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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 #2

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The manuscript describes the interpretation of LC-MS and MS-MS investigations from reaction chamber experiments of alpha-pinene ozone experiments. The focus is the structural characterization of higher molecular weight dimer esters. One of the conclusions of the manuscript is the proposal of a connection between the formation of the dimeric esters and the formation of highly oxidized dimers often observed in CIMS measurements. In general, the paper is well written and presents an interesting topic that is well suited to be published in ACP. The formation of higher molecular weight

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Discussion paper

compounds is still a topic of considerable interest, especially in connection with atmospheric new particle formation. Although the first observation of the dimers in biogenic SOA is already 20 years ago, the detailed structures and especially the formation pathways of these compounds are still unclear. In my opinion the most interesting aspect of the manuscript is the suggestion of an reaction of a peroxy- and an alkoxy-radical to form a dimer with a trioxide bridge, followed by a decomposition to form the observed stabile ester dimers. Such a pathway would finally bridge the observation of gas phase HOMs with the well-known dimer esters as identified by the traditional trace analytical community (e.g. using LC-MS). Therefore, in my opinion the manuscript is well suited to be published in ACP after considering the following minor comments.

Minor comments: The suggestion that an peroxy radical is involved in the formation of the 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., Müsgen, P., Rohrer, F., Rudich, Y., Springer, M., Tillmann, R., and Wahner, A.: Suppression of new particle formation from monoterpene oxidation by NOx, 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.

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?

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