahnt et al., 2018).

The high abundance of dimer esters detected in freshly formed α-pinene derived SOA particles (Kristensen et al., 2016) suggests that these compounds may be important for the initial formation and growth of atmospheric particles; a hypothesis supported by saturation vapor pressure estimates reported in Kristensen et al. (2017) classifying dimer esters as ELVOC with vapor pressures suitable for gas-to-particle phase conversion at room temperatures. Furthermore, recent studies show that dimer esters and other oligomeric compounds in atmospheric aerosol are strongly correlated with cloud condensation nuclei activity thus suggesting a significant impact on climate (Kourtchev et al., 2016).

In contrast to dimer esters, few studies have identified particle phase HOMs and thus their fate upon gas-particle partitioning remains elusive. Recently, Zhang et al. (2017) identified highly oxidized monomers ($C_{8-10}H_{12-18}O_{4-9}$) and dimers ($C_{16-20}H_{24-36}O_{8-14}$) in α-pinene derived SOA particles using Na^+ attachment during electrospray ionization. The dimers identified by Zhang et al. (2017) show a somewhat different chemical formula and degree of oxidation than the gas-phase HOM dimers previously identified by Ehn et al. (2014), where the observed dimer composition was $C_{19-20}H_{28-32}O_{11-18}$. This can be attributed to decomposition of the hydroperoxides functionality of HOMs from processes such as photolysis, thermolysis and solvation, yielding alkoxy radicals, esters, and other moieties. The chemical formulas of the dimeric compounds in Zhang et al. (2017)

show good resemblance to the dimer esters published in Kristensen et al. (2016), characterized as $C_{15\text{-}19}H_{24\text{-}30}O_{5\text{-}10}$. This raises the important question, how different types of identified dimers, including HOMs and dimer esters, are related via gas-particle partitioning, chemical reactions or other processes.

The Aarhus Chamber Campaign on HOMs and Aerosols (ACCHA) presented in this work was designed s to elucidate the formation of HOMs and dimer esters from the dark ozonolysis of α-pinene at different temperatures. The effect of temperature and α-pinene concentration on SOA formation and composition on the formation of HOMs and dimer esters is investigated through a series of chamber experiments at temperatures prevailing at the latitudes of the boreal forests (Hakola et al., 2009) i.e. from 20 to -15 °C.

The results of ACCHA are presented in multiple publications. The elemental composition of the bulk α-pinene SOA by High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) is reported in the companion paper by Jensen et al (2019). A study presenting factor analysis of PTR-ToF-MS data includes a case study from the ACCHA campaign (Rosati et al., 2019). The formation of gas-phase HOMs as measured by nitric acid-based Chemical Ionization Atmospheric Pressure interface Time of Flight (CI-APi-ToF) mass spectrometer is presented in the work by Quéléver et al. (2019).

In the current work, we present the effect of temperature and α-pinene concentrations on the formation and molecular composition of SOA particles formed from ozone-initiated oxidation of α-pinene. Specifically, we investigate the contributions of organic acids and dimer esters to α-pinene SOA formed at temeratures of 20, 0, and -15 °C and examine the changes in molecular composition arising from heating and cooling of SOA particles.

2. Method

2.1 Chamber experiments

Dark ozonolysis of α-pinene was conducted in the Aarhus University Research on Aerosol (AURA) smog chamber. The chamber is described in detail in Kristensen et al. (2017). In short, the AURA chamber consists of a 5 m^3 Teflon bag situated in a 27 m^3 temperature controlled cold room. The chamber temperature can be varied from -16 °C to +26 °C. The temperature and relative humidity are monitored in the center of the Teflon bag by a HC02 probe coupled to a HygroFlex HF320 transmitter (Rotronic AG, Switzerland). Additional instrumentations are situated in air-conditioned (at constant 20°C) laboratory surrounding the cold room. In the current study, the chamber was operated using dry purified air (active carbon, Hepa) at atmospheric pressure. Ozone (O_3, ~100 ppb) was added to the chamber using an ozone generator (Model 610, Jelight Company, Inc.) and the concentration of O_3 and oxides of nitrogen (NO and NO_2~~NO_x~~) were monitored by UV photometric (O342 Module, Environment S.A.) and chemiluminescent monitors (AC32M, Environment S.A.), respectively. A known amount of VOC was added to a 10 mL glass manifold, evaporated and transferred to the chamber through a stainless-steel inlet (Diameter = 10 mm, Length = 100 cm) using heated (70 °C) N_2-flow. The concentration of the added VOC was monitored using a Gas Chromatograph with Flame Ionization Detector (Agilent 7820A GC-FID, with a time resolution of 6 min) and a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF- 783 MS 8000; IONICON, Innsbruck, Austria) sampling through stainless steel outlets located opposite of the VOC inlet (distance between inlet and outlet ~ 1.6 m). Particle size distributions were measured using a scanning mobility particle sizer (SMPS) system including a Kr-85 neutralizer (TSI 3077A) and an electrostatic classifier (TSI 3082) coupled with a nano water-based condensation particle counter (CPC, TSI 3788). The SMPS system was optimized for measurements of particles in the range of 10 – 400 nm with a sampling time of 80 s (60 s upscan, 20 s downscan, aerosol flow rate = 1.6 L min^{-1} , sheath flow rate = 5 L min^{-1}). In addition, the total particle number concentration of particles with diameter (D_p) larger than ~1.4 nm was measured by a Particle Size Magnifier (PSM A10, Airmodus, (Vanhanen et al., 2011), sample flow = 2.5 L min^{-1}, time resolution = 1 s) operated in fixed saturator flow mode. SMPS and PSM measurements were performed as close as possible to the cold room trough insulated tubing extending ~ 40 cm and ~ 10 cm from the cold room, respectively, thus minimizing residence time and potential influences caused by temperature variations.

The chemical composition of gas-phase HOMs were measured using a nitric acid-based Chemical Ionization Atmospheric Pressure interface Time-of-Flight mass spectrometer (CI-APi-ToF, Tofwerk A.G., Switzerland / Aerodyne Research Inc., USA) presented by Junninen et al. (2010) and Jokinen et al. (2012). An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc., (DeCarlo et al., 2006)) was deployed to measure real-time, non-refractory particulate matter. In addition, SOA molecular composition with respect to organic acids and high-molecular-weight dimer esters was investigated through off-line filter analysis of the formed α-pinene derived SOA performed using an Ultra High-Performance Liquid Chromatograph coupled to the electrospray ionization source of a Bruker Daltonics quadrupole time-of-flight mass spectrometer (UHPLC/ESI-qToF-MS). Filter sampling was performed once no additional growth in SOA mass was evident from the SMPS and no α-pinene could be detected by the GC-FID. All filter samples were collected by a low volume sampler onto 47 mm 0.20 micrometer PTFE filters (Advantec) situated in stainless steel filter holders at a flow rate of ~27 L min^{-1} once no additional growth in SOA mass was evident from the SMPS and no α-pinene could be detected by the GC-FID. After collection, the filter samples were stored at -20 °C until extraction and analysis.

A total of 12 α-pinene oxidation experiments conducted in the AURA smog chamber are presented here (Table 1). Each experiment was performed at temperatures close to either 20, 0 or -15 °C to investigate the effect of temperature on the formation and composition of both gas and particle phase organics from dark ozonolysis of α-pinene. Five experiments were conducted with the injection of 10 ppb α-pinene (~0.32 µL, 99%, Sigma Aldrich, Exp. 1.1-1.5) into the ozone-filled chamber (~100 ppb O_3). These experiments include oxidation at constant temperatures 20, 0 and -15 °C (Exp. 1.1, 1.2 and 1.3) and two temperature ramp experiments (Exp. 1.4 and 1.5). The ramp experiments were performed by injection of α-pinene at a fixed 20 °C (Exp. 1.4) or -15 °C (Exp. 1.5) temperature followed by subsequent ramping to -15 or 20 °C, respectively. In both experiments the temperature ramping was initiated approximately 40 min after the injection of α-pinene, hence before the SOA mass formation plateaued. In Exp. 1.4 a decrease in temperature from 20 °C to -15 °C was achieved in ~ 100 min, while in Exp. 1.5 heating of the chamber from -15 °C to 20 °C was performed in ~ 140 min. Note that small variations in RH (< 25 %) are observed in between all conducted experiments arising from heating or cooling of the dry chamber air (Table 1).

To investigate the effect of α-pinene concentration on the SOA formation and composition three experiments were performed with 50 ppb of α-pinene (~1.6 µL, 99%, Sigma Aldrich) at 20, 0 and -15 °C (Exp. 2.1-2.3) and repeated (Exp. 2.3b and Exp. 3.1-3.3).

~~The injection of α-pinene in the 10 and 50 ppb experiments described above (Exp. 1.1-2.3) was conducted with a N_2 flow rate of 15 L min^{-1}. To examine the effect of the injection flow rate, the 50 ppb α-pinene Exp. 2.1-2.3 were repeated using an N_2 injection flow of 30 L min^{-1} (Exp. 3.1-3.3).~~ All experiments were performed without the addition of an OH-scavenger to the chamber.

Throughout this paper SOA density is assumed to be 1 g cm^{-3} as in Kristensen et al. (2017).

