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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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First, I would like to say to the authors and to anyone else who reads interactive comments how impressed I am with the experimental design and interpretation of MSn data. A lot of hard work went into this study. Thanks for an enjoyable read!

Interpretation of MSn data in general, and product ion signal intensities in particular, is impeded by the fact that ions readily undergo structural rearrangements that often can't be predicted ahead of time, causing misinterpretation. The strength of this study is the

presentation of two different sets of data (with/without methylation) for two different species (MW 358 and 368), all of which point to the same conclusion with regard to positional isomers. This gives substantial confidence in the conclusions.

Specific comments and questions:

Please comment about why positive ion ammonia adducts were studied 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?

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?

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 H2O molecule), which would be much harder for the MW 368 structure a in Figure 1.

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.

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.

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?

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.

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 MSn work might be exploited more fully to perhaps rule in/out certain reaction pathways.

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