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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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We would like to thank the reviewer for their careful reading of the manuscript and helpful comments which have made the paper stronger. Please find below responses to your comments.

The manuscript reports high quality chamber experiments on photooxidation of α-pinene with various NOx concentrations. The gas phase composition was monitored by a CIMS system. Under low-NOx conditions a-pinene hydroxy hydroperoxides and pinonaldehyde are reported as major products and their formation pathways are discussed with focus on the RO2+HO2 reactions. A kinetic model was developed to cal-

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Interactive Discussion

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culate OH concentrations and branching ratios. Under high-NOx conditions pinonaldehyde, organonitrates and the isomerization products of alkoxy radicals are observed as the major products with implications on the understanding of OH radical regeneration. It was also found that especially the concentrations of PAN compounds are depending on the actual NO2 level. Consequently, the paper fits to the scope of ACP and it will contribute to understand the gas phase chemistry of biogenic VOCs. The paper is well written and conclusions made are sound. We recommend publishing the manuscript in ACP, however, have some minor comments on the manuscript.

1. Minor revisions: Line 307: From a physico-chemical point of view, pinonaldehyde is not really nonpolar, it just contains no acidic hydrogen, therefore the positive mode needs to be used.

Reply: We have reworded the sentence, “Pinonaldehyde is neither acidic nor is the complex with CF3O- significantly strong to be detected in the negative mode and thus is observed only in the positive mode of the CIMS.”

2. In Equations (4) + (5) O2 is missing on the right side of the equations

Reply: Fixed

3.Line 371: α-pinene oxide has a relatively low polarity but it is again not nonpolar (see above). Arguing about this kind of ion formation should discuss gas phase acidities or gas phase basicities (or proton affinities).

Reply: The sentence has been amended to, “a-pinene oxide is neither acidic nor is the complex with CF3O- significantly strong to be detected in the negative mode and thus is observed only in the positive mode. . .”

4. Line 396f: ”. . . forming an acyl peroxy radical” after O2 addition. . ... ?

Reply: Yes, we have added that to the sentence, thank you.

5. Line 405 and 422: Did the authors measure synthesized reference peroxyacids to

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be absolutely sure about these products or were they “just” tentatively identified based on the interpretation of the mass spectra?

Reply: The assignment of the peroxyacids are based off of analysis of the mass spectrum and known acyl peroxy radical chemistry. In addition, we have synthesized peracetic acid as a calibration source in the past and have observed that it is ionized at its molecular mass +85 (complex) with a small fraction at molecular mass +65 (+ CF3O- - HF). Reanalysis of the data shows similar time traces at m/z 285, 265, and 219 (molecular mass of pinonic peracid +85, +65, +19 respectively) providing further evidence to the formation of pinonic peracid. The observation of the signal at m/z 265 and has been added to the text and figure 2 and a discussion about the known ionization behavior of peracetic acid has been added to the text.

6. Figures 1+2: To avoid confusion of the reader between molecular ions of complexes the authors should consider to mentioned the ion compositions (complexes of CF3 or HF) in the captions again.

Reply: They have been added.

7. Figure 6 and related text: Acronyms for the compounds would facilitate the reading.

Reply: We appreciate the comment, however, the three a-pinene hydroxy hydroperoxides are discussed in three places in the text and typically are just split into two categories, beta-hydroxy hydroperoxides and ring opened hydroxy hydroperoxides. In one instance we do separate the two beta-hydroxy hydroperoxides from each other, but we feel that the full description of them while they are being discussed presents the best representation. Added to this, an acronym that would be descriptive enough to distinguish between the three would be cumbersome itself (i.e. B-APINENEOHOOH-1 for the beta hydroxy hydroperoxide with the OOH group on the tertiary carbon) and would require the reader to remember what each meant instead of having it described in words.

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