2.2 Off-line particle analysis by UHPLC/ESI-qTOF-MS

Collected particle filter samples were extracted and analyzed for organic acids and dimer esters. Filter extraction was performed using a 1:1 mixture of methanol and acetonitrile (HPLC grade, Sigma Aldrich). 0.2 µg of camphoric acid recovery standard was added to the filter sample prior to the addition of the extraction mixture to minimize uncertainties related to the off-line extraction and analysis. The samples were placed in a cooled ultrasonic bath for 15 min after which the filters were removed and the extracts filtered through a Teflon filter (0.45 µm pore size, Chromafil). The extraction solvents were then removed by evaporation over gentle N_2 flow and the residues were dissolved by adding 0.2 mL MilliQ water with 10 % acetonitrile and 0.1 % acetic acid. The reconstituted samples were placed in a cooled ultrasonic bath for 5 min and the extract transferred to a HPLC sample vial for analysis. To ensure complete transfer of organics from the evaporated extracts, additional reconstitution were performed with 0.2 mL MilliQ water with 50 % acetonitrile and 0.1 % acetic acid. Both sample solutions (10 % and 50 % acetonitrile reconstitution) were analyzed by UHPLC/ESI-qTOF-MS immediately after extraction.

The HPLC stationary phase was a Waters Acquity UPLC Ethylene Bridged Hybrid C18 column (2.1 x 100 mm 1.7 um) while the mobile phase consisted of acetic acid 0.1% (v/v) in MilliQ water (eluent A) and acetic acid 0.1% (v/v) in acetonitrile as eluent B. The operating conditions of the mass spectrometer have been described elsewhere (Kristensen and Glasius, 2011). Quantification of the organic acids was performed from eight-level calibration curves (0.1 to 10.0 μg mL^{-1}) of the following acids: cis-pinic, cis-pinonic acid, terpenylic acid, diaterpenylic acid acetate (DTAA), 3-methyl-butane tricarboxylic acid (MBTCA). The analytical uncertainty is estimated to be < 20 % for carboxylic acids. Due to lack of authentic standards, the dimer esters were quantified using DTAA as surrogate standard. DTAA was chosen due to its structural similarities with that of the dimer esters (dicarboxylic acid with ester functionality) as well as similar UHPLC retention time.

3. Results and discussions

A representative example of the results obtained from the conducted smog chamber experiments is shown in Fig. 1. Following injection of α-pinene into the ozone-filled chamber at constant temperature and RH, rapid particle formation is captured by the PSM (measuring particles >1.4 nm) and, shortly after, the SMPS (10-400 nm). In all conducted experiments, maximum particle number concentrations were obtained within 10 minutes after α-pinene injection followed by decay ascribed to wall loss and particle aggregation. Particle number concentrations shown in Fig. 1 (lower panel) are wall-loss corrected. During the course of the experiment, decrease in ozone and α-pinene concentration is accompanied by increase in particle SOA mass concentration as measured by the SMPS. Figure 1 (upper panel) shows wall-loss-corrected SOA mass concentration obtained from ozone-initiated oxidation of 50 ppb α-pinene (measured by GC-FID). Wall loss corrections were based on first order fits to the SOA mass or number concentration after peak. The grey shaded area represents the time of filter sampling for off-line chemical analysis by UHPLC/ESI-qTOF-MS. Similar figures showing data from all conducted experiments are presented in Supplementary Information.

3.1 Particle formation rates and SOA mass yields

Figure 2A-B show the total particle number concentration (# cm^{-3}) as measured by the PSM (D_p> 1.4 nm) at 20, 0 and -15 °C as a function of time after injection of 10 ppb and 50 ppb α-pinene, respectively. The maximum total particle number concentrations in all experiments are listed in Table 1. Particle formation in terms of number concentrations from the dark ozonolysis of α-pinene at both 10 ppb and 50 ppb VOC concentrations show negative dependence on temperature as has also been reported previously (Jonsson et al., 2008;Kristensen et al., 2017). Maximum particle formation rates (# cm^{-3} s^{-1}) are estimated from linear fits to the experimental time series of total particle number concentration measured by the PSM (Fig. 2A-B ~~inserts~~). Due to in inhomogeneous mixing in the beginning of the experiments (when the particle formation is most efficient) as well as uncertainties related to the PSM cut-off, the presented particle formation rates should be considered rough estimates and likely not accurate formation rates of e.g. 2 nm particles. However, ~~I~~it is clear that lower temperatures result in higher particle formation rates from ozone-initiated oxidation of α-pinene at both low (10 ppb) and high (50 ppb) VOC concentration. At both α-pinene concentrations, a significantly higher particle formation rate is observed when oxidation takes place at 0 °C compared to oxidation performed at 20 °C, with the formation rates being ~ 6 and ~ 20 times higher at 0 °C than at 20 °C, at 10 ppb and 50 ppb α-pinene experiments, respectively. In comparison, the maximum particle formation rate at both α-pinene concentrations only increased by a factor of 1.5 when performing the oxidation at -15 °C compared to 0 °C. Figures 2C-D show the evolution of the wall-loss-corrected SOA mass concentration (μg m^{-3}) measured by SMPS as a function of time after α-pinene injection. Agreeing with previous studies, SOA mass and mass yields are higher at lower temperatures (Jonsson et al., 2008;Saathoff et al., 2009;Pathak et al., 2007;Kristensen et al., 2017). The reported 18 and 43 % mass yields at 20 °C and -15 °C, respectively, (50 ppb α-pinene, 100 ppb O_3) are in excellent agreement with previous values of 21 % and

39 % from similar oxidation experiments (50 ppb α -pinene, 200 ppb O_3) performed in the same chamber (Kristensen et al., 2017). Compared to experiments performed at 20 °C, temperatures of 0 °C and -15 °C respectively result in ~ 50 % and ~ 150 % higher SOA mass concentrations. Interestingly, SOA mass concentration in both 10 and 50 ppb α-pinene oxidation experiments show almost identical response to temperature going from reaction temperatures of 20 °C to -15 °C. In Fig. 2C and 2D the maximum SOA mass is obtained faster at higher reaction temperatures than at lower temperatures. For both low (10 ppb) and high (50 ppb) α-pinene ~~loadings~~concentrations, maximum SOA mass is reached ~~after~~ approximately 140 min, 200 min and 250 min after α-pinene injection at 20, 0 and -15 °C, respectively. This is attributed to the faster reaction of α-pinene with ozone at higher temperatures, which is also evident from the calculated α-pinene loss rates shown in the insert in Fig. 2D (50 ppb, GC-FID derived; due to the detection limit of the GC-FID no loss rates could be calculated for 10 ppb α-pinene experiments). Compared to oxidation experiments performed at 20 °C, loss rates of α-pinene were found to be 11 % and 22 % lower at 0 °C and -15 °C reaction temperature, respectively. These results are in good agreement with temperature dependent reaction rates of ozone with α-pinene reported by Atkinson et al. (1982) predicting a 16 (± 4) % and 28 (± 6) % lower reaction rate at 0 °C and -15 °C, respectively, relative to the reaction rate calculated at 20 °C. The discrepancy between measured and literature-derived values is likely due to the presence of OH radicals in the current study. Despite the lower reaction rate for α-pinene ozonolysis at low temperature, the particle number concentration data, in Fig. 2, show significantly faster particle formation in cold experiments.

3.2 Particle size distributions and sub-10 nm particles

Figure 3A shows the particle size distributions as recorded by the SMPS after max. SOA mass concentration was reached in (10 ppb) and high (50 ppb) concentration α-pinene oxidation experiments at 20, 0 and -15 °C. At both α-pinene concentrations, lower reaction temperatures result in larger particles consistent with the higher SOA masses at 0 °C and -15 °C in Fig. 3C and 3D. The time evolutions of the particle size distribution measured over time (Fig. 3B) shows that particles formed at 20 °C are initially larger than the particles formed at the two lower temperatures (0 °C and -15 °C). However, during the course of the experiments, particles formed at the lower temperatures grow more rapidly to larger sizes compared to particles formed at 20 °C. This is likely attributable to enhanced condensation of organics onto the formed particles at lower temperatures.

Figure 4A shows the total particle number concentration (# cm^{-3}) obtained by the PSM (D_p> 1.4 nm) and SMPS (D_p in the range 10-400 nm) respectively as a function of time after α-pinene injection (10 ppb) at both 20 and -15 °C. The differences in the total particle number concentrations derived by the two instruments corresponds to the number concentrations in the size range of 1.4 nm to 10 nm. Comparing experiments performed at 20, 0 and -15 °C temperatures in Fig. 4B (10 ppb α-pinene), it is clear that the presence of sub-10 nm particles is higher at the lower reaction temperatures and that the largest temperature dependence is in the range 20 °C to 0 °C.

According to Fig. 4A, sub-10 nm particles constitute ~10 and 25 % of the total particle number concentration at 20 and -15 °C, respectively, even 30 min after α-pinene injection where particle number concentrations have peaked. The size distributions obtained from the SMPS (Fig. 4C), however, indicating very few particles in the smaller size-ranges (i.e. below 20 nm, Fig. 4C insert) at this time of the experiments. A possible explanation for the high sub-10 nm particle number concentration is the presence of a particle distribution mode below the detectable range of the SMPS. Supporting this, Lee et al. (2016) reported an absence of particles in the size range between 3 and 8 nm in ambient air particle measurements (1-600 nm particle size distribution range combining PSM and SMPS data) during the Southern Oxidant and Aerosol Study (SOAS) field campaign. To our knowledge, the current work represents the first indication of this observed “gap” in the particle size distribution in smog chamber experiments, thus emphasizing the need for further studies of sub-10 nm particle formation and detection from VOC oxidation.

