

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.

kasper.kristensen@eng.au.dk

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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.

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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-particle 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 show-

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ing newly formed 20–70 nm particles showed enhancement in alkanolic 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 alkanolic 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; Claićin et al., 2018)?

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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

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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 (ClaiňĆin 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 (ClaiňĆin 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 partitioning 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 $\mu\text{g m}^{-3}$ 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 °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-

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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

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(RC = O), alcohols (ROH), carboxylic acids (ROOH) to form hydroperoxy esters and secondary ozonides and water vapor to form hydroxy hydroperoxides (ClaiřĆin et al., 2018; Zeng et al., 2020). ClaiřĆin et al. (2018) stated that the only known gas-phase mechanism for forming esters in their experiments was the reaction of Cl with carboxylic acids under dry conditions. ClaiřĆin 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. Mőller 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 Cl with oxidation products with various functionalities. As we cannot exclude other formation pathways (i.e. sCl 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 (sCl) 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, Clafin et al. (2018) stated that the only known gas-phase mechanism for forming esters in their experiments was the reaction of sCl with carboxylic acids under dry condition. As the reactions of sCl 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

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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 sCl 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 sCl 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 sCl + 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 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 tem-

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perature 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

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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 proceed 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. Clafin et al. (2018) showed that the autoxidation and radical termination reactions of the Criegee Intermediate RO₂ (CI-RO₂) radicals may result in a plethora of different products covering a range of oxidation states and functionalities; including multifunctional RO₂ 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, α -alkoxyalkyl hydroperoxides (AAAHs), and α -AAHP, respectively (Chhantyal-Pun et al., 2018; McGillen et al., 2017; Khan et al., 2018; Clafin 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 (Clafin et al., 2018; Zhao et al., 2018b). Here, CI-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 NO_x 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

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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

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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.

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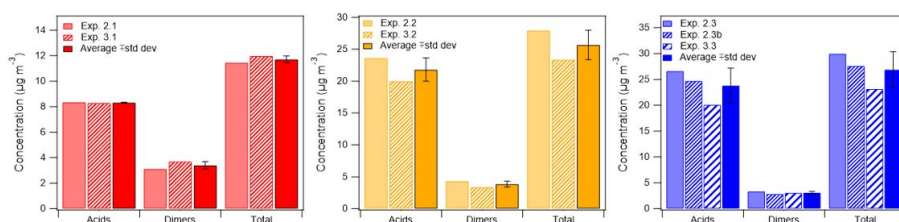


Figure S3. Concentrations ($\mu\text{g m}^{-3}$) of acids and dimers from UHPLC/ESI-qTOF-MS analysis of repeated experiments performed at 50 ppb α -pinene and 20 °C (Exp. 2.1 & 3.1), 0 °C (Exp. 2.2 & 3.2) and -15 °C (Exp. 2.3a, 2.3b & 3.3). Bars to the right (dark colored) represent average concentrations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

Fig. 1. Figure S3 added to SI

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