

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.

Anonymous Referee #2

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The manuscript reports high quality chamber experiments on photooxidation of α -pinene with various NO_x concentrations. The gas phase composition was monitored by a CIMS system. Under low-NO_x conditions α -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 calculate OH concentrations and branching ratios. Under high-NO_x 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

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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.

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.

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

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).

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

Line 405 and 422: Did the authors measure synthesized reference peroxyacids to be absolutely sure about these products or were they "just" tentatively identified based on the interpretation of the mass spectra ?

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

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

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