

Interactive comment on “ α -Pinene Nitrates: synthesis, yields and atmospheric chemistry” by S. X. Ma et al.

Anonymous Referee #2

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This manuscript describes the organic synthesis, smog chamber yields, and OH loss rate constants for a subset of hydroxynitrates from α -pinene. The detection technique used here, GC-TSD, speciates the isomers of α -pinene nitrates. The determined yields are then combined with structure-activity relationships to propose a reaction mechanism. This work is expected to be of great interest to the community, and will hopefully motivate a continued interest in determination of organic nitrate yields from other biogenically important monoterpenes. Publication in ACP is recommended following the authors' attention to the following points.

As stated in the manuscript, the two previously reported α -pinene nitrate yields are markedly different (18% and <1%) (Noziere et al. 1999; Aschmann et al. 2002). There is some disagreement regarding the phase of the organic nitrates (gas vs. particle)

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formed in these experiments. Noziere et al. suggests most of the organic nitrates in their study remain in the gas phase, while Aschmann propose organic nitrate aerosol partitioning and particle wall loss as one possible explanation for differences in yields. Rollins et al. (2010) determines 15-18% of the SOA molecules formed from α -pinene oxidation in the presence of NO are organic nitrates, suggesting partitioning of the organic nitrates into the aerosol phase. Given the seeming importance of the phase of the organic nitrates from this photooxidation system, the reviewer would like to see the authors explain more about whether their sampling technique would observe particulate nitrate. Or, perhaps give reasons why they believe all the organic nitrogen is in the gas phase (i.e. experiment set-up, OH exposure. . .). The addition of this information would help relate the three studies.

A few more details regarding the decision to apply the determined sensitivity of APN-A for all the nitrate isomers would be useful. Does this synthesis produce the purest product? How stable was this nitrate in the Teflon bag? Why not check the purified APN-C as well?

What are the approximate synthetic yields of each of the three methods for synthesis?

What are the approximate OH concentrations in the photooxidation experiments? In the OH rate constant determination experiment?

Other comments:

page 6851, lines 24/25: should be NO and NO_x concentrations?

page 6847, line 2: The rate constant of α -pinene + OH is a factor of 2 lower than isoprene + OH, as is the reported lifetime in Atkinson and Arey (2003). What is the origin of the factor of 3?

Page 6846, lines 19-24: Guenther et al, 2003 should be Guenther et al., 1993 (Guenther et al. 1993). Also, all these units should be Tg C yr⁻¹.

Page 6850, lines 25-27: I find this sentence unclear. Was EI used to identify APN-A,

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and CI and negative CI were used to identify APN-C?

Aschmann, S. M., R. Atkinson and J. Arey: Products of reaction of OH radicals with alpha-pinene. *Journal of Geophysical Research-Atmospheres*, 107(D14), 2002.

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Guenther, A. B., P. R. Zimmerman, P. C. Harley, R. K. Monson and R. Fall: Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *Journal of Geophysical Research-Atmospheres*, 98(D7), 12609-12617, 1993.

Nozriere, B., I. Barnes and K. H. Becker: Product study and mechanisms of the reactions of alpha-pinene and of pinonaldehyde with OH radicals. *Journal of Geophysical Research-Atmospheres*, 104(D19), 23645-23656, 1999.

Rollins, A. W., J. D. Smith, K. R. Wilson and R. C. Cohen: Real Time In Situ Detection of Organic Nitrates in Atmospheric Aerosols. *Environmental Science & Technology*, 44(14), 5540-5545, 2010.

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