3.3 Molecular composition

Figure 5 shows the detailed chemical composition of SOA with respect to organic acids and dimer esters at different temperatures (20 °C, 0 °C, and -15 °C) and at two different concentrations of α-pinene (10 ppb and 50 ppb, respectively). The acids and dimer esters identified are similar to those in Kristensen et al. (2017), where suggestions for molecular structures are given. Significantly higher particle concentrations of α-pinene-derived organic acids are evident at the lower 0 and -15 °C temperatures compared to 20 °C supporting increased condensation of organics at lower temperatures. The total contributions of the identified acids to the formed SOA mass in experiments with an initial α-pinene concentration of 10 ppb are 17 %, 25 % and 32 % at 20, 0 and -15 °C, respectively. In comparison, in 50 ppb α-pinene oxidation experiments, the acids contribute to the formed SOA with 18 %, 38 % and 28 % respectively. For comparison, the fraction of acids was 20 % at 20 °C and 31 % at -15 °C of total SOA mass in experiments with 50 ppb of α-pinene and 200 ppb of ozone (Kristensen et al. 2017). Comparing mass fractions of acids at 20 °C and -15 °C, the mass fraction seems to be highly dependent on temperature and much less dependent on VOC concentration or VOC:O_3 ratios.

In all experiments, pinic acid was found to be the dominant identified organic acid, constituting between 5 and 9 % of the formed SOA mass with highest contributions at lower reaction temperatures. A negative dependence of concentration with temperature is observed for six of the ten identified organic acids: pinonic acid, pinalic acid, oxopinonic acid, OH-pinonic acid, pinic acid and terpenylic acid. Diaterpenylic acid acetate (DTAA), diaterpenylic acid (DTA) and 3-methyl-butanetricarboxylic acid (MBTCA), however, show lower concentrations at the lower temperatures compared to at 20 °C. The effect of temperature seems to correlate with the O:C ratio (i.e. degree of oxidation of the organic acids) as shown in Fig. 5. Acids with lower O:C-ratios (O:C < 0.4) are found at higher concentrations at lower temperatures (0 and -15 °C). This can likely be attributed to an enhanced condensation of these species onto the SOA particles at temperatures of 0 and -15 °C. In contrast, although contributing significantly less to the SOA mass, the more oxidized compounds (O:C > 0.4, DTAA, DTA and MBTCA) show an opposite trend with respect to temperature (Fig. S3). As MBTCA, DTAA and DTA are hypothesized to be formed from gas-phase oxidations involving OH-radicals (Szmigielski et al., 2007;Vereecken et al., 2007;Müller et al., 2012;Kristensen et al., 2014), their lower concentrations at lower reaction temperatures could be explained by (1) changes in reaction pathways or branching of the intermediates of MBTCA, DTAA and DTA, (2) lower gas-phase concentration of the first generation of oxidized organic compounds due to higher degree of condensation (e.g. MBTCA is formed from gas-phase oxidation of pinonic acid), and (3) reduction of OH radical production and hence reduced oxidation by OH-radicals at lower reaction temperatures (Jonsson et al., 2008;Tillmann et al., 2010). The former (1) is supported by Müller et al. (2012) and Donahue et al. (2012a) reporting lower particle-phase MBTCA correlating with decreased pinonic acid vapor fractions at lower temperatures. Both explanations are supported by lower O:C ratios of the total α-pinene-derived SOA formed at the lower temperatures as reported in Jensen et al. (2020).

A total of 30 dimer esters were identified in the collected SOA particle samples, from both 10 and 50 ppb α-pinene ozonolysis experiments. In the 10 ppb α-pinene experiments, total concentrations of dimer esters of 0.64, 0.51 and 0.46 µg m^{-3} were found in SOA particles formed at 20, 0 and -15 °C, respectively, thus showing a small positive dependence on temperature. The corresponding mass fractions were: 11.1 %, 7.5 % and 3.8 %. For particles formed from higher 50 ppb α-pinene concentrations, the temperature dependence is less obvious with total dimer ester concentration of 3.1, 4.3, and 3.3 µg m^{-3} at 20, 0, and -15 °C, respectively. The corresponding mass fractions of the dimer esters are: 8.9 %, 8.0 % and 3.9 %, thus similar to fractions reported for the 10 ppb α-pinene oxidation experiments, thus, as in the case of the organic acids, the mass fraction of dimer esters seems to be highly dependent on temperature and much less dependent on VOC concentrations or VOC:O_3 ratios.

In relation, Kourtchev et al. (2016) observed a positive relationship between temperature and oligomer fraction in aerosol samples collected at Hyytiälä in summer 2011 and 2014 but ascribed this to differences in the VOC emissions. However, the current study, indicates that temperature alone may influence the formation of dimeric compounds thus supporting to the ambient observation in Kourtchev et al. (2016).

~~This is somewhat contradictory to previously published findings by Kourtchev et al. (2016) showing increased particle fraction of oligomeric compounds at higher VOC precursor concentrations.~~

Looking at the concentrations of the ~~(~~30~~)~~ individual dimer esters, their formation is affected differently by the reaction temperature (Fig. 5). ~~As an example, the particle-phase concentration of the MW368 dimer ester (pinonyl-pinyl ester, $C_{19}H_{28}O_7$) is increases at lower temperatures, while the opposite is seen for the MW358 dimer esters (pinyl-diaterpenyl ester, $C_{17}H_{26}O_8$). Figure 6A shows the yields of the identified dimer esters at -15 ° C relative to 20 °C (yield (-15 °C) / yield (20 °C)) as a function of the number of carbon atoms in the dimer esters. From this, it is clear that the effect of temperature on the formation of individual dimer esters is compound specific. Of the 30 dimer esters, increased particle concentrations at lower temperatures is most often related to species with high carbon number (i.e. C_{19} species). Also,~~ Fig. 6A shows that the Figure 6A shows the yields of the identified dimer esters at -15 ° C relative to 20 °C (yield (-15 °C) / yield (20 °C)) as a function of the number of carbon atoms in the dimer esters. From this, it is clear that the effect of temperature on the formation of individual dimer esters is compound specific. Of the 30 dimer esters, increased particle concentrations at lower temperatures is most often related to species with high carbon number (i.e. C_{19} species). Also, Fig. 6A shows that the temperature effect on the dimer ester concentration to a large extent depends on the O:C ratio (indicated by color scale) of the individual species. This is highlighted also in Fig. 6B showing a more significant decrease in relative yields of dimer esters with higher oxygen number (i.e. more oxidized) at the lower -15 °C temperature in both 10 ppb and 50 ppb α-pinene experiments. Accordingly, the dimer esters are grouped based on their O:C ratios, with the more oxidized dimer esters having an O:C > 0.4; the O:C value above which all dimer esters show decreased concentration at the lower -15 °C compared to 20 °C (Figure S5). The total concentrations of the low (< 0.4) and high (> 0.4) O:C dimer esters are shown in Fig. 5B and 5D inserts. ~~temperature effect on the dimer ester concentration to a large extent depends on the O:C ratio (indicated by color scale) of the individual species. This is highlighted also in Fig. 6B showing a more significant decrease in relative yields of dimer esters with higher oxygen number (i.e. more oxidized) at the lower -15 °C temperature in both 10 and 50 ppb α-pinene experiments. Accordingly, the dimer esters are grouped based on their O:C ratios, with the more oxidized dimer esters having an O:C > 0.4. The total concentrations of the low (< 0.4) and high (> 0.4) O:C dimer esters are shown in Fig. 5B and 5D inserts. Recently, gas-phase RO_2–RO_2 reactions followed by particle phase decomposition of the resulting diacyl peroxides have been suggested as a possible mechanism for the formation of dimer esters from α-pinene ozonolysis (Zhang et al., 2015). As the decomposition of diacyl peroxides and the subsequent formation of dimer esters is suggested to increase at higher temperatures, this could indicate that the formation of the high O:C dimer esters proceed through the suggested RO_2-RO_2 reaction pathway, thus explaining increased concentrations at higher temperatures. Also, it is worth considering that the lower O:C dimer esters (such as the MW368 pinonyl-pinyl ester) may be composed of diacyl peroxides or acyloxyalkyl hydroperoxides, thus explaining the observed increased concentrations of these species at the lower temperatures owing to the suggested unstable nature of hydroperoxide-containing compounds (Krapf et al., 2016) .~~

~~Thermodynamics also need to be considered as possible explanation for the observed temperature responses of the high and low O:C dimer esters. As reported in Kristensen et al. (2017), the identified dimer esters span across a wide range of volatilities. Here, many of the low O:C dimer esters may be sufficiently volatile to allow considerable fractions to exist in the gas phase at high temperature. Consequently, the increased particle-phase concentration observed at the lower temperatures may solely be attributed to enhanced gas-to-particle phase partitioning of these species. Supporting this, Mohr et al. (2017) identified dimeric monoterpene oxidation products ($C_{16-20}H_yO_{6-9}$) in both particle and gas phases in ambient air measurements in the boreal forest in Finland.~~

3.4 Temperature ramping

Normann Jensen et al. (2020) present a detailed analysis on changes in AMS derived elemental chemical composition during temperature ramps in the ACCHA campaign and show that temperature at which the particles are formed to a large extend determines the elemental composition also after subsequent heating or cooling by 35 °C. During two temperature ramp experiments, we also studied how the concentration, mass fraction and molar yields of carboxylic acids and dimer esters as identified in the off-line analysis varied. The experiments involving temperature ramps were conducted to examine whether the observed effect of temperature on the dimer ester concentration is attributed to gas-to-particle partitioning or stabilization/decomposition of the hydroperoxide-containing species.

