

# ***Interactive comment on “The Aarhus Chamber Campaign on Highly Oxidized Multifunctional Organic Molecules and Aerosols (ACCHA): Particle Formation and Detailed Chemical Composition at Different Temperatures” by Kasper Kristensen et al.***

**Kasper Kristensen et al.**

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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  $\alpha$ -pinene SOA for-

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mation and composition at different temperatures (20 °C, 0 °C, and -15 °C) 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  $\alpha$ -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

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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  $-15^{\circ}\text{C}$  compared to  $20^{\circ}\text{C}$ . Unfortunately, this is not clearly stated in the manuscript. We have thus added a figure to the SI (Figure S4) showing dimer ester yields at  $-15^{\circ}\text{C}$  relative to  $20^{\circ}\text{C}$  (yield @  $-15^{\circ}\text{C}$  / yield @  $20^{\circ}\text{C}$ ) 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  $-15^{\circ}\text{C}$  compared to  $20^{\circ}\text{C}$  (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).”

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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 RO<sub>2</sub>-RO<sub>2</sub> 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 CO<sub>2</sub>). 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 °C or -15 °C, the SOA mass do not merge to the level in constant 20 °C or -15 °C. 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

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role in total 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  $0.3 \mu\text{g m}^{-3}$  increase in organic acid concentration making up  $\sim 15\%$  of the reported  $2 \mu\text{g m}^{-3}$  increase in SOA mass compared to the constant  $20^\circ\text{C}$  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  $\alpha$ -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  $20^\circ\text{C}$  to  $-15^\circ\text{C}$ . 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  $\text{NO}_3$ -CIMS should be discussed more extensively. Further, it is true that at lower temperature, HOM formation via  $\text{RO}_2$  autoxidation is limited, bimolecular  $\text{RO}_2$  reaction is expected to increase. But this does not necessarily mean that  $\text{RO}_2$ - $\text{RO}_2$  dimer formation is going to be enhanced. How about  $\text{RO}_2 + \text{HO}_2$  and  $\text{RO}_2 + \text{RO}_2$  which lead to monomeric

products? These two reactions are both temperature dependent and are likely more important than RO<sub>2</sub> autoxidation (5-10%) and RO<sub>2</sub>+RO<sub>2</sub> to ROOR (5 – 10%). Thus, the temperature effects on RO<sub>2</sub> + HO<sub>2</sub> and RO<sub>2</sub> + RO<sub>2</sub> could more likely govern the changes in RO<sub>2</sub> 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, RO<sub>2</sub> + RO<sub>2</sub> 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, see below) 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-RO<sub>2</sub> reactions. Also, as suggested by the reviewer the influence of HO<sub>2</sub> + RO<sub>2</sub> competition is also discussed.

Section 3.5 (revised): “Gas-phase formation of dimer esters from  $\alpha$ -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,  $\alpha$ -acyloxyalkyl hydroperoxides ( $\alpha$ -AAHPs) (Zhao et al., 2018a; Kristensen et al., 2016). In relation, Clafin 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.

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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  $\alpha$ -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, C19H28O7) and MW 358 (pinyl-diaterpenyl ester, C17H26O8) 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  $\text{RO}_2 + \text{R}'\text{O} \rightarrow \text{RO}_3\text{R}$  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

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5- and 7-hydroxy-pinonic acid involved in the formation of the two C<sub>19</sub>H<sub>28</sub>O<sub>11</sub> HOM species decomposing to the MW 368 and MW 358 dimer esters, respectively; or (2) temperature-dependent decomposition and rearrangement of the C<sub>19</sub>H<sub>28</sub>O<sub>11</sub> 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<sub>19</sub> 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<sub>2</sub>, 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

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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 proceed through reaction of products from RO<sub>2</sub> autoxidation. The involved oxidation state of these products may vary depending on the degree of autoxidation undertaken by the RO<sub>2</sub> radical as well as the radical termination of these including unimolecular processes leading to loss of OH or HO<sub>2</sub> or bimolecular reactions with NO, HO<sub>2</sub> or other RO<sub>2</sub> 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. Clafin et al. (2018) showed that the autoxidation and radical termination reactions of the Criegee Intermediate RO<sub>2</sub> radicals may result in a plethora of different products covering a range of oxidation states and functionalities; including multifunctional RO<sub>2</sub> radicals, hydroperoxide, carbonyl, alcohol, carboxylic and peroxy-carboxylic acid, dialkyl and diacyl peroxides. Of these, carbonyls, alcohols and carboxylic acids react readily with sCl resulting in dimeric compounds such as secondary ozonides,  $\alpha$ -alkoxyalkyl hydroperoxides (AAAHs), and  $\alpha$ -AAHP, respectively (Chhantyal-Pun et al., 2018; McGillen et al., 2017; Khan et al., 2018; Clafin et al., 2018). In addition, gas-phase RO<sub>2</sub>–RO<sub>2</sub> reactions have been proposed as conceivable mechanism for the formation of dimers from  $\alpha$ -pinene ozonolysis (Clafin et al., 2018; Zhao et al., 2018b). Here, RO<sub>2</sub> produced from the isomerization or decomposition of Criegee Intermediates are suggested to participate in RO<sub>2</sub>–RO<sub>2</sub> reactions resulting in dialkyl or diacyl peroxides. The formation of dimer esters through reactions of RO<sub>2</sub> is supported by an observed decrease in dimer ester concentrations at higher levels of NO<sub>x</sub> 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<sub>2</sub> cross-reactions as likely route of gaseous dimer formation. The RO<sub>2</sub>–RO<sub>2</sub> reaction is expected to compete with the reactions of RO<sub>2</sub> with HO<sub>2</sub> 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  $\alpha$ -pinene with

