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Atmospheric Chemistry and Physics Discussions

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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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 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

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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.

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.

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

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.

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

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).

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

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

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?

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

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.

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.

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 syn-conformation (see, for example, recent work by Vereecken and Peeters on beta-pinene, PCCP, 14, 3802).

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 “perxide” 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?

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

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

Supplemental Material: Fourth box down, “perxide” should be “peroxide”.

Page 2: Rate constant for HO2 + HO2 should be around 2.5 x 10(-12) at atmospheric pressure.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 6447, 2012.