Figure 7A shows the SOA mass formation (wall-loss corrected) from the 10 ppb α-pinene oxidation experiments performed at constant 20 °C (Exp. 1.1) and -15 °C (Exp. 1.3) and from the two temperature ramping experiments (Exp. 1.4 and 1.5) in which the chamber temperature was ramped up or down ~ 40 min after injection of α-pinene. In the ~ 40 min following the injection of α-pinene, SOA mass in both ramp experiments show good agreement with the constant temperature experiments performed at similar starting temperature (Exp. 1.1 and 1.3). Likewise, particle formation rate and maximum particle number concentration obtained in Exp. 1.4 and 1.5 prior to temperature changes (Table 1) also resembles that of Exp. 1.1 and 1.3. Thus the initial evolution of the particle formation in Exp. 1.1 (constant 20 °C) and Exp. 1.4 (ramp experiment initiated at 20 °C) and experiment 1.3 (constant -15°C) and Exp. 1.5 (ramp experiment initiated at -15 °C) are comparable.

From Fig. 7A, cooling and heating the chamber imply a quasi-immediate effect on the SOA mass concentration. In Exp. 1.4, decreasing the temperature results in a maximum SOA mass concentration being ~ 30 % higher than the maximum SOA mass in Exp. 1.1 performed at a constant 20 °C (8 versus 6 µg m^{-3}). Reversely, heating the chamber from -15 to 20 °C (Exp. 1.5) results in a ~ 30 % lower SOA mass (10 versus 15 µg m^{-3}) compared to SOA formed and kept at -15 °C (Exp. 1.3). The changes in particle size distributions as a result of temperature ramping (Fig. 7B) are attributed to evaporation during heating and condensation during cooling. Interestingly, despite the loss or gain of particle mass during temperature ramping the SOA mass concentration is closer to the experiments performed at the initial temperature rather than the final temperature even after a temperature ramp of 35 °C. This, in turn, suggests that the formation conditions to a large extent govern the type of SOA that was formed, rather than the conditions the SOA was later exposed to.

Figure 8 shows the concentrations, mass fractions and molar yields of organic acids and dimer esters in SOA particles from constant temperature oxidation experiments at 20 and -15 °C (Exp. 1.1 and 1.3, respectively) and from the two temperature ramp experiments (Exp. 1.4 and 1.5). Upon heating SOA particles from -15 to 20 °C, a loss of particle mass (5 µg m^{-3}, Fig. 7) was observed and is attributed to evaporation of organics. This is supported by a 2.8 µg m^{-3} lower organic acid concentration in particles exposed to heating in Exp. 1.5 compared to particles formed at the constant -15 °C (Exp. 1.3), accounting for ~ 60 % of the evaporated organics. These results underline the semi-volatile nature of the identified organic acids (i.e. pinalic acid, pinonic acid, oxopinonic acid, OH-pinonic acid, pinic acid, terpenylic acid and terebic acid) and show that these acids are readily removed from organic aerosols during heating thus explaining previously reported reduced aerosol mass fraction from heating α-pinene SOA (Pathak et al., 2007). In contrast, cooling of the formed SOA particles in Exp.1.4 resulted only in a small 0.3 µg m^{-3} increase in organic acid concentration making up ~ 15 % of the reported 2 µg m^{-3} increase in SOA mass compared to the constant 20 °C experiment. These results indicate limited gas-to-particle phase condensation of the semi-volatile organic acids upon cooling the SOA. The current findings are in agreement with that of Zhao et al. (2019) who found that during cooling of α-pinene SOA particles the resulting mass growth was largely over predicted by the applied volatility basis set model. As suggested in Zhao et al. (2019) the observed limited condensation of semi-volatiles to SOA particles during cooling is likely attributed to an expected high particle viscosity at the relative low RH conditions of the performed oxidation experiments. Under these conditions, condensed SVOCs are likely confined at the near-particle-surface region thus impeding further partitioning of the gas-phase SVOCs (Renbaum-Wolff et al., 2013). In the current study, this is supported by the relatively small increase in organic acids (Fig. 8) as well as almost negligible increase in particle size (Fig. 7B) observed upon cooling the SOA particles from 20 °C to -15 °C. Also, if SVOCs reside near the particle surface, this would indeed explain the effective evaporation of these compounds (i.e. the identified organic acids, Fig. 8) and subsequent reduction in particle size (Fig. 7B) observed in Exp. 1.5.

Figure 8 reveals that heating and cooling of α-pinene-derived SOA particles results in insignificant or small changes in the concentrations, mass fractions, and molar yields of dimer esters when compared to experiments performed at constant temperatures. This indicates that the dimer esters are not subjected to evaporation or decomposition within the studied temperature range and timeframe. Also, the results indicates that the SOA particle dimer ester concentration is, within the timeframe of the performed experiments, unaffected by any changes to the particle phase-state associated with either the performed cooling or heating of the particles. This could thus suggest that the formation of dimer esters proceed through gas-phase mechanism rather than reactions in the particle phase. Thus, ~~T~~the~~se~~ results show that the concentration of the dimer esters in SOA from α-pinene oxidation is largely determined by the temperature by which the SOA is formed rather than subsequent exposure to higher or lower temperatures.

3.5 Dimer ester formation ~~and HOMs~~

Gas-phase formation of dimer esters from α-pinene ozonolysis has been suggested to proceed through the reaction of stabilized Criegee Intermediate (sCI) with carboxylic acids resulting in the formation of a class of ester hydroperoxides, α-acyloxyalkyl hydroperoxides (α-AAHPs) (Zhao et al., 2018a;Kristensen et al., 2016). In relation, Claflin et al. (2018) stated that the only known gas-phase mechanism for forming esters in their experiments was the reaction of sCI with carboxylic acids under dry condition. As the reactions of sCI are expected to be temperature-dependent this could explain the lower formation of some of the identified dimer esters (the high O:C dimers) in the current study. Also, as suggested by Kristensen et al. (2017), temperature-modulated condensation of the gas-phase carboxylic acid precursors may also contribute to the observed temperature effects on the formation of dimer esters. As the condensation of the carboxylic acids is vapor pressure dependent it is expected that the less volatile (i.e. more oxidized) species are more effectively depleted from the gas phase at lower temperatures hence hindering their gas-phase reactions with the sCI and reducing formation of the more oxidized dimer esters. Consequently, at the lower temperatures the formation of dimer esters is more likely to proceed through reactions of sCI with the more volatile and less oxidized carboxylic acids species thus potentially explaining the observed increased formation of the low O:C dimer esters in the 0 °C and -15 °C experiments. In addition to the observed temperature dependence of the low O:C dimer esters an increased stability of hydroperoxide-containing species in SOA particles is expected at lower temperatures (Zhao et al., 2018a).

While the formation of α-AAHPs through sCI + carboxylic acids is a plausible mechanism related to many of the dimer esters identified in the current study, this may not be true for all species. In particular, studies on the MW 368 dimer ester (pinonyl-pinyl ester, $C_{19}H_{28}O_7$) and MW 358 (pinyl-diaterpenyl ester, $C_{17}H_{26}O_8$) conclude that the chemical structures of these esters do not include hydroperoxide functionalities (Beck and Hoffmann, 2016;Kahnt et al., 2018). Consequently, Kahnt et al. (2018) recently suggested an alternative mechanism for the formation of these species involving gas-phase formation and subsequent rearrangement of unstable $C_{19}H_{28}O_{11}$ HOM species formed from $RO_2 + R'O \rightarrow RO_3R$ reaction of an acyl peroxy radical and an alkoxy radical. Specifically, Kahnt et al. (2018) explains that the $C_{19}H_{28}O_{11}$ HOM species decompose through the loss of oxygen or ketene resulting in the formation of the MW 368 dimer ester (pinonyl-pinyl ester, $C_{19}H_{28}O_7$) and the MW 358 dimer ester (pinyl-diaterpenyl ester, $C_{17}H_{26}O_8$), respectively. Interestingly, in the current study, the particle-phase concentration of the MW 368 dimer ester increases at lower temperatures, while the opposite is seen for the MW 358 dimer esters (Fig. 5), thus indicating significant differences in the mechanism responsible for the formation of these particular dimer esters. In accordance with the mechanism suggested by Kahnt et al. (2018), the different responses to temperature of the two dimer esters could be explained by (1) a temperature modulated formation of the alkoxy radicals related to the 5- and 7-hydroxy-pinonic acid involved in the formation of the two $C_{19}H_{28}O_{11}$ HOM species decomposing to the MW 368 and MW 358 dimer esters, respectively; or (2) temperature-dependent decomposition and rearrangement of the $C_{19}H_{28}O_{11}$ HOM species suppressing the more complex decomposition and rearrangement mechanism in which carbon-containing entities (e.g. ketene) is expelled from the HOM.

However, these explanations are not supported by the temperature ramping experiments performed herein indicating that the formation of the dimer esters is determined by the initial reaction temperature and remains relatively unaffected by heating or cooling. In addition, although accounting for the differences in the temperature response of the MW 368 and MW 358 dimer esters, and to some extent the increased particle concentration of many higher carbon number dimer esters (i.e. C_{19} species, Fig 6A), a temperature-modulated decomposition does not solely explain the observed decrease in relative yields of dimer esters with higher oxygen number (Fig. 6B). To explain this, the formation and subsequent decomposition of more oxidized HOMs need to be considered as possible precursors for the more oxygen-rich dimer esters.

