

Interactive comment on “Dimer esters in α -pinene secondary organic aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity” by K. Kristensen et al.

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We would like to thank the reviewers for their thorough reviews and suggestions. We have considered all comments carefully and our replies are listed below. It is our feeling that this process has contributed to improve the manuscript.

Sincerely, Kasper Kristensen and Marianne Glasius on behalf of all authors

Reply to Anonymous Referee #4:

General Comments: This is a detailed study of dimer formation from α -pinene oxidation. The manuscript is nicely written and provides convincing evidence that dimers are
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formed in the gas phase through the sCI. This conclusion is important since it provides a reasonable explanation for nucleation of secondary organic particles in the absence of inorganic species e.g. sulfuric acid and ammonia.

Major comment: The terminology “dimer esters” in the title and text is not optimum and should be changed. Indeed, the main conclusion of the work is that “dimer esters are not formed through the currently postulated particle-phase esterification of carboxylic acids” (conclusion section). As the authors point out, this conclusion is supported by experimental kinetics studies (reference cited in the conclusion section should be Heaton et al., 2007) and by computational chemistry (DePalma, 2013). In particular, the DePalma study shows that ester formation from acid monomers is thermodynamically unfavourable either in the gas or particle phase under atmospherically relevant conditions. The DePalma conclusion concerning esterification should be emphasized in both the introduction and conclusion since it directly supports the conclusion of this manuscript. The problem with the use of “dimer esters” especially in the title is that an un-careful reader will mistakenly associate these species with a classical esterification process, which is counterproductive with respect to the conclusion of this paper. In fact, the results of this paper argue strongly for a change in the way the scientific community refers to these species. Accordingly, it is better to use “dimers” or “covalent dimers” in the title and text. Then, discuss in the next to last paragraph of the introduction section why these species have been (acceptably) referred to as esters in the past (molecular weights and elemental formulas are consistent with ester formation; MS/MS data are consistent with monomer acid building blocks). This would set up the key conclusion of the work that while these dimers may share structural features with the products of esterification, they clearly are not formed by esterification.

Reply: We agree with the referee that the terminology “dimer esters” can be somewhat misleading and have changed “dimer esters” to “dimers” in the title and text as suggested by the referee. Heaton et al., (2007) is now cited in the conclusion section as suggested. The previous reasoning and origin of the terminology “dimer ester” is now

mentioned in the introduction as suggested by the referee.

Minor comment: Section 2.2 – Specify the NO_x detection limit to quantify what is meant by “very low” concentration.

Reply: As NO_x has never been injected into the indoor chamber and it was continuously flushed with clean house air prior to each experiment, NO_x is expected to be below 1 ppbv in this chamber, hence the term “very low” concentration. We have added this information to the manuscript to avoid any misunderstandings.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 32529, 2013.

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