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Atmospheric Chemistry and Physics Discussions

Interactive comment on "$\vec{\alpha}$-Pinene Nitrates: synthesis, yields and atmospheric chemistry" *by* S. X. Ma et al.

Anonymous Referee #1

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The manuscript reports the syntheses of 4 alpha-pinene hydroxy nitrates and their detection and quantification in the OH radical initiated oxidation of alpha-pinene an important biogenic VOC. From their data the authors have been able to estimate the total nitrate yield (RONO2) and also calculate the relative branching ratios of the nitrate precursor radicals (RO2). The authors have also determined rate coefficients for the reaction of OH with two of the alpha-pinene hydroxy nitrates and have estimated overall lifetimes for these compounds. The work has been performed in a large volume Teflon chamber using GC-TSD for detection of the nitrates and other standard techniques for O3, NOx etc. The results are all new and are a valuable addition to our understanding of NOx cycling in the troposphere. The authors have years of experience in working with organic nitrates and the work on a first glance appears to be of a very high standard. The manuscript is also very well written and the results are clearly and logically

presented.

The paper helps enormously to resolve the discrepancy in the literature on the nitrate yield from the reaction of OH with alpha-pinene with the present results supporting the work of Noziere et al. (1999).

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 1where 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 wal-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). Magsunaga and Ziemann (Aerosol Science and Technology, 44:881–892, 2010) have shown that this can be substantial and fairly rapid for some compounds.

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 H2O2 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.

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 RO2+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.

The kinetics section on APN looks fine and based on the number of primary, secondary and tertiary abstractable H-atoms and neighbouring functional groups the different in relativity of APN-A and APN-C of nearly a factor of two seems reasonable.

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.

Page 1: Title – chemistry with a capital C Page 2, line 19: Librando and Tringali (2005) is not in the reference list Page 7, line 13: .....it is a possible product..... Page 9, line 5: "identified" should be "identical" Page 14, line 22: ...higher than the estimated value.... Page 23, Line 24: Libardoni et al. is not referenced in text

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6845, 2011.