A detailed study on the formation of HOMs during the ACCHA campaign is presented by Quéléver et al. (2019). Here, significantly lower (by orders of magnitude) HOM gas-phase concentrations are observed in -15 °C experiments compared to 20 °C experiments. As the HOMs form through autoxidation of RO_2, low temperatures and thus decreased autoxidation is expected to result in lower formation of HOMs, with reduced formation of the more oxygenated species. Interestingly, however, Quéléver et al. (2019) observed no correlation between the degree of oxidation (i.e. O:C-ratio) of the identified HOMs and the magnitude by which the formation of these was reduced at lower temperatures. This is in contrast to the observed temperature effects on the formation of the identified dimer esters presented in the current study (Fig. 7), and thus rule out the formation and decomposition of more oxidized HOMs as mechanism for the formation of more oxygen-rich dimer esters. In Quéléver et al. (2019), one possible interpretation of the observed temperature effect on HOMs is that the rate-limiting step in the autoxidation chain takes place already in the first steps of autoxidation~~in RO_2 radicals with six or fewer oxygen atoms~~. This is supported by the observed decreased concentration of dimer esters with a higher number of oxygen atoms, which also indicates that the formation of the identified dimer esters likely proceeds through reaction of products from RO_2 autoxidation~~RO_2~~. The involved oxidation state of these products may vary depending on the degree of autoxidation undertaken by the RO_2 radical as well as the radical termination of these including unimolecular processes leading to loss of OH or HO_2 or bimolecular reactions with NO, HO_2 or other RO_2 resulting in the formation of ROOR dimers. As the autoxidation as well as the bimolecular reactions of peroxy radicals are temperature-dependent, these processes may provide explanation for the observed response to temperature of the different dimer esters. Claflin et al. (2018) showed that the autoxidation and radical termination reactions of the Criegee Intermediate RO_2 radicals may results in a plethora of different products covering a range of oxidation states and functionalities; including multifunctional RO_2 radicals, hydroperoxide, carbonyl, alcohol, carboxylic and peroxycarboxylic acid, dialkyl and diacyl peroxides. Of these, carbonyls, alcohols and carboxylic acids reacts readily with sCI resulting in dimeric compounds such as secondary ozonides, α-alkoxyalkyl hydroperoxides (AAAHs), and α-AAHP, respectively (Chhantyal-Pun et al., 2018;McGillen et al., 2017;Khan et al., 2018;Claflin et al., 2018). In addition, gas-phase RO_2–RO_2 reactions have been proposed as conceivable mechanism for the formation of dimers from α-pinene ozonolysis (Claflin et al., 2018;Zhao et al., 2018b). Here, RO_2 produced from the isomerization or decomposition of Criegee Intermediates are suggested to participate in RO_2-RO_2 reactions resulting in dialkyl or diacyl peroxides. The formation of dimer esters through reactions of RO_2 is supported by an observed decrease in dimer esters concentrations at higher levels of NOx in ambient air measurement in Hyytiälä, Finland (Kristensen et al., 2016) and supports the formation proposed by several studies (Ehn et al., 2014;Berndt et al., 2018;Zhao et al., 2018b) involving RO_2 cross-reactions as likely route of gaseous dimer formation. The RO2–RO2 reaction is expected to compete with the reactions of RO_2 with HO_2 radicals. In the absence of an OH-scavenger, the performed oxidation experiments will include the formation of OH-radicals from the gas-phase reaction of α-pinene with O_3. The formed OH-radicals reacts readily with O_3 yielding HO_2-radicals available for RO_2-HO_2 reactions. As both reactions (O_3 + α-pinene and O_3 + OH) have a positive temperature dependence, the formation of HO_2 and its subsequent reaction with RO_2 is expected to increase at the higher reaction temperatures. In Simon et al. (2020) the higher concentration of HO_2 leads to an increased competition with the RO_2-RO_2 self-reaction, which reduced the formation of HOM dimers but increased HOM monomers. However, in the current study, reduction in the concentration of dimer esters due to increased RO_2-HO_2 competition at higher temperatures is only observed in the case of the low O:C dimer esters. In the case of the higher O:C dimers, it appears that a suppressed competition of HO_2 with RO_2 at the lower temperatures is less important compared to the reduced availability of more oxidized species for dimer ester formation. We propose that, although different in chemical structures and O:C-ratios, dimer esters and HOMs may be linked via their formation mechanisms, both involving RO_2 autoxidation. The particle-phase dimer esters and the gas-phase HOMs may merely represent two different fates of the RO_2 radicals. If conditions are favorable and efficient autoxidation takes place, this will result in the formation of HOMs, which by the definition recommended by Bianchi et al. (2019) in this case means any molecule with 6 or more oxygen atoms that has undergone autoxidation. On the other hand, dimer esters could be the product of RO_2 cross reactions or reactions of sCI with the autoxidation termination products with O:C ratios influenced by the number of potential autoxidation steps undertaken by the involved RO_2 species prior to reaction or termination (Fig. 9). Whether the formation of dimer esters proceeds through ROOR dimer formation from RO_2-RO_2 cross reactions or through monomeric compounds reacting with sCI is yet to be determined.

Lastly, thermodynamics need to be considered as a possible explanation for the observed temperature responses of the high and low O:C dimer esters. As reported in Kristensen et al. (2017), the identified dimer esters span across a wide range of volatilities. Here, many of the low O:C dimer esters may be sufficiently volatile to allow considerable fractions to exist in the gas phase at high temperature. Consequently, the increased particle-phase concentration observed at the lower temperatures may solely be attributed to enhanced gas-to-particle phase partitioning of these species. Supporting this, Mohr et al. (2017) identified dimeric monoterpene oxidation products ($C_{16-20}H_yO_{6-9}$) in both particle phase and gas phases in ambient air measurements in the boreal forest in Finland.

~~The observed response to temperature of the different dimer esters may thus be ascribed to the oxidation state of RO_2 species available for gas-phase reactions. At the lower reaction temperatures, the RO_2 autoxidation is limited, thus favoring the formation of low O:C dimer esters through reaction of less oxidized RO_2 species. Likewise, the higher O:C dimer esters thus only form if sufficient degree of autoxidation of the RO_2 is allowed before bimolecular cross-reaction takes place and the dimer esters are formed.~~

~~We thus propose that, although different in chemical structures and O:C-ratios, dimer esters and HOMs may be linked through their formation mechanisms, both involving RO_2 autoxidation. The particle-phase dimer esters and the gas-phase HOMs may merely represent two different fates of the RO_2 radicals. If conditions are favorable and efficient autoxidation takes place, this will result in the formation of HOMs, which by the definition recommended by Bianchi et al. (2019) in this case means any molecule with 6 or more oxygen atoms that has undergone autoxidation. On the other hand, dimer esters could be the product of RO_2 cross reactions, with O:C ratios influenced by the number of potential autoxidation steps undertaken by the involved RO_2 species prior to reaction (Fig. 9). In this case, if either RO_2 has undergone autoxidation, the resulting dimers would classify as HOM, regardless whether the ultimate fate is a dimer peroxide or dimer ester. The formation of dimer esters through reactions of RO_2 is supported by an observed decrease in dimer esters concentrations at higher levels of NOx in ambient air measurement in Hyytiälä, Finland (Kristensen et al., 2016) and supports the formation proposed by several studies (Ehn et al., 2014;Berndt et al., 2018;Zhao et al., 2018) involving RO_2 cross-reactions as likely route of gaseous dimer formation.~~

4. Conclusions

The formation of SOA from dark ozonolysis of α-pinene is highly influenced by temperature. At sub-zero temperatures, such as -15°C, more effective nucleation gives rise to significantly higher particle number concentration compared to similar experiments performed at 20 °C, where the vast majority of laboratory studies are conducted. In addition, the SOA mass concentration resulting from α-pinene ozonolysis shows a strong temperature dependence attributed to increased condensation of semi-volatile oxidation products at lower temperatures. This is supported by higher concentration of semi-volatile organic acids, such as pinic acid and pinonic acid, in SOA particles formed at 0 °C and -15 °C compared to particles formed at 20 °C. In addition to organic acids, the contribution of high-molecular-weight dimer esters to the formed SOA is also affected by temperature. Underlining the chemical complexity of α-pinene SOA, the 30 quantified dimer esters showed different behaviors with respect to temperature, with the suppressed formation of the more oxidized dimer esters (O:C > 0.4) at low reaction temperatures. This feature is not seen in the case of the least oxidized dimer esters (O:C < 0.4), showing a small increase in particle concentration at lower temperatures. Similar to the high O:C dimer ester compounds, α-pinene ozonolysis experiments performed at lower temperatures result in lower HOM formation in the gas-phase. We suggest that the identified dimer esters may form through RO_2 cross-reactions or sCI reactions both likely involving hydroperoxide-containing compounds from autoxidation. The identification of dimer esters in SOA would thus signify a specific termination pathway and fate of the RO_2 radicals, and link these molecules more close to HOMs than earlier thought.~~We suggest that the identified dimer esters may form through RO_2 cross-reactions likely involving hydroperoxide-containing compounds from autoxidation. The identification of dimer esters in SOA would thus signify a specific termination pathway and fate of the RO_2 radicals, and link these molecules more close to HOMs than earlier thought~~. These results indicate that temperature not only affects the formation of SOA mass in the atmosphere but also alters the chemical composition through condensation and evaporation of semi-volatile species, changes in the formation of HOMs and finally in the reaction pathways leading to the formation of dimer esters having high and low O:C-ratios.

