

Interactive comment on “ α -pinene photooxidation under controlled chemical conditions – Part 1: Gas-phase composition in low- and high-NO_x environments” by N. C. Eddingsaas et al.

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We thank you for your careful review of our manuscript; your comments and suggestions are appreciated and have made the paper stronger. Please find below responses to your comments and the changes made to the manuscript.

This manuscript presents measurements of oxygenated products from the photooxidation of alpha-pinene under two regimes – one where the organic peroxy radical chemistry is dominated by reaction with HO₂, and the other where it is dominated by reaction with NO. The measurements are made using chemical ionization mass spectrometry (both positive- and negative-ion modes). The manuscript offers a fairly detailed look

C3069

at the suite of gas-phase reaction products formed from alpha pinene, and the results are simulated using a detailed chemical mechanism. It would have been nice if other, corroborative measurements had been available (e.g., CO, HCHO by FTIR, NO, NO₂); consequently the paper relies much on implications based on the model. The paper is also a little short on details in places. However, the measurements seem to have been carefully done, and, where available, the model results fit the measurements well. The presentation of the paper is reasonable. At times the writing is imprecise, but not enough to obscure the meaning. In addition to my comments below, it could benefit from a final careful reading. One particular thing to note is that it sometimes refers to a singular product, when it is clear that a class of products is meant (e.g. the hydroxyhydroperoxide, the peroxy radical). The manuscript can be published after consideration of the following comments.

Reply: Along with CIMS data we continuously monitor NO, NO_x, O₃, RH, and temperature as indicated in the experimental section. Monitoring O₃ gave us proof that we were reacting α -pinene with OH and not O₃. NO and NO_x monitoring was performed to make sure that under high-NO_x conditions, NO stayed in high enough concentration that peroxy radicals would react with NO, or in some cases acylperoxy radicals react with NO₂. Thank you for pointing out about the chemical classes, we have gone through the paper and fixed this.

1. Main Text P 6648, lines 4-7. I know that you're trying to say that at low [pinene] most of the OH reacts with H₂O₂, but that may not be apparent to the casual reader. Please rephrase so that it says what you actually mean.

Reply: Edited the sentence to read; "... under low-NO_x conditions is reaction with HO₂, produced from reaction of OH with H₂O₂, and under..."

2. P 6649, line 28. Grammar: "structure" and "are" do not agree.

Reply: Structure changed to structures

C3070

3. P 6450. What was the duration of a typical experiment (or the range). Figures 3 and 4 show data out to 18 hours. A comment here on the observed (or expected) wall losses would also be appropriate. An overview Table of experiments conducted, and the conditions used, would also be nice.

Reply: We have run experiments where the lights were extinguished after photooxidation occurred and no gas phase loss of any species was observed. The data from these experiments can be seen in part 2 of this series of papers. A statement discussing the observation of no wall loss after the lights had been turned off has been added to the experimental section. A table listing all experiments performed has been included, the table lists concentration of α -pinene, OH source, aerosol seed particles (if added), and duration of experiment.

4. P 6450, line 23. Mention here what type of lights were used.

Reply: The following has been added: "40 W black lights (Sylvania F40/350BL) with emission peak emission at 352 nm were used in both chambers. The light intensity as a function of wavelength (300-800 nm) was measured using a Licor (LI-1800) spectroradiometer."

5. Page 6453, lines 5-19. This description of the chemistry is a nice touch. I was easily able to estimate the OH, HO₂ and RO₂ from the information given (and agree that it should be dominated by HO₂ + RO₂).

Reply: Thank you

6. Page 6453, line 22. Here for example you say THE resulting hydroxyl alkyl radical, when there are two.

Reply: Thank you, we have fixed this throughout the paper and have been changed the statements to peroxy radicals, a number of peroxy radicals, or something equivalent.

7. Page 6454, line 18. PANs are mentioned in passing here, but not how they were detected. How many were there?

C3071

Reply: The end of the paragraph has been amended: "however, it was determined that higher NO₂ concentration exists during methyl nitrite photolysis due to the increased production of peroxyacetyl nitrates (PANs), as detected by CIMS in the negative mode, which result from the reaction of RO₂ + NO₂. More details on the detection of and the specific PANs detected will be discussed in section 3.3."

8. Page 6454, last line, and Figure 3A. Is the vertical scale meant to convey any information? Arbitrary units multiplied by 0.5 are still arbitrary. Are they normalized by a sensitivity factor, to make them proportional to concentration?

