

Interactive comment on “Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a mass spectrometric study of SOA aging” by L. Müller et al.

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The authors would like to thank the reviewer for her thorough reading. Below, we respond to the comments.

General comments: In this study, sound evidence is provided that pinonic acid, a first-generation alphapinene secondary organic aerosol (SOA) product, serves as a gas-phase precursor for 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), supporting a proposal previously made in Szmigielski et al. (2007). Mechanistic pathways for the

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formation of MBTCA are given and discussed in detail. I argue, however, that based on several reasons the mechanism involving hydrogen abstraction at the C-7 atom of pinonic acid should be retained in the main text, as will be outlined in the specific comments below. The aging of two well-known first-generation alpha-pinene SOA products pinonic acid and pinic acid through OH-initiated reactions is examined in detail. This methodological approach, however, has some limitations that should be addressed in the introduction. A model consisting of only these two single products is far too simple to simulate aging of alpha-pinene SOA in the atmosphere. Besides pinonic and pinic acid there is another important first-generation alpha-pinene SOA product, i.e., the lactone-containing terpenoic acid terpenylic acid (Claeys et al., 2009), which should not be overlooked and participates in SOA aging. This process also involves esterification reactions in the particle phase, such as, for example, the formation of higher-MW diesters and organosulfates. The results obtained in this study should more thoroughly be discussed in the context of previous studies that are available on this topic. There is an issue with this manuscript because recent SOA studies related to the current study are either not cited or in the case they are cited not properly cited. In particular, it is hard for me to accept that the authors do not properly cite our article reporting for the first time the structural elucidation of 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (Szmigielski et al., 2007). There is only a very vague reference to our article (page 19445 – line 18), somewhat out of context. Furthermore, in the Szmigielski et al. (2007) article we proposed a possible mechanism starting from pinonic acid involving H abstraction at the C-7 position to explain the formation of MBTCA. In the section of the main text dealing with the mechanism a reference to our article would have been appropriate.

Specific comments: (1) Introduction – last paragraph: some background information on MBTCA would be appropriate in this paragraph. The authors state in the abstract that MBTCA is known product. MBTCA is indeed known to the authors (not necessarily to the SOA community) but unlike pinic and pinonic acids MBTCA is not a well-known product and has only been recently structurally elucidated and proposed

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as a suitable terpene SOA tracer (Szmigielski et al., 2007). A reference to the latter study and some related relevant studies (for which I refer to Zhang et al., 2010) would be appropriate. I think this could best be done at the end of the paragraph. A search on the Web-of-Science with “3-methyl-1,2,3-butanetricarboxylic acid” as topic only gives 6 references, the first one being Szmigielski et al. (2007), much less than for “pinic acid” and “pinonic acid” for which 91 and 107 references were found, respectively, showing that MBTCA is indeed not well known. I suggest that the authors add a few lines in the introduction and explain why MBTCA is monitored, as was, for example, properly done in the recent study by Zhang et al. (2010), who measured pinic and pinonic acids and MBTCA in ambient fine aerosol collected over a whole year in Mainz, Germany, and stated in their introduction: “Pinic acid as a dicarboxylic acid and pinonic acid as an oxocarboxylic acid are major products of the ozonolysis or OH-initiated oxidation of pinene (here and below pinene stands for both alpha- and beta-pinene) (Atkinson and Arey, 2003; Hatakeyama et al., 1989, 1991; Yu et al., 1999a). Further reaction of the initial oxidation products of pinene leads to highly oxidized, acyclic, polar compounds (3-hydroxyglutaric acid and 3-methyl-1,2,3-butanetricarboxylic acid, 3-MBTCA) (Szmigielski et al., 2007; Kourtchev et al., 2009; Jaoui et al., 2005). 3-MBTCA is formed by OH-initiated oxidation of cispinonic acid (Szmigielski et al., 2007) and was first detected in aerosol samples from Amazonia and Belgium (Kubatova et al., 2000, 2002).”

Reply: The criticism of the reviewer is justified. The introduction was edited as the reviewer suggested and significant citations were added.

(2) Introduction: I also miss a discussion of the recent article by Zhang et al. (2010), which is most relevant to the present study. In the Zhang et al. (2010) study pinonic acid, pinic acid, and MBTCA were measured in ambient fine aerosol collected over a whole year in Mainz, Germany, and it could be demonstrated that MBTCA shows a strong Arrhenius-type correlation with inverse temperature, indicating that OH-initiated oxidation of pinonic acid is a rate-limiting step in its formation and that MBTCA is a suitable tracer for the aging of biogenic SOA by OH radicals.

Reply: The reviewer is correct so far as a citation of the Zhang et al. article is appropriate in the context to the present paper. Therefore, the citation was included. However, the authors decided not to discuss the article by Zhang et al. in detail. Actually, the chamber results presented here were already used as a basis for the interpretation of the field data showing the temperature dependence of MBTCA in the particle phase, which strongly confirms the gas phase oxidation mechanism (Zhang, 2010).

(3) Introduction – page 19445 - line 21: the authors write: “The third possible reaction pathway is the formation of oligomers, which means the combination of smaller molecules to a larger one. In these oligomerization reactions less volatile compounds will almost always be formed (Kalberer et al., 2004; Muller et al., 2008, 2009).” The literature cited here is far from up-to-date. Substantial progress has been made in the past two years with respect to the structural elucidation of high-MW dimers of the diester type containing pinic acid and hydrolysis products of the recently reported lactone-containing terpenoic acids [i.e. terpenylic (Claeys et al., 2009) and terebic acid (Yasmeen et al., 2010)] as monomeric units. The recent articles by Yasmeen et al (2010) and Gao et al. (2010) are relevant in the context of alpha-pinene-related oligomers.