With respect to dimer esters, no decomposition or evidence of partitioning changes between the aerosol and the gas phase were observed from heating or cooling the SOA particles, suggesting that 1) the formation and, consequently, concentration of dimer esters is dictated by the VOC oxidation conditions and 2) once formed, dimer esters remain in the particle phase, representing a core compound within SOA and thus an efficient organic carbon binder to the aerosol phase. In relation, the presented results from temperature ramping show that final SOA mass concentration obtained from dark ozonolysis of α-pinene is more dependent on the initial reaction temperatures rather than temperatures to which the formed SOA is subsequently exposed. In conclusion, this means that the changes at ambient temperatures in areas in which emissions and oxidation of VOCs, such as α-pinene, is likely to result in significant changes to the resulting SOA mass as well as the chemical composition of the SOA. As global temperatures are expected to rise, especially in the Nordic regions of the boreal forests, this means that although less SOA mass is expected to form from the oxidation of emitted biogenic VOCs, the temperature-induced changes to the chemical composition may result in more temperature resistant SOA influencing cloud-forming abilities from increased content of oligomeric compounds (i.e. dimer esters).

Author contributions

MB, ME,~~ and~~ MG, and HBP supervised the ACCHA campaign. KK, LLJQ, SC, ME, and MB designed the experiments. KK, LNJ, SC initialized the chamber for experiments. KK and LNJ measured and analyzed the aerosol phase. KK, BR, and RT measured and analyzed the VOCs and their oxidation production. LLJQ performed the measurement and analyzed the gas-phase HOMs. JE guided and helped with the interpretation of the dimer ester data and formation pathways. KK prepared the manuscript with the contributions from all co-authors.

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Table 1. Overview of conducted α-pinene ozonolysis experiments

ID	Date	Exp. Type	α-pinene (ppb)	~~α-pinene injection flow (LPM)~~	Ozone (at injection) (ppb)	Temp. [a] (at injection) (°C)	RH [a] (at injection) (%)	Temp. avg. [b] (°C)	RH avg. [b] (%)	VOC loss rate [c] (h^{-1})	Max SOA mass [d] ($\mu g\ m^{-3}$)	Max particle number [d] (10-400nm) ($\#\ cm^{-3}$)	Max particle number (>1.4nm) ($\#\ cm^{-3}$) [e]
1.1	20161202	Low load, 20 °C	10	~~15~~	104	20.2	0	20.3 (±0.1)	0.8 (±0.8)	N/A	6	$3.9\cdot10^4$	$5.2\cdot10^4$
1.2	20161208	Low load, 0 °C	10	~~15~~	105	0.9	2.9	0.7 (±2.7)	7.1 (±4.1)	N/A	9	$7.9\cdot10^4$	$17.0\cdot10^4$
1.3	20161207	Low load, -15 °C	10	~~15~~	106	-13.7	8	-14.7 (±0.1)	12.9 (±5.3)	N/A	15	$7.4\cdot10^4$	$19.5\cdot10^4$
1.4	20161209	Low load, 20 to -15 °C	10	~~15~~	103	19.9	0		N/A	N/A	8	$4.4\cdot10^4$	$8.4\cdot10^4$
1.5	20161220	Low load, -15 to 20 °C	10	~~15~~	113	-14	11.7		5.3 (±4.0)	N/A	10	$9.4\cdot10^4$	$20.0\cdot10^4$
2.1[∞]	20161212	High load, 20 °C	50	~~15~~	105	19.8	0	20 (±1.1)	1.1 (±1.3)	1.0	50	$8.2\cdot10^4$	$11.0\cdot10^4$
2.2	20161219	High load, 0 °C	50	~~15~~	107	-0.4	6.9	-0.3 (±0.1)	6.9 (±0.8)	0.9	65	$19.0\cdot10^4$	$>70.0\cdot10^4$*
2.3a	20161213	High load, -15 °C	50	~~15~~	101	-13.1	6.7	-14.9 (±0.6)	11.9 (±4.3)	0.8	120	$24.0\cdot10^4$	$>70.0\cdot10^4$*
2.3b[∞]	20161221	High load, -15 °C	50	~~15~~	113	-14.0	19.8	-15.0 (±0.2)	24.7 (±3.6)	0.8	131	$16.0\cdot10^4$	$51.2\cdot10^4$
3.1	20170112	High load, 20 °C	50	~~30~~	100	20.3	0	20.1 (±0.5)	2.4 (±2.0)	1.1	50	$7.8\cdot10^4$	$8.4\cdot10^4$
3.2	20170116	High load, 0 °C	50	~~30~~	105	0.2	8.6	0.0 (±0.1)	8.7 (±1.1)	1.0	78	$25.0\cdot10^4$	$>70.0\cdot10^4$*
3.3	20170113	High load, -15 °C	50	~~30~~	105	-14.5	11.2	-14.8 (±0.6)	15.8 (±4.5)	0.9	115	$23.0\cdot10^4$	$>70.0\cdot10^4$*

[a] Temperature and RH measured in centre of Teflon bag,

[b] Average temperature and RH (±std.dev.) over the entire experiment,

[c] VOC loss rates are estimated from GC-FID measurements

[d] Measured by SMPS (10-400nm), [e] Measured by PSM (>1.4nm),

* PSM overloaded

∞ Temperature ramps were performed after the stable temperature phase and is presented in Jensen et al., (2020~~19~~).

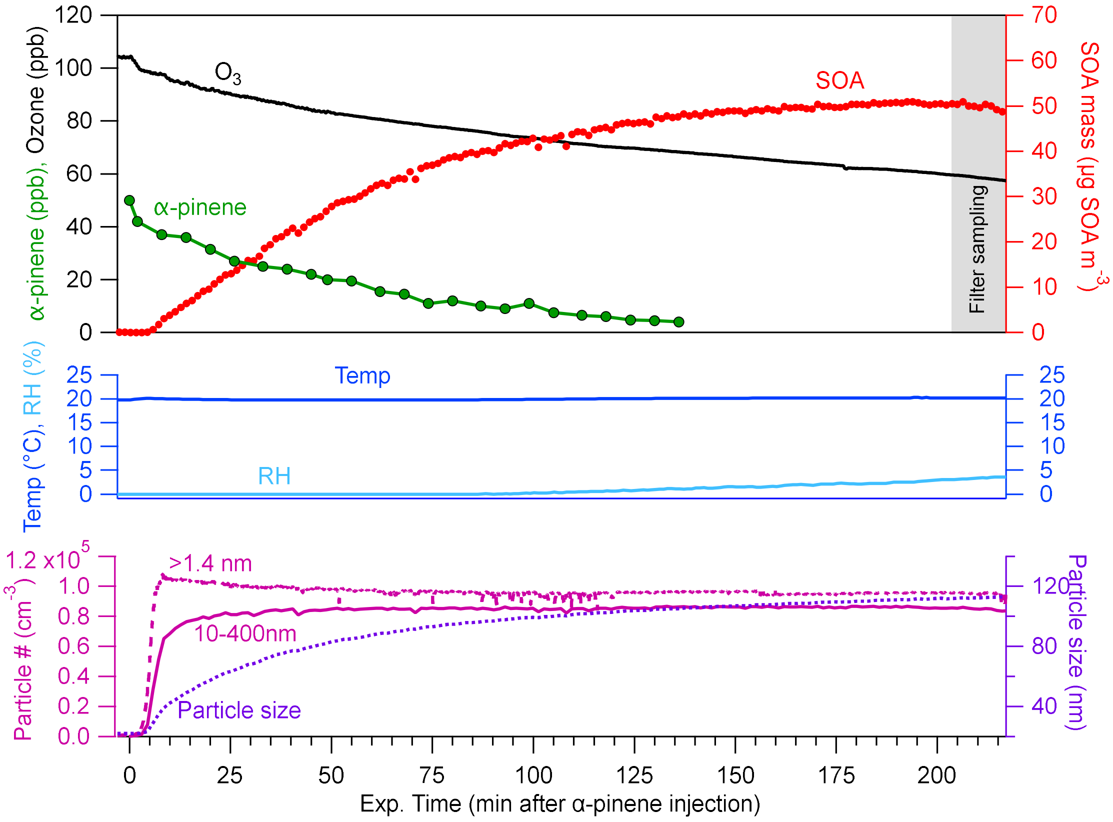


Figure 1. Concentration of O_3 (ppb, black), α-pinene (ppb, green), wall-loss corrected SOA mass (µg m-3, red) and particle number concentration (# cm^{-3}, measured by PSM (>1.4nm) and SMPS (10-400nm), dark red) and the geometric mean particle size (nm, by SMPS, violet) along with recorded RH (%, teal) and temperature (°C, blue) during a 50 ppb α-pinene oxidation 1070 experiment performed at 20 °C (Exp. 2.1).

