

# Reply to referees: $\alpha$ -Pinene Nitrates: Synthesis, Yields and Atmospheric Chemistry” by

S. X. Ma et al.

We would like to thank the two anonymous referees for their constructive comments and general encouragement which helped us improve the paper. All the points raised by the reviewers have been answered below and in the revised manuscript, where indicated below.

## Comments/Changes, Referee #1

### *Major comments:*

1. On the top of page 9 the authors talk about alleviating adsorptive losses of the APNs on GC-TSD. How big a problem was this and was it the same for all of the APN? Such a loss is certainly not reflected in the yields given in Table 1 where the quoted error is quite low. What error has been given to the yield 2 sigma? How long were the yield experiments? is there a danger of some chemical processing on the reactor walls with wall-gas phase partitioning on the time scale of the experiments which might affect yields and perhaps give some unwanted nitrates (i.e. memory effects from past experiments). Matsunaga and Ziemann (Aerosol Science and Technology, 44:881 - 892, 2010) have shown that this can be substantial and fairly rapid for some compounds.

Reply: The "conditioning" for APNs is essentially similar as described in detail in Muthuramu et al., 1993. We now cite that paper in the sentence referring to conditioning, page 9 line 5. We believe that conditioning involves occupying column active sites with the APNs, at which irreversible adsorption takes place. Once those sites are occupied, minimal loss takes place for subsequent injections. That is the observation discussed in the Muthuramu paper. The yield experiment lasts typically 3-5 h. Our measured wall loss rate constants are relatively slow ( $\tau \sim 6-18$  hrs), and we clean the chamber until no species are observed. However, we have carefully calculated/estimated our yield uncertainties, and all numbers reported now have appropriate uncertainties, as shown in Table 1 of the revised manuscript.

2. Also at the top of page 9 the authors state that the system was calibrated with APN-A and have assumed the same sensitivity for the other APNs. I am not so sure that I feel so confident with this assumption, for example, the properties of ortho-nitrophenol are quite different to that of para-nitrophenol because of the intramolecular and intermolecular H bonding, respectively in the compounds. APN-A and APN-B will have intramolecular H bonding whereas the other two will not. Again on page 9, why was H<sub>2</sub>O<sub>2</sub> used as the OH radical source and not isopropyl nitrite as in the product study. Was this an instrumental, or radical concentration issue? Please

elaborate.

Reply: The sensitivity of the thermionic specific detector (TSD) to APNs is dependent on the structure of the nitrogen in the molecule. If the nitrogen structure between two molecules with the same carbon number is similar, the sensitivity for the APNs is similar (Meng et al., 1998). In our case, we calibrated our GC/TSD using both pure synthesized APN-A and APN-C (quite different structures), the sensitivity ratio  $S_{\text{APN-A}}/S_{\text{APN-C}}=1.05$ , so we assumed the same sensitivity for the other APNs. This difference is now properly reflected in our reported uncertainties. We use  $\text{H}_2\text{O}_2$  as the OH radical source in the kinetics section, not isopropyl nitrite as in the product study, because we have intended to measure the free  $\text{NO}_2$  yield from OH reaction with the  $\alpha$ -pinene nitrates. However, we are not able to discuss those experiments in this paper.

3. On page 13, how large was the correction of the APN yield due to secondary reaction with the OH radical? I suspect it was minor with the possible exception of APN-D. I agree with the authors that I would expect the alpha branching ratios for APN-A and APN-B to be similar, however, the estimation is based on an OH addition ratio 65:35 and computed branching ratios for P2OH which associated uncertainties. Are the uncertainties on the  $\text{RO}_2+\text{NO}$  branching ratio in table just the uncertainties in the APN yields or do they also include errors on the different terms used to calculate the gamma values? If not they should so that has a better idea of the real uncertainty in the branching ratios. The example on page 14 for C14 alkyl nitrates shows how large discrepancies between experiment and estimated values can be.

Reply: Each APN concentration was corrected using the correction factor F, to account for OH scavenging of nitrate species. An average correction factor F would be 1.022 for APN-A, 1.048 for APN-B, 1.036 for APN-C, 1.263 for APN-D. The F factor rapidly increased with time, particularly for APN-D whose OH rate constants are larger. The original uncertainties in the  $\text{RO}_2+\text{NO}$  branching ratio in Table 1 of the revised manuscript now include appropriate uncertainties in the different terms used to calculate the gamma values, some of which do indeed have large uncertainties.