Reply: You make a valid point, the signal is in arbitrary units and the trace for pinonaldehyde, the one divided by two, is from the positive mode while the others are from the negative mode. As the axis is in arbitrary, the X0.5 has been removed.

9. Page 6456, line 18. "Teresa et al" should be "Raventos Duran et al." (in reference section, also).

Reply: Fixed

10. Page 6457, line 7. Detection of alpha-pinene oxide. Is there any evidence for dehydration of alcohols after protonation in positive mode? Could the pinene oxide actually be a fragment from the diol (which would be at m/z 171, and dehydrates to m/z 153)? Both 153 and 171 are listed in Figure 1. This is quite common in PTRMS detection. More details of the detection are required here.

Reply: The following has been added to the discussion of α -pinene oxide detection in the text. " α -pinene oxide is not acidic nor binds sufficiently with CF₃O⁻ to be observed in the negative mode and therefore is observed only in the positive mode at m/z 153 and 171 as confirmed by direct injection of α -pinene oxide into the chamber. Further evidence of α -pinene oxide formation is presented in part 2 of this series of paper where SOA composition is discussed."

In addition, it is stated in the previous paragraph in the paper that diols are not ob-

C3072

served. Diols would be observed in CIMS negative mode, and are not observed; therefore the ions at pos m/z 153 and 171 cannot be diols.

11. Page 6458, paragraph beginning line 10. This was a little difficult to follow. The text bounced between discussing alpha-pinene oxidation and pinonaldehyde oxidation. There were also some comments like (line 17) "The contribution of pinonic acid. . . causes the slow gas-phase loss of these two ions". Please try to be more precise. The ions are not in the chamber, the neutrals are. The appearance of the acids causes the signals at those masses to decay more slowly than if they had been just due to one product.

Reply: The paragraph has been rewritten.

12. P 6459, last line and Figure S2. I have to say, these isomerizations seem pretty unlikely to me. As a result of the double ring structure, the peroxy group and the H-atom are pointing in opposite directions, and the C-C-C-O framework is locked in an unfavorable configuration. Some abstraction from the methyl groups may be possible in the synconformation (see, for example, recent work by Vereecken and Peeters on beta-pinene, PCCP, 14, 3802).

Reply: We agree with your assessment. The text and figure S2 has been modified to the following, "When OH adds to the tertiary carbon of the double bond the resulting peroxy radical can form a seven member ring with the hydrogen of either the secondary carbon in the four membered ring or one of primary carbons attached to the four member ring. After isomerization, reaction with O₂ and HO₂ will form an α -pinene hydroxy dihydroperoxide which would be detected at m/z 303. See Fig. S2 for proposed mechanism."

13. Page 6460, line 3. change "perixide" to "peroxide", Page 6461, line 12. Seems to have an extra word or two (which. . .with)?, Page 6462, line 7. change "perixide" to "peroxide", Page 6463, line 1. change "clousure" to "closure", Page 6465, line 13. Presumably the isomerization first forms an alkyl radical, not an alkoxy?

C3073

Reply: all have been fixed

14. Page 6466. Is it possible to extract a rate constant for OH + norpinonaldehyde from the data?

Reply: No, the timeframe of the experiments is not long enough. We see the formation of norpinonaldehyde but not the loss.

15. Page 6466, line 12. "This is expected. . ." Please be more explicit (secondary product, NO₂/NO higher. . . or fewer C-H sites to abstract from?).

Reply: The sentence has been replaced by the following, "Pinonaldehyde PAN is formed from an acyl peroxy radical while pinonaldehyde nitrate is formed from an alkyl peroxy radical. The formation of an acyl peroxy radical is favored over the formation of an alkyl peroxy radical from H-abstraction of pinonaldehyde and thus pinonaldehyde PANs is expected to be formed in higher yield than pinonaldehyde nitrate."

16. Supplemental Material: Fourth box down, "perixide" should be "peroxide".

Reply: Fixed

17. Page 2: Rate constant for HO₂ + HO₂ should be around 2.5×10^{-12} at atmospheric pressure.

Reply: That is correct and what was used in the model, it was written incorrectly.

18. Top of third page: In the reaction channels for APINENEOHOO + HO₂, the fourth channel (APINENEOH) is the major channel (50%), but this product is not listed anywhere. The second channel should probably have an HO₂ product, too, since the radical reacts with O₂ to make PINON.

Reply: You are correct that "APINENEOH other products" does not appear elsewhere in the mechanism, this is because the path was not further analyzed and accounts for some of the unaccounted for carbon from the first oxidation step. Thank you for pointing out that the second channel should have an HO₂ in it, it has been added.

C3074

C3075