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Atmospheric Chemistry and Physics Discussions

Interactive comment on "LC-MS analysis of aerosol particles from the oxidation of α-pinene by ozone and OH-radicals" *by* R. Winterhalter et al.

Anonymous Referee #3

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This paper describes results from experiments taken in the EUPHORE smog chamber on reaction products formed from the oxidation of a-pinene with ozone, OH radicals, and its photo-oxidation in the presence or absence of NOx. In principle, the topic of the manuscript is of great interest for the readers of "ACP", and the paper presents a great deal of results. The main purpose of the paper was the identification of reaction products, in my opinion the identification and quantification is not convincing (see my comments). However the authors may be correct for the identification but this need more explanation on how this was done? As a consequence, I recommend the paper to be reworked before publication.

1. Page 7, 2nd paragraph, in the photooxidation experiments, most of the products were below the instrument detection limit as reported by the authors. Hence, Table 5 and Figure 5b show that all products were identified and quantified (except for Mw =

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200)? Need comments from the authors! It seams to me not consistent!

2. There are two products commercially available (norpinic acid and 2-hydroxy-3-pinanone) that the authors didn't use in this study for identification and quantification. For example, the authors suggest for m/z 168 two possible compounds (2-hydroxy-3-pinanone and 8-hydroxy-menthen-6-one (5-(1-hydroxy-1methyl-ethyl)-2-methyl-cyclohex-2-enone) and if 2-hydroxy-3-pinanone was used, the assignment may be more straightforward. The authors need to comment why those standards were not used.

In addition, in my opinion, since the reaction products from the oxidation of a-pinene lead to a complex mixture (between 16 and 20 reaction products), and as the author know how difficult to identify these complex mixture, it seams to me that if authentic standards exist commercially, the authors need to take advantage of that.

3. Page 10, line 13, "For correction aerosol loss the ratio of corrected to measured SOA was used." How the correction was made? From Figure 4a for example, the loss of particles is very high (measured and corrected), could the authors comment here? It seams to me that the loss in the EUPHORE chamber may be low as reported for other smog outdoor chambers that exit in the world with similar volume to surface ratio!

4. Page 11, line 14, "Also the yield of pinonic... other studies." Need reference(s)

5. Section 3.4, first paragraph, Could the authors report how much NOx was released from the wall since they can be measured with their "NOx-meter", and if this amount can explains the amount of ozone formed (may be need a very simple calculation)!!

6. Page 14, line 8, The formation of pinonaldehyde and OH-pinonaldehyde, keto-pinonaldehyde and most of the pathways reported here were reported in the literature. Could the authors give the original references for these pathways?

7. The name "Pinolic acid" should be deleted from the text, Tables and Figures, because of the confusion it may cause to the readers and leave only the IUPAC nomen-

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clature for this compound.

8. Could the authors specify which pinalic acid they are talking about (see Yu et al. 1999 for pinalic 3-acid and pinalic 4-acid).

9. On page 19, line 6 "Finally the yield of particulate products was calculated versus reacted -pinene, which has been corrected for loss processes by the use of the chemically inert tracer SF6." SF6 cannot be used for loss process for a-pinene, it can accounts only for dilution but not for wall loss in the chamber?

10. Why the yield increase for observed products (see paragraph 3, page 11)?

11. The results (yields) of the photo-oxidation of a-pinene in the presence of NOx need to be compared with other studies that exist in the literature. Note that other studies were undertaken w/o seed aerosol!

12. Page 15, line 5, "The main course...(88%))" need reference!

13. Page 15, line 15, "But there has been....end of paragraph" there is other studies that report OH reaction with a-pinene and need to be referenced in addition to Larsen et al., 2001)!

14. Please give how much seed concentration was used (also need to be mentioned in table 1).

Comments

The chromatogram showed by Larsen et al. 2001 for the OH reaction of a-pinene (Figure 4) looks different then the one reported here and much peaks were observed. Did the authors observe m/z 215 and 231 as in Larsen et al. 2001 since I there the same instrument or similar one that was used?

Glasius et al observe a very intense peak for 10-hydroxy-pininic acid from the ozonolysis of myrtenol (Fig. 5) using APCI(+). Why in this study the authors report that acids are not suitable when APCI(+) was used (low response to acids)? Also similar if not

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the same instrument was used!!

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