4. Finally the authors assume the Henry's law constant for all the APNs is similar to that for beta-hydroxy alkyl nitrates. While I agree that this is probably valid for APN-A and APN-B, I am not so sure that it will apply for the other APNs where the physical properties could be quite different.

Reply: We believe you are right, the Henry's law constant for all the APNs is different, however, since we have no other information about the Henry's law constants for comparable size and polarity hydroxy nitrates, we only state in the paper on page 19/20 that we have assumed this is a reasonable estimate. We note that wet deposition is, on average, a minor loss term.

*Minor comments*

1. Page 1: Title - chemistry with a capital C.

Reply: The title now reads as " $\alpha$ -Pinene Nitrates: Synthesis, Yields and Atmospheric Chemistry".

2. Page 2, line 19: Librando and Tringali (2005) is not in the reference list.

Reply: Now Librando and Tringali (2005) is in the reference list.

3. Page 7, line 13: .....it is a possible product.....

Reply: The sentence has been corrected as suggested by the reviewer.

4. Page 9, line 5: "identified" should be "identical".

Reply: We now use the word "identical" instead of "identified", as suggested by the reviewer.

5. Page 14, line 22: ...higher than the estimated value....

Reply: The sentence has been corrected as suggested.

6. Page 23, Line 24: Libardoni et al. is not referenced in text.

Reply: Libardoni et al. has been deleted now.

### Comments/Changes, Referee #2

#### *Major comments:*

1. 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.

Reply: The reaction of OH radicals with  $\alpha$ -pinene can produce at least seven organic nitrates, which will likely partition to the aerosol phase, as observed by Rollins et al. (2010b). In our experiment,  $\alpha$ -pinene, isopropyl nitrite (IPN) and NO were injected into the chamber without seed particles,  $\alpha$ -pinene was consumed under conditions without any O<sub>3</sub> production, and thus the aerosol yield was very low, and we thus believe that our organic nitrate yields, taken from initial slopes, are not influenced by loss to the aerosol phase.

2. 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?

Reply: See point #2 above in response to Reviewer #1, regarding the sensitivity for APNs. Two  $\alpha$ -pinene hydroxy nitrates (APN-A and APN-C) were purified by silica gel column chromatography from method 1 and method 3, respectively. APNs are low in volatility and adsorptive, making chamber wall loss a potentially significant non-photochemical depletion process for the hydroxy nitrates during chamber experiments. The wall loss first order rate constant in 5500L chamber for APN-A is

$1.5 \pm 0.7 \times 10^{-5} \text{ s}^{-1}$  and for APN-C is  $4.9 \pm 1.2 \times 10^{-5} \text{ s}^{-1}$ . The uncertainties related to wall loss and differential detector sensitivities are incorporated into the overall uncertainties now reported in Table 1 of the revision.

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

Reply: The calculated yield of APN-A from method 1 is 2.6% and the yield of APN-C from method 3 is 2.8%. We don't get pure products from method 2, and don't know the yield from method 2, but the estimated yield is lower than 3%. This is why purification by column chromatography was needed.

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

Reply: For the product yield experiments, we calculate an average steady state OH concentration in the chamber of  $\sim 1.5\text{-}2.4 \times 10^7 \text{ molecules/cm}^3$ . In the OH rate constant determination experiments, the calculated steady state OH concentration was  $\sim 2\text{-}7 \times 10^6 \text{ molecules/cm}^3$ .

#### *Minor comments*

1. Page 6851, lines 24/25: should be NO and NO<sub>x</sub> concentrations?

Reply: it should be NO and NO<sub>x</sub> concentrations, thanks for the correction.

2. Page 6847, line 2: The rate constant of  $\alpha$ -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?

Reply: We appreciate this question, the rate constant of  $\alpha$ -pinene + OH should be a factor of 2 lower than isoprene + OH.

3. Page 6846, lines 19-24: Guenther et al, 2003 should be Guenther et al., 1993. Also, all these units should be Tg C yr<sup>-1</sup>.

Reply: The revised manuscript now cites Guenther et al. 1993, and all the units are reported as Tg C yr<sup>-1</sup>.

4. Page 6850, lines 25-27: I find this sentence unclear. Was EI used to identify APN-A, and CI and negative CI were used to identify APN-C?

Reply: APN-A and APN-C identification was accomplished by both EI and CI.

#### *New Reference:*

Chin.-Kai Meng, Response of Nitrogen-Phosphorus Detectors to Different Structural Nitrogen Compounds, Hewlett Packard Application Brief, Hewlett-Packard Company, Wilmington, DE, USA, February 1998.