

***Interactive comment on “High-molecular-weight esters in  $\alpha$ -pinene ozonolysis secondary organic aerosol: Structural characterization and mechanistic proposal for their formation from highly oxygenated molecules” by Ariane Kahnt et al.***

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We would like to thank the reviewer for thoughtful and constructive comments, and for the general appreciation of the study.

Our responses to the specific comments are as follows:

Reviewer: Please comment about why positive ion ammonia adducts were studied

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as opposed to protonated or metal cationized molecules (positive spectra) or deprotonated molecules (negative spectra). I'm guessing that the additional fragmentation step of the ammonia adducts (initial loss of ammonia) takes away some internal energy of the ions, making subsequent fragmentation of  $MH^+$  more controlled and easier to interpret. Also, how intense are the ammonia adducts of these ions relative to other adducts? Was the solvent composition modified to enhance ammonia adduction?

Response: The simple reason why in the positive ion mode ammonia adducts were selected is that under the LC conditions used these ions were more abundant than the protonated molecules, while metal-cationized molecules were not observed. The ion abundance ratios  $[M + NH_4]^+ / [M + H]^+$  were 13.0, 15.6, 38 and 7.7, for the MW 358 ester, MW 368 ester, MW 358 ester trimethylated derivative and MW 368 ester dimethylated derivative, respectively. Ammonia adducts were formed because the buffered aqueous LC mobile phase with pH 3 contained ammonium formate (50 mM). The LC solvent composition was thus not modified to enhance ammonia adduction. Upon collisional activation in the ion trap, the ammoniated adducts lose ammonia, resulting in the protonated molecules, of which the fragmentation can readily be explained.

Reviewer: Scheme 1. Should the dotted line for pathway b in the  $m/z$  359 structure be pointed to the left rather than to the right?

Response: Yes, this is indeed wrong. Scheme 1 will be corrected in the revised manuscript.

Reviewer: Page 11, line 296. While I appreciate the authors point regarding the strength of the signal intensity of  $m/z$  351 with respect to the two positional isomers, I think a much more compelling observation is the high intensity of  $m/z$  333 ion (loss of the second  $H_2O$  molecule), which would be much harder for the MW 368 structure a in Figure 1.

Response: We thank the reviewer for this input. The main text will be changed accordingly to include this observation. The loss of a second molecule of water would indeed

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be more difficult to explain with positional isomer a.

Reviewer: Page 12, lines 314-319. This discussion (fragmentation of the cyclobutane ring) is perhaps the weakest of the arguments made by the authors regarding positional isomers since it is based on previous measurements of the fragmentation of monomer compounds in negative ion mode. Nonetheless, it is consistent with other fragmentation products for MW 368 that point to positional isomer b in Figure 1.

Response: The discussion of the fragmentation of the dimethylcyclobutane ring is indeed based on previous measurements of the fragmentation of monomer compounds (pinic acid and norpinic acid) in negative ion mode but we would like to retain this argument in favor of positional isomer b.

Reviewer: Figures 4 and 5. I found the dotted lines within the structures in these figures to be distracting. The lines do indicate where the molecule is ultimately going to break, but the ammonia adduct decomposes to the protonated molecule first, which is not clear from the structure. I think it is better to keep the format of these structures similar to Figures 2 and 3.

Response: For clarity, the dotted lines will be removed in Figures 4 and 5. We fully agree with the reviewer.

Reviewer: Page 12, section 3.2.1. Before launching into the gas phase formation mechanism, the authors should state (if it is the case) that there are no direct analogues to MW 358, 368 in the CI-APiTOF mass spectra. If MW 358 and 368 were produced in the gas phase, do you expect they would be sensitively detected by CI-APiTOF?

Response: As suggested, it will be stated that there are no direct analogues to the MW 358 and 368 esters in the CI-APiTOF mass spectra. But it is hard to predict whether the CI-APiTOF MS technique with nitrate clustering would be sensitive to the detection of these compounds. As far as we understand the CI-APiTOF MS technique is very sensitive to the detection of peroxy compounds.

