

## ***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 his thorough reading. Below, we respond to each comment made by the reviewer.

**General comments** This paper studies low-volatility products of the OH-initiated oxidation of pinic and pinonic acid, and cross-compares the results to  $\alpha$ -pinene + OH/O<sub>3</sub> experiments. The results indicate formation of methyl-butanetricarboxylic acid (MBTCA) from pinonic acid, and no sizable reaction for pinic acid. Based on relative gas phase /

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SOA fractions of pinic versus pinonic acid, and on the correlation of MBTCA formation with modelled pinonic acid gas phase concentrations in the  $\alpha$ -pinene experiments, the authors conclude that MBTCA formation occurs in the gas phase. The yield of MBTCA from pinonic acid was also estimated experimentally. Some possible formation routes for MBTCA from the OH-initiated oxidation of pinonic acid are proposed and discussed; their derivation relies on structure-activity relationships available in the literature. The observation of MBTCA from pinonic acid oxidation is an important contribution to our understanding of SOA formation and aging. By inference, one can expect many similar compounds in the terpene oxidation to yield analogous compounds with high O/C ratio. Furthermore, the experiments suggest that such high degrees of oxidation can be achieved already in the gas phase, an important element in SOA formation and growth. An elucidation of the chemistry is necessary for a proper understanding of the SOA chemistry, though the open questions surrounding the proposed pathways indicate that our understanding of acid formation in the gas phase is still far from complete. Note: an in-depth assessment of the experiments themselves is outside the area of expertise of the current reviewer.

**Specific comments** page 19454, lines 7-12. This reasoning is only correct if the gas phase rate coefficients are also similar. The rate coefficients have not been mentioned yet, and only the rate coefficient for pinonic acid is shown later.

**Reply:** The reviewer is correct, however, we believe that the differences in volatility (due to the different functionalities) are much more important here than potential differences in the OH rate constant.

page 19456, lines 4-7. Strictly speaking, these percentages need to be rescaled to account for the minor abstraction of the acid hydrogen, not included in the total rate coefficient by Vereecken and Peeters, 2002. (see e.g. Khamaganov et al. J. Phys. Chem. A. 2006, 110, 12852-12859 for acetic acid + OH). It might be worthwhile to mention here that the percentages, and the total rate coefficient, are subject to considerable uncertainty.

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Reply: The percentages were rescaled as suggested by the reviewer.

Page 19457, line 2. The use of the rate constants by Atkinson (2007) and Kroll and Seinfeld (2008) might be inappropriate for many of the reaction involved, as these recommendations do not contain data on many of the substituents and functionalities in the intermediates of importance here. For the alkoxy radical decomposition, this includes e.g. the effect of cyclic substituents, strained ring opening, and CO<sub>2</sub> elimination. These influences are discussed in Vereecken and Peeters (2009) as cited in the paper. For the H-migrations, the mentioned papers do not rigorously account for migrations across larger or smaller spans than 1,5-H-shift, and furthermore likely do not properly account for the effect of substituents in the cyclic H-migration transition states. See Vereecken and Peeters "A structure–activity relationship for the rate coefficient of H-migration in substituted alkoxy radicals" PCCP 2010, 12, 12608-12620 for a discussion of this latter aspect; it also includes a SAR that attempts to model these effects explicitly. The use of these theory-based SARs changes the predicted product distribution significantly; at the very least, they identify a number of reaction steps that need to be assessed (see below).

Reply: We thank the reviewer for his very detailed and well-founded discussion of the mechanism. The authors are aware of the fact that the yield calculations presented in the present paper are just rough estimates and far away from drawing a complete and accurate picture of the processes being involved in the formation of MBTCA. We added a discussion of the critical points in Pathway A and Pathway B.

Page 19457, Pathway A : 1,5-H-shift in R34: Higher level theoretical calculations (Vereecken and Peeters, 2010) suggests that H-migration of an aldehyde-H might have a higher barrier than previously obtained at lower levels of theory. In that case, formation of a C8 dialdehyde-carboxylic acid would be the dominant route, which could be partially oxidized to MBTCA similar to the scheme for P25 -> P28. Fate of R36: CO<sub>2</sub> elimination is not mentioned in the current paper, yet could also be an important pathway, with a barrier of < 2 kcal/mol and a rate of appr. 1E12 s<sup>-1</sup> (Vereecken and Peeters,

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2009), compared to 7.5E7 s<sup>-1</sup> for the alpha-OH 1,5-H-shift (Vereecken and Peeters, 2010). Vereecken and Peeters (2009) discuss an example of the CO<sub>2</sub> elimination vrs. H-migration problem.

Reply: See comment above

Page 19458, Pathway B : Application of the SAR by Vereecken and Peeters, 2009, leads to barriers of 0.3 kcal/mol and 1.6 kcal/mol for the two competing ring opening channels in R22, yielding a yield of 9% for R23. Furthermore, with such very low barriers, the reactant can still be chemically activated when decomposing, further enhancing the yield of R23. Within the uncertainty of the SAR, then, the proposed ring opening of R22 might be significantly more important than currently indicated. Application of the same decomposition SAR to R23 yields a CH<sub>2</sub>O elimination at k(283K) = 4.8E4s<sup>-1</sup>, again increasing the predicted mass flux to P25. The reaction with O<sub>2</sub> does not slow down as much with decreasing temperature. The H-migration from R28 to R29 again might have to compete against CO<sub>2</sub> elimination, which has a much more favorable entropic factor.

Reply: See comment above

Page 19459, acylperoxy + HO<sub>2</sub>. A more recent measurement of the ozone+acid channel is e.g. Jenkin, Hurley and Wallington, PCCP 9, 3149 (2007), or Le Crâne, Rayez, Rayez and Villenave, PCCP 8, 2163 (2006).

Technical corrections page 19450, line 11: typo "Magda Claeys"

Reply: Has been corrected

page 19455, line 22: typo "make MBTCA from pinonic acid"

Reply: Has been corrected

Page 19457, line 27: typo "Fantechi et al."

Reply: Has been corrected

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Figure 2 : The arrows for +TME seem to be missing from 4:15 <-> 6:30.

Reply: Has been corrected

Figure 5, reaction chain C3, step 2: This is a ring opening, not a 1,5-H-shift

Reply: Has been corrected

Figure 6 : a higher-resolution version of this figure is needed. Reaction R27 -> R28: indicate +NO, -NO<sub>2</sub>.

Reply: Has been corrected

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