

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.

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 reviewer #1: Magda Claeys

General Comments:

This is a very fine manuscript. The comprehensive study presents detailed insights into the experimental conditions under which high-molecular weight dimers from alpha-pinene are formed. This is an actual topic in atmospheric sciences as high-molecular weight products are likely involved in new particle formation under ambient conditions. Unambiguous evidence is provided that high-molecular weight diesters are formed through ozonolysis and not through OH-initiated oxidation of alpha-pinene, and involve the participation of a stabilized Criegee intermediate (sCI), thus revising a previous formation mechanism, proposed in Yasmeeen et al. (2010), where the high-molecular weight diesters have been explained by esterification of monomeric terpenoic acids in the particle phase. A reasonable explanation is given why in field studies conducted at K-puszt, Hungary, or the Blodgett forest, USA, the high-molecular weight diesters are mainly detected during night-time when ozone chemistry may occur. Evidence is also provided that diaterpenylic acid acetate (DTAA) is formed through OH-initiated oxidation of alpha-pinene and does not serve as a monomer for the MW 358 dimer.

Specific comments:

1) Introduction – page 32532 - lines 5-14; Figure 1: known reactions are discussed here for the sCI which lead to first-generation products such as pinonaldehyde and pinic acid; especially, the formation of pinic acid is relevant as it is incorporated into high-molecular weight diesters with MW 358 and 368. However, nothing is said about reactions that lead to terpenylic acid, which is also incorporated into high-molecular weight dimers with MW 344 and 358. In this respect, a pathway involving ozonolysis of alpha-pinene and campholenic aldehyde, previously suggested by Claeys et al. (2009), has been supported in recent studies by Iinuma et al. (2013) and Kahnt et al. (2014; in press). The reaction of alpha-pinene and ozone leads to alpha-pinene oxide, which can rearrange to campholenic aldehyde. As campholenic aldehyde contains a double bond it can react further with ozone to form terpenylic aldehyde, which can be further oxidized in the particle phase to terpenylic acid. It is worth noting that a sCI has been proposed to play a role in the formation of terpenylaldehyde through ozonolysis of campholenic aldehyde (Claeys et al. 2009; supporting information; Scheme S2).

Refs.:

Iinuma, Y.; Kahnt, A.; Mutzel, A.; Boge, O.; Herrmann, H.: Ozone-driven secondary organic aerosol production chain, Environ. Sci. Technol., 47, 3639–3647, 2013.

Kahnt, A.; Iinuma, Y.; Mutzel, A.; Boge, O.; Claeys, M.; Herrmann, H.: Campholenic aldehyde ozonolysis: a mechanism leading to specific biogenic secondary organic aerosol constituents, Atmos. Chem. Phys., 14, in press; doi:10.5194/acp-14-1-2014 (Atmos. Chem. Phys. Discuss., 13, 22487-22534, 2013).

Reply: We agree with the referee that the formation of terpenylic acid should be mentioned in the manuscript as well. The suggested citations have now been added along with short description of the formation of terpenylic acid from α -pinene, as described by the referee.

2) Introduction – page 32533 – lines 19-29: Reference should be made to the article by Hoffmann et al. (1998); this could best be done in the paragraph, where arguments are given against the proposed esterification mechanism. This is in my opinion the first article where

mention is made of high-molecular weight compounds in an α -pinene ozonolysis smog chamber experiment, including the major MW 358 compound, which is shown to be formed in the gas phase concomitantly with *cis*-pinic acid, *cis*-pinonic acid and a MW172 monomer, tentatively attributed to *cis*-norpinic acid. At a later stage, the MW172 monomer was structurally revised as the lactone-containing terpenylic acid (Claeys et al., 2009).

Ref.:

Hoffmann, T.; Bandur, R.; Marggraf, U.; Linscheid, M.: Molecular composition of organic aerosols formed in the α -pinene/O₃ reaction: Implications for new particle formation processes, *J. Geophys. Res.-Atmos.*, 103, (D19), 25569-25578, 1998.

Reply: We agree with the referee and have added a reference to the article by Hoffman et al. (1998) acknowledging their first observation of high-molecular weight compounds in α -pinene ozonolysis smog chamber experiment.

3) *Experimental – page 32538 – lines 17-28: It is not completely clear how the quantitation was done. Was there any correction done for losses of the analytes during sample workup? Was an internal recovery standard used to compensate for losses during sample workup?*

Reply: No correction for losses of analytes was conducted as no internal recovery standard was used during sample workup. The extraction efficiency has later been tested by extraction and analysis of filters spiked with pinic acid, pinonic acid, terpenylic acid, diaterpenylic acid and MBTCA resulting in an above 80% recovery of all compounds.

4) *Page 32538 – lines 25-26: The dominant acids in the low α -pinene OH-initiated oxidation experiments with the OH radical are MBTCA and DTAA. With respect to the formation mechanism of MBTCA, sufficient information and citations to previous work are given at various places in the text. However, with respect to the formation of DTAA, reference to previous work is missing. The authors could refer to Claeys et al. (2009), where DTAA has been explained through OH-initiated oxidation of α -pinene (Scheme 2 in the cited article). It is worth mentioning that part of this pathway has been previously suggested in a theoretical study by Vereecken et al. (2007).*

Ref.:

Vereecken, L.; Muller, J.-F.; Peeters, J.: *Low-volatility polyoxygenates in the OHinitiated atmospheric oxidation of alpha-pinene: impact of non-traditional peroxy radical chemistry*, *Phys. Chem. Chem. Phys.*, 9, 5241–5248, 2007.

Reply: We thank the referee for this comment and have added the suggested citations regarding the formation of DTAA.

5) Page 32541 – line 10: *A novel dimer ester with MW 388, also previously observed by Gao et al. (2010), is detected. Has MS/MS been performed to obtain information about the monomeric residues? If so, it would be worthwhile to include this information.*

Reply: MS/MS spectra have been added to the supplementary material, but no conclusions have been derived regarding the monomers.

Technical corrections:

Abstract – page 32531 – line 4: replace “gas-phase” by “gas phase”

Page 32534 – line 23: replace “detector” by “detection”

Page 32538 – line 12: replace “inlet” by “source”

Page 32541 – line 11: replace “esters” by “ester”

Page 32541 – line 16: replace “pininc” by “pinic”

Page 32547 – lines 6, 8 and 16: replace “gas-phase” by “gas phase”

References: titles of journal articles should not be capitalized; the ref. Gao et al. (2010) should be corrected.

Figure S1: the structure of MBTCA should be corrected; the structure is correct in Table 2 of the main text; also, replace “Diaterpenylci” by “Diaterpenylic”.

Reply: All technical corrections proposed by the reviewer have been corrected accordingly. We thank the referee for bringing these to our attention.

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 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 “dimers 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.

Relevant changes made in the manuscript:

In addition to the changes stated above the following relevant changes have been made in the manuscript:

Quality of Figure 2, 5, 9, 12 and 6S has been improved.

P32539, Line 6: “hydroxyperoxy” has been changed to “alkyl peroxy”

P32536, Line 6: “Temperature” has been changed to “temperature” in brackets