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Reviewer: Sections 3.3.2 and 3.3.3. My understanding of gas phase radical-radical chemistry is that these types of reactions are relatively unconstrained - they occur with high probability and it is mostly a matter of which two specific species happen to collide first. With that in mind, it seems that this discussion and accompanying schemes 5 and 6 give a rationalization for the formation of MW 358 and 368, but they do not explain the preference for the specific positional isomers that were identified.

Response: We believe that the discussion accompanying schemes 5 and 6 provides a reasonable rationalization for the formation of the MW 358 (isomer a) and MW 368 (isomer b). For the formation of the other positional isomers, one would have to consider the formation of isomeric monomeric radicals. For example, the formation of MW 368 (isomer a) would require the formation of a C<sub>10</sub>H<sub>15</sub>O<sub>5</sub> radical, containing the carboxyperoxy radical at the opposite methylcarboxyperoxy substituent and would require one or more steps.

Reviewer: Given that identification of positional isomers is a key element of this study, can the authors explain this preference? Furthermore, why do you have the expectation that MW 358 and 368 must be produced from dimer precursors that were initially formed in the gas phase? Could it be possible that these species are formed from reactive nonvolatile monomers (peroxy compounds?) that condense to the particle phase and then react very quickly to make the dimer products? It seems that the positional isomer preference demonstrated by the MS<sub>n</sub> work might be exploited more fully to perhaps rule in/out certain reaction pathways.

Response: As discussed in the manuscript, we propose that the MW 358 and 368 esters are produced from unstable dimer precursors that are initially formed in the gas phase. An argument in favor of this hypothesis, mentioned in the manuscript, is that the proposed gas phase precursors, i.e., isomeric C<sub>19</sub> peroxy species, are unstable (lines 357 - 365). This is supported by an alpha-pinene ozonolysis flow tube experiment reported by Krapf et al. (2016), where in addition to the C<sub>19</sub>H<sub>28</sub>O<sub>11</sub> species also C<sub>19</sub> species are detected corresponding to the conversion of one acyl hydroperoxy group

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(C<sub>19</sub>H<sub>28</sub>O<sub>10</sub>), the conversion of two acyl hydroperoxy groups (C<sub>19</sub>H<sub>28</sub>O<sub>9</sub>), the loss of oxygen (C<sub>19</sub>H<sub>28</sub>O<sub>9</sub>), and the loss of oxygen combined with the conversion of one acyl hydroperoxy group (C<sub>19</sub>H<sub>28</sub>O<sub>8</sub>). As clearly stated in the manuscript, the proposed formation pathways should be regarded as tentative.

We think that it is rather unlikely that the MW 358 and 368 esters are formed in the condensed phase by reactive monomers containing peroxy groups. In an earlier study (Yasmeen et al., 2010) we have proposed that the MW 358 ester is produced in the condensed phase by reaction between pinic acid and the lactone-containing terpenylic acid, but a subsequent study by Kristensen et al. (2014) provided evidence that this pathway is not supported and that a gas-phase formation pathway should be considered. In the cited study, the formation of dimers has been shown to occur only during ozonolysis of  $\alpha$ -pinene and not through OH-oxidation, suggesting that these dimers originate via the gas-phase reaction of a stabilized Criegee intermediate formed by ozonolysis of  $\alpha$ -pinene. This mechanism is supported by the increase in the formation of dimers observed at higher RH, explained by increased stabilization of the Criegee intermediate. This has been addressed in the introduction where we write: “Efforts to understand ester formation from  $\alpha$ -pinene ozonolysis have also been actively undertaken. Yasmeen et al. (2010) proposed that ester formation took place in the particle phase by esterification of cis-pinic acid with terpenylic acid but this mechanism was not retained in later studies. Kristensen et al. (2014) demonstrated their formation through gas-phase ozonolysis and supported the participation of a stabilized Criegee intermediate, as previously suggested for the formation of unstable high-molecular-weight compounds that play a role in new particle formation (Ziemann, 2002; Bonn et al., 2002; Lee and Kamens, 2005).”

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