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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Determination of alpha;-pinene-derived organic nitrate yields: particle phase partitioning and hydrolysis" *by* J. D. Rindelaub et al.

Anonymous Referee #1

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General comments

This manuscript describes environmental chamber experiments aimed at investigating the gas and aerosol phase chemistry of organic nitrates derived from alpha-pinene under conditions of varying seed aerosol acidity and relative humidity (RH). The main finding of the work is that the gas and aerosol phase chemistry of the organic nitrates are coupled on the time scale of the experiments, with the gas phase production of organic nitrates in competition with aerosol phase consumption of nitrates. This finding is important in that it suggests that aerosol phase partitioning of organic nitrates may be an important sink for NOx, with a corresponding important effect on air quality.

The work has been carefully planned and executed, and the manuscript is clearly written. For these reasons, this study is quite appropriate for Atmospheric Chemistry and Physics.

One potential inconsistency in the results cited by the authors concerns the lack of detection of the expected nitrate hydrolysis product, pinanediol. However, Bleier et al. (J. Phys. Chem. A, 117, 4223-4232, 2013) recently reported that the hydrolysis of alpha-pinene oxide leads to the ring-opened product, trans-sobrerol, rather than the ring-retaining product, pinanediol. Since both the anticipated dominant organic nitrate product in this work and alpha pinene oxide should hydrolyze through a common tertiary carbocation intermediate, it seems reasonable to expect that trans-sobrerol would also be a hydrolysis product in the present system. Since trans-sobrerol is commercially available (sold as trans-p-menth-6-ene-2,8-diol), the authors could quite easily confirm or refute the presence of trans-sobrerol as a product, which could help to further elucidate their proposed mechanism for organic nitrate hydrolysis.

Specific comments

p. 3306, line 21: Since the Shepson group has extensive experience detecting and quantifying organic nitrates via GC-MS methods, there must be a compelling reason that the authors chose to use FT-IR methods instead. It would be helpful to readers to understand why the FT-IR detection method was selected.

p. 3306, line 28: Since tetrachloroethylene has quite a congested IR spectrum in the region of interest for organic nitrates, I'm assuming that solvent properties dictated this choice. Again, it would be useful to explicitly explain this choice.

p. 3307, line 18: How sensitive are the derived organic nitrate product yields to the assumptions concerning OH rate constants and NOx recycling efficiency?

p. 3317, line 18: Since the partitioning efficiency is apparently very high at RH > 20% for the alpha-pinene derived organic nitrates, it leads one to consider whether isoprene-derived organic nitrates might also be able to partition significantly (even though one would expect that isoprene-derived organic nitrate partitioning coefficients are probably significantly smaller than the alpha-derived organic nitrates). Given the relative dearth of elevated RH chamber experiments, do the authors think that this kind of partitioning is possible for isoprene-derived organic nitrates but has simply has not been observed because of the experimental conditions used in previous studies?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 3301, 2014.