

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.

Ariane Kahnt et al.

magda.claeys@uantwerpen.be

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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: The suggestion that an peroxy radical is involved in the formation of the

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dimers also fits to the observation of an suppression of NPF as observed in: Wildt, J., Mentel, T. F., Kiendler-Scharr, A., Hoffmann, T., Andres, S., Ehn, M., Kleist, E., M \ddot{u} sgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R., and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NO $_x$, Atmos. Chem. Phys., 14, 2789-2804, <https://doi.org/10.5194/acp-14-2789-2014>, 2014. The authors might consider to also refer to this work.

Response: We thank the reviewer for this input. This study will be mentioned in the revised manuscript.

Reviewer: I might have missed that in the text but are there indications if the final dimeric ester products (i.e. MW 358 and 368) can also be detected in the gas phase? If not, do the authors believe that this is a consequence of the (non) ionization of the esters in their measurements or an indication that the formation of the final products takes place in the particle phase?

Response: We are not aware that the final dimeric MW 368 and 358 esters can also be detected in the gas phase by the CI-API-TOF technique with nitrate clustering. It is well possible that the latter technique is not sensitive to the detection of the MW 368 and 358 esters. As far as we understand the CI-API-TOF MS technique is very sensitive to the detection of peroxy compounds. A similar comment was also made by reviewer #1. In response, as suggested by this reviewer, it will be stated in the revised version that there are no direct analogues to the MW 358 and 368 esters in the CI-API-TOF mass spectra. It is hard to say at which stage (gas or condensed phase) and to which extent the final products will be formed from the unstable gas-phase peroxy precursors but there is evidence from an α -pinene ozonolysis flow tube experiment reported by Krapf et al. (2016) that degradation already takes place under the flow tube conditions: in addition to the C $_{19}$ H $_{28}$ O $_{11}$ species also C $_{19}$ species are detected corresponding to the conversion of one acyl hydroperoxy group (C $_{19}$ H $_{28}$ O $_{10}$), the conversion of two acyl hydroperoxy groups (C $_{19}$ H $_{28}$ O $_9$), the loss of oxygen (C $_{19}$ H $_{28}$ O $_9$), and the loss of oxygen combined with the conversion of one acyl hydroperoxy group (C $_{19}$ H $_{28}$ O $_8$).

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