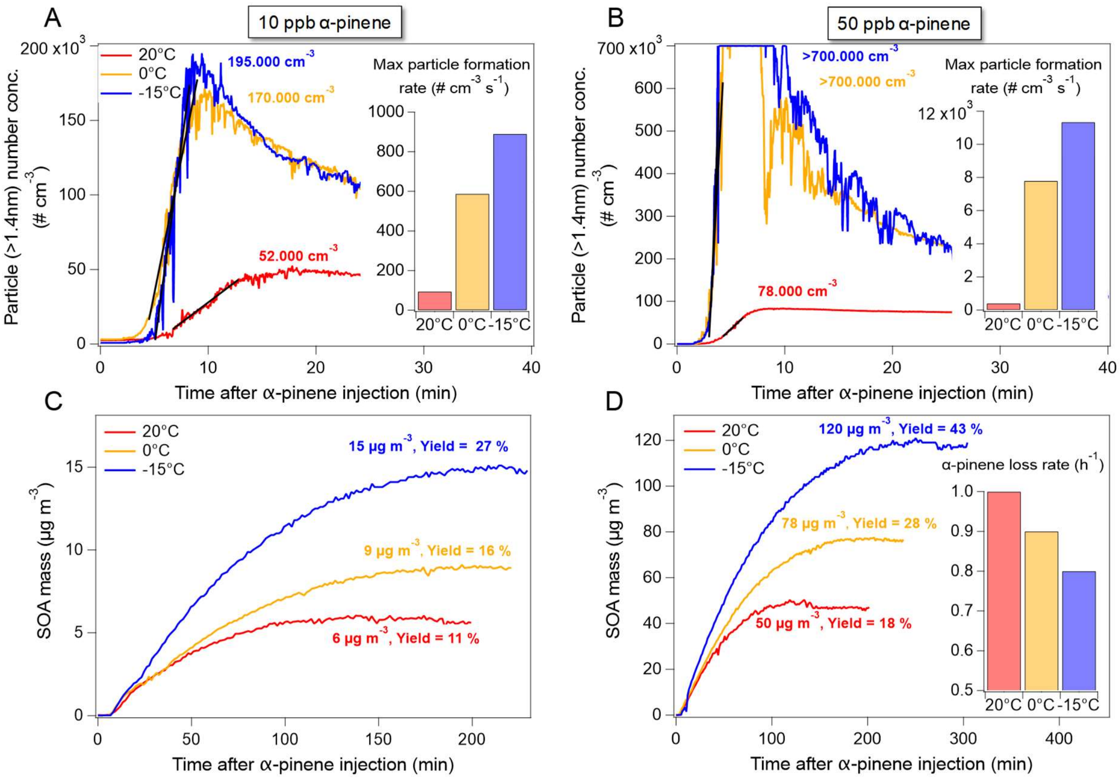


Figure 2. Effect of reaction temperature and initial VOC loading on SOA formation: Particle number concentration (A, B) and wall-loss-corrected SOA mass concentration (C, D) at α-pinene concentrations of 10 ppb (A, C) and 50 ppb (B, D). Inserts show particle formation rates (# cm^{-3} s^{-1}) as estimated from linear fits to the experimental data (A, B). The insert in D shows the loss rate of α-pinene (h^{-1}) at different temperatures as derived from an exponential fit to the measured concentration of α-pinene.

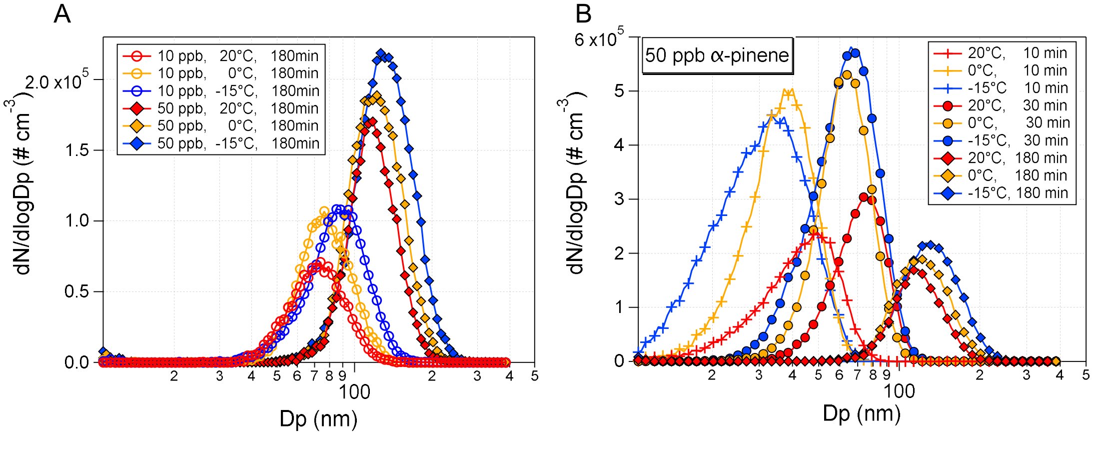


Figure 3. **A)** Particle size distribution recorded 180 minutes after the ozone-initiated oxidation of 10 (Exp. 1.1-1.3) and 50 ppb (Exp. 2.1-2.3) α-pinene performed at 20 °C (red), 0 °C (orange), and -15 °C (blue). **B)** Particle size distribution recorded at 10, 30 and 180 minutes after injection of 50 ppb α-pinene at 20 °C (Exp. 2.1, red), 0 °C (Exp. 2.2, orange), and -15 °C (Exp. 2.3, blue).

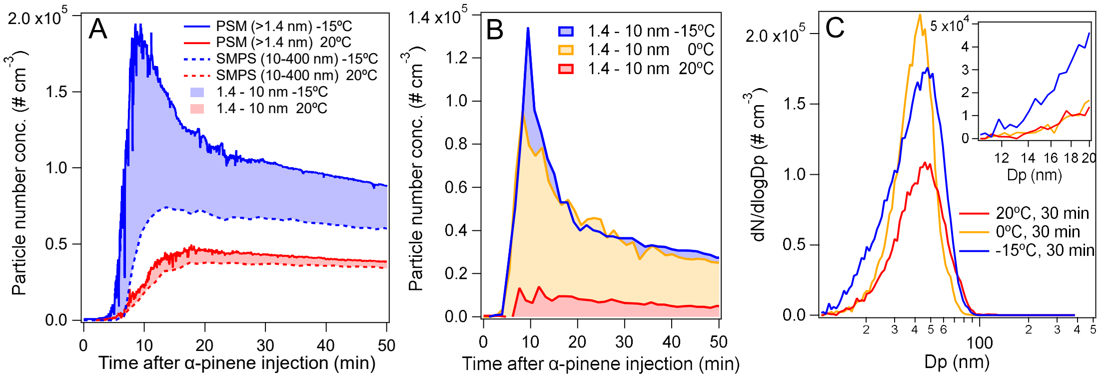


Figure 4. **A)** Effect of temperature on particle number concentrations (# cm^{-3}) as derived from the SMPS (10-400 nm particle size range, broken line) and PSM (>1.4 nm particle size range, solid line) in experiments with an initial α-pinene concentration of 10 ppb. (Exp. 1.1, red, and Exp. 1.3, blue). **B)** Particle number concentrations (# cm^{-3}) of 1.4 – 10 nm particles in experiments with an initial α-pinene concentration of 10 ppb performed at -15°, 0 °C and 20 °C (Exp. 1.1, 1.2, and 1.3, respectively). **C)** Particle size distributions recorded 30 minutes after the ozone-initiated oxidation of 10 ppb α-pinene performed at 20 °C (red), 0 °C (orange), and -15 °C (blue) (Exp. 1.1-1.3).

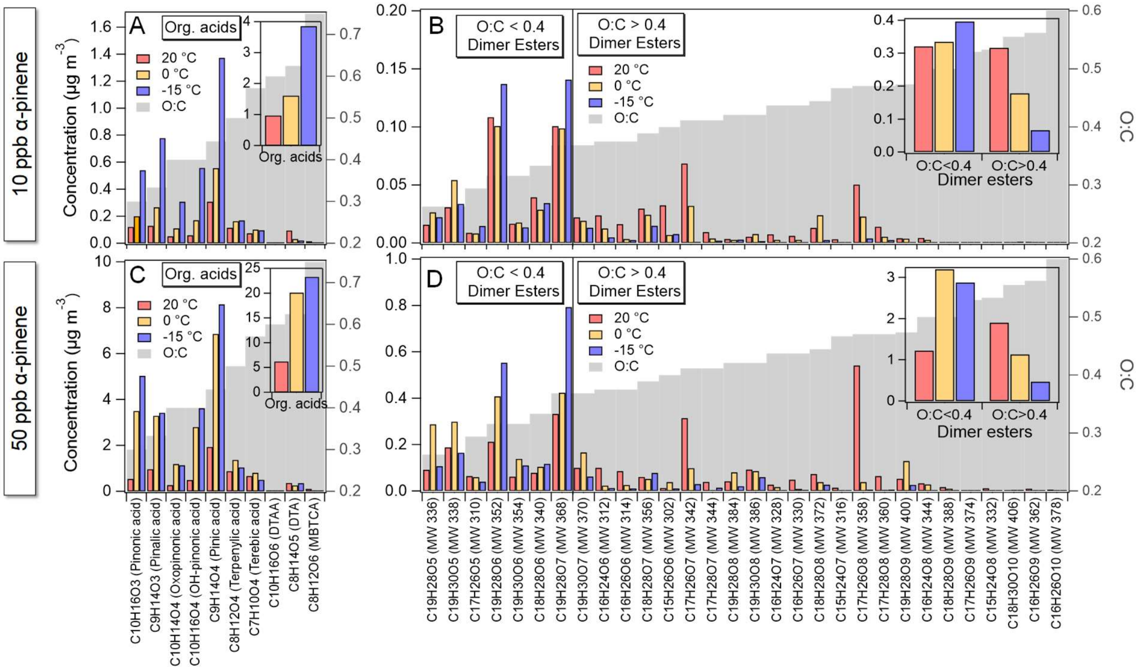


Figure 5. LC-MS results showing concentrations (µg m^{-3}, left axis) of acids and dimer etsers as well as O:C ratios (grey bars, right axis) of these at 20 °C (red), 0 °C (orange), and -15 °C (blue) for the two α-pinene loadings; 10 ppb (top panels **A** and **B**), 50 ppb (bottom panels **C** and **D**). Inserts show the total concentrations of the identified organic acids and dimer esters (O:C < 0.4 and O:C > 0.4)