Reply: The criticism of the reviewer is justified. The introduction was edited as the reviewer suggested and significant citations were added.

(4) Section 3.2 OH-initiated aging of pinic and pinonic acid; page 19453 – line 8: Along with the generation of MBTCA, a simultaneous increase in signal intensity of the mass traces of m/z 199, m/z 213, m/z 215, m/z 229 and m/z 231 was observed. Some explanation should be given about the possible chemical nature of these compounds. For example, the m/z 199 compound most likely corresponds to an isomer of hydroxypinonic acid, i.e., 10-hydroxypinonic acid (Glasius et al., 2009; Yu et al., 1999).

Reply: Actually, as we already stated in the text, we do not want to speculate about the chemical nature of these trace substances due to the lack of authentic standard substances and insufficient data to assign specific compounds. As the reviewer cor-

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rectly stated (comment (6)), m/z -values from an online measurement are not sufficient to prove the chemical nature of an intermediate. However, we do not rule out that m/z 199 is e. g. 10-hydroxypinonic acid but there are simply not sufficient LC/MS data to prove this hypothesis. Nevertheless, some of the traces observed are discussed in the context of the mechanisms.

(5) Section 3.3 Formation mechanism: a substantial effort is done to come up with feasible formation pathways leading to the formation of MBTCA. The authors argue that the pathway starting with H-atom abstraction from the C-7 atom (pathway C and C') should be abandoned (and therefore do not discuss it in the main text), the rationale being that H-abstraction by OH radicals from the C-7 atom of pinonic acid has the lowest theoretically predicted rate constant (Table 2) and thus is assumed to be a minor reaction channel right from the beginning of the reaction sequence (about 1%). In our MBTCA article (Szmigielski et al., 2009) we have considered this pathway taking into account that it leads to the formation of other tracers of alpha-pinene, namely, pinic acid and 10-hydroxypinonic acid. Furthermore, it allows one to explain the formation of 3-hydroxyglutaric acid (Claeys et al., 2007) (for a possible mechanism, see Kourtchev et al., 2009; supplement), as well as that of another minor hydroxydicarboxylic acid, i.e., 3-hydroxy-4,4-dimethylglutaric acid (Claeys et al., 2007). Thus, it can be argued that the mechanism involving H abstraction at the C-7 position (but not necessarily starting at that position, see below), as originally proposed in Szmigielski et al. (2007), is a valid and uniform pathway not only leading to MBTCA, but also to pinic acid, pinalic acid, 10-hydroxypinonic acid, 3-hydroxyglutaric acid, and 3-hydroxy-4,4- dimethylglutaric acid. This pathway thus has the merit that it is supported by experimental data. Furthermore, experimental evidence shows that the rate of formation of MBTCA through photooxidation of alpha-pinene is very comparable to that of pinic acid, consistent with the same pathway being followed (Claeys et al., 2007). Note that in the cited article MBTCA was still not structurally elucidated and is referred to as "2 hydroxy- 4-isopropyladipic acid" (of which the structure was later revised to MBTCA). However, I would not exclude that the initial hydrogen abstraction is at the favored C-2 position (or another favored posi-

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tion), and that subsequently a hydrogen rearrangement takes place. The acetyl group is sterically well oriented (cis relative to the carboxymethylene group), so that the radical site originally created at C-2 could be neutralized by abstraction of a hydrogen atom from the terminal C-7 position. I am aware that such hydrogen rearrangements also occur in the formation of isomeric pinanediol nitrooxy organosulfates (Surratt et al., 2008).

Reply: In fact we follow a different approach than the reviewer in her original paper. We now included a specific reference to that paper and a short discussion about alternative pathways, however, without going into too much detail. Overall, future work has to bring more light into the detailed chemical mechanism of the oxidation mechanisms of PA in the gas phase.

(6) Section 3.3 Formation mechanism: with respect to pathways A and B proposed to be the favored ones, experimental evidence is still needed to firmly support them; the detection of compounds with certain m/z values corresponding to postulated intermediates is not sufficient.

Reply: See reply to comment (4)

(7) Section 3.3 Formation mechanism: page 19455 – line 11-14: the authors write: “An additional puzzle is the speed of the MBTCA formation; in all cases (e.g., Fig. 2) the tricarboxylic acid signal rises almost immediately after the onset of pinonic acid oxidation. The MBTCA thus behaves like a first-generation oxidation product, despite having two additional acid moieties.” This is fully in line with our earlier observations, see Claeys et al. (2007), Figure 4. It can be seen in that figure that MBTCA [still referred to as 2 hydroxy-4-isopropyladipic acid; see comment (5)] and pinic acid show similar formation behaviors during the first 6 hours of the alpha-pinene irradiation.

Reply: We agree.

Technical corrections: - Fig. 6: it was impossible to read the schemes; a higher resolu-

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tion figure is needed.

Reply: Figure 6 was recreated with a higher resolution

- Page 19450 – line 11: replace “Clayes” by “Claeys”, and “Antwerpen” by “Antwerp”.

Reply: The typo was certainly changed and we apologize for it.

- Page 19453 – line 4: deprotonated MBTCA; the term “molecular ion” is reserved for an ion formed by the removal of one or more electrons to form a positive ion (in the case of electron ionization) or the addition of one or more electrons to form a negative ion (in the case of electron capture). Terms relating to mass spectrometry can be found in the following publication: “Standard definitions of terms relating to mass spectrometry (IUPAC Recommendations 2006)” by Murray et al.

Reply: The term has been changed according to IUPAC recommendations

- Page 19457 – line 10 (and many places elsewhere): the carbon positions should not be indicated with a subscript. A subscript is reserved for denoting the number of atoms in a molecule. It is correct to write “C-2” or “C(2)” or “C2”.

Reply: The subscriptions have been changed

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