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O3. The formed OH-radicals reacts readily with O3 yielding HO2-radicals available for RO2-HO2 reactions. As both reactions ( $O_3 + \alpha$ -pinene and  $O_3 + OH$ ) 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

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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<sub>16</sub>–20H<sub>y</sub>O<sub>6</sub>–9) in both particle and gas phases in ambient air measurements in the boreal forest in Finland.”

Technical comments:

1. Line 41. 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.  $\alpha$ -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

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as possible to the cold room through insulated tubing extending  $\sim 40$  and  $\sim 10$  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  $\alpha$ -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.

Reply: The following sentence has been added (Line 181-183) “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).”

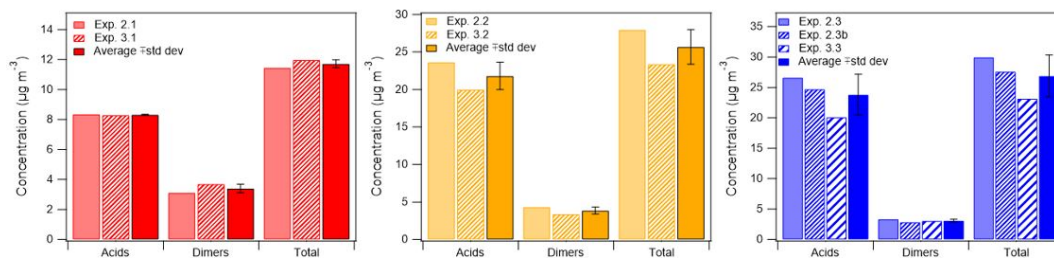
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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-99>, 2020.

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Discussion paper





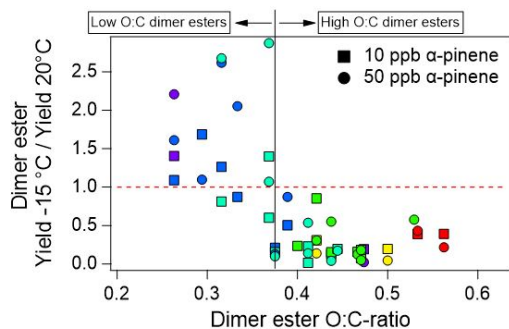
**Figure S3.** Concentrations ( $\mu\text{g m}^{-3}$ ) of acids and dimers from UHPLC/ESI-qTOF-MS analysis of repeated experiments performed at 50 ppb  $\alpha$ -pinene and 20 °C (Exp. 2.1 & 3.1), 0 °C (Exp. 2.2 & 3.2) and -15 °C (Exp. 2.3a, 2.3b & 3.3). Bars to the right (dark colored) represent average concentrations and associated standard deviations.

**Fig. 1.** Figure S3 added to SI

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Discussion paper





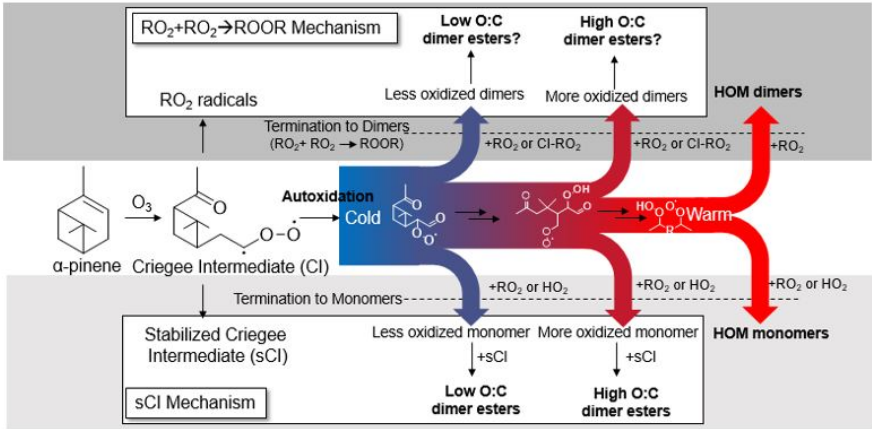
**Figure S4.** Comparison of relative yields (yield at -15 °C / yields at 20 °C) for specific dimer esters as a function of dimer ester O:C ratio in 10 and 50 ppb  $\alpha$ -pinene ozonolysis experiments. Vertical line indicates the O:C value (0.38) above which all dimer esters show a decrease in concentration at -15 °C compared to 20 °C.

**Fig. 2.** Figure S4 added to SI

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**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.

**Fig. 3.** New Figure 9

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