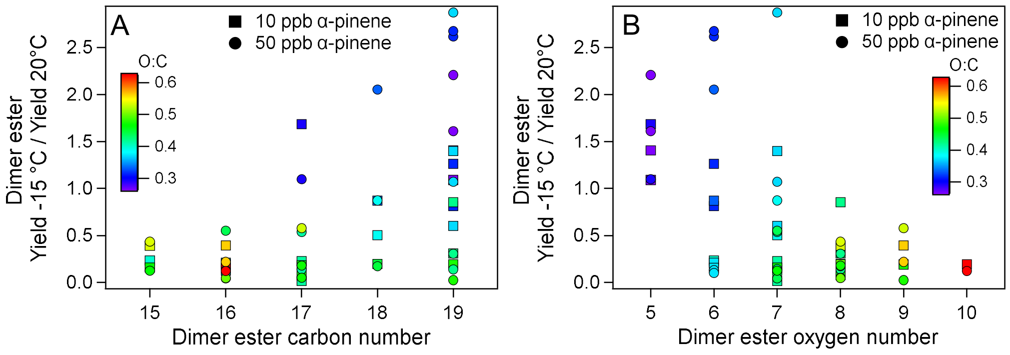


Figure 6. Comparison of relative yields (yield at -15 °C / yields at 20 °C) for specific dimer esters as a function of dimer ester carbon number (**A**) and oxygen number (**B**) in 10 and 50 ppb α-pinene ozonolysis experiments. Color scale indicates the O:C ratio of the dimer esters.

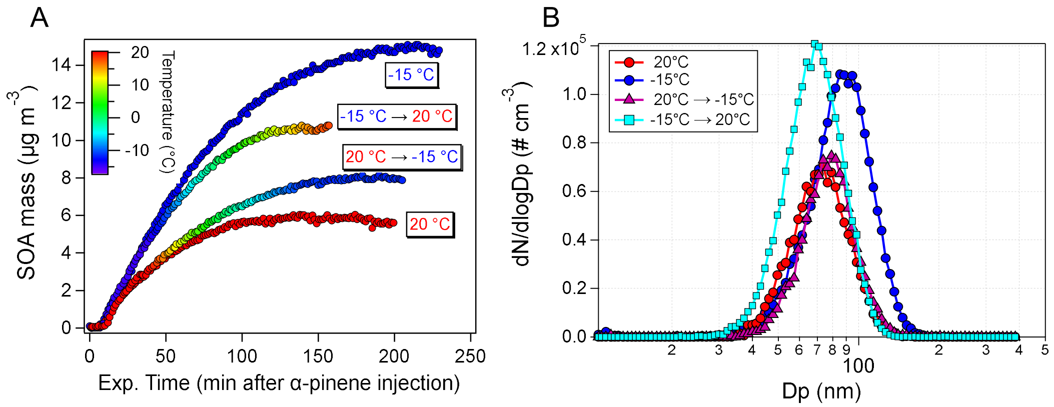


Figure 7. Effect of ramping temperature (20 °C → -15 °C, Exp. 1.4, and -15 °C → 20 °C, Exp. 1.5) on the wall-loss corrected SOA mass concentration (**A**) and final particle size distribution (**B**) from ozonolysis of 10 ppb α-pinene. For comparison, results from constant -15 °C and 20°C temperature experiments (Exp. 1.1 and Exp. 1.3, respectively) are also shown.

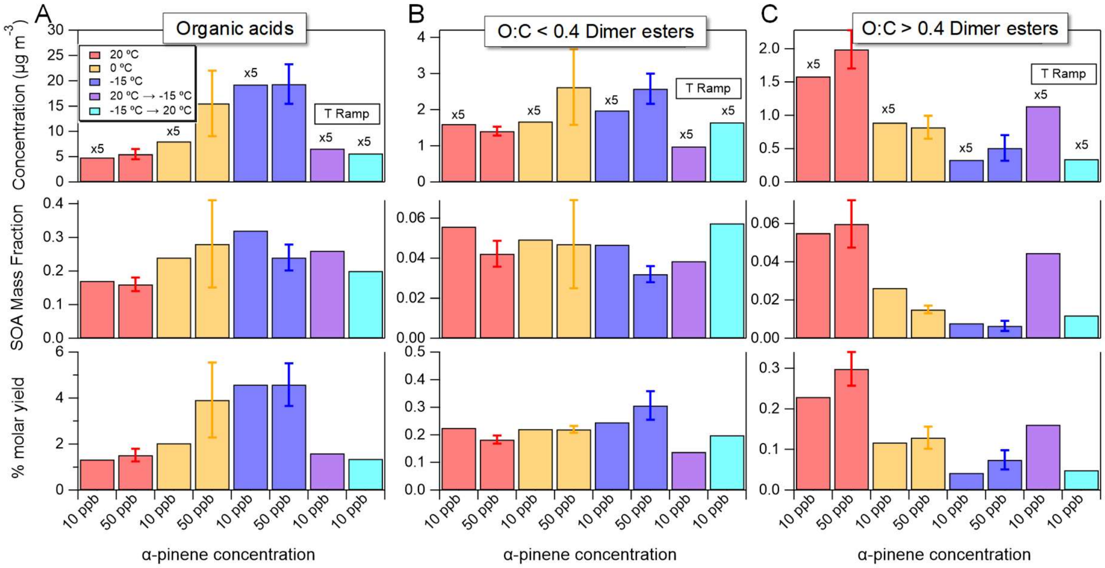


Figure 8. Effect of α-pinene concentration and temperature on the mass concentrations (µg m-3), SOA mass fractions, and molar yield of the identified organic acids (column A), low O:C (<0.4) dimer esters (column B) and high O:C (>0.4) dimer esters (column C). Note that the concentrations (µg m-3) of organic acids and dimer esters related to the 10 ppb α-pinene oxidation experiments have been multiplied with a factor of 5 (top panels). For the 50 ppb pinene oxidation experiments average values are reported from Exp. 2.1-2.3 and Exp. 3.1-3.3. Error bars represent one standard deviation.

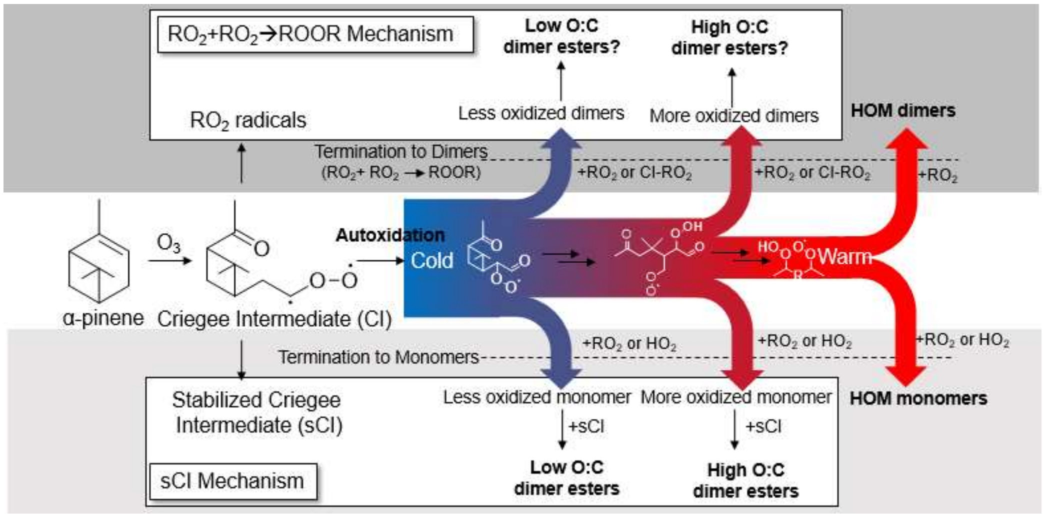
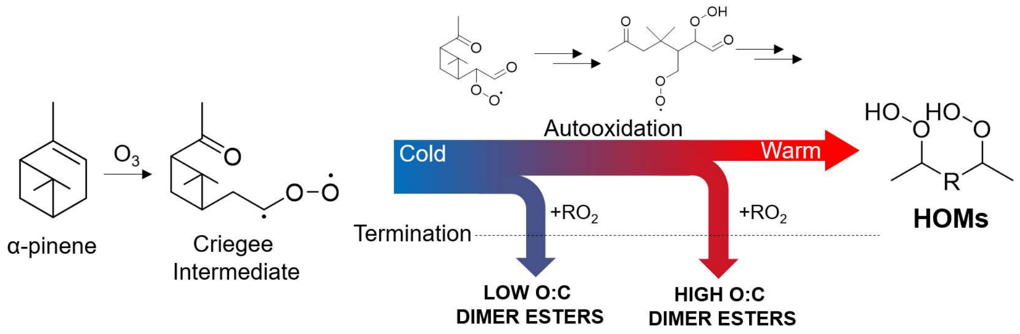


Figure 9. Illustration of two suggested mechanism for dimer esters: 1) RO$_2$-RO$_2$ radical reactions forming ROOR dimers (upper) or 2) reactions of stabilized Criegee Intermediates (sCI) with monomers from RO$_2$ termination reactions with RO$_2$ or HO$_2$ (lower). The O:C of the resulting dimer ester is governed by the degree of autoxidation before radical termination.



~~**Figure 9.** Illustration of the proposed relation between low O:C (< 0.4) and high O:C (> 0.4) dimer ester formation and HOMs.~~

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