

Interactive comment on “Chemical Composition and Hydrolysis of Organic Nitrate Aerosol Formed from Hydroxyl and Nitrate Radical Oxidation of α -pinene and β -pinene” by Masayuki Takeuchi and Nga L. Ng

Anonymous Referee #2

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Overview

Takeuchi et al. report on systematic photochemical reaction chamber studies of particle-phase organic nitrate hydrolysis rates and hydrolysable fractions following the oxidation of alpha- and beta-pinene by both OH and NO₃ radicals, representing daytime and nighttime oxidation chemistry, respectively. Understanding the fate of organic nitrates in aerosol is important to assess its role in the cycling of criteria air pollutants: NO_x, O₃, and particulate matter. This paper elucidates transformations of organic nitrates from two of the most atmospherically abundant monoterpenes: alpha- and

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beta-pinene and provides insights into their lifetimes under lab-simulated daytime and nighttime oxidant conditions. The study appears to have been carefully executed with the proper tools and the paper itself is well written, although there are several points that require clarification, as outlined in my critique. The study is timely, sound, and contributes to new knowledge, which after considering my comments, I think is suitable for publication in Atmospheric Chemistry and Physics.

Comments

(1) Page 6, line 133: Please elaborate. What “negligible impact” on the results concerning hydrolysis was there?

(2) Page 10, line 233: This is likely the case for beta-pinene + NO₃, but alpha-pinene + NO₃ leads to very low ON yields (preferably forming volatile pinonaldehyde) and low SOA yields as discussed in Fry et al. (2014) as well as for γ -terpinene + NO₃ as discussed in Slade et al. (2017). Favorability of nitrated to non-nitrated organics following NO₃ oxidation vs. OH oxidation in the presence of NO will depend on the degree of branching on the carbon of the C-ONO₂ bond. As stated, it is a bit oversimplified, please revise accordingly.

(3) Concerning my second comment, it would be helpful if the authors included a discussion on the difference in the degree of nitration between the beta-pinene and alpha-pinene systems under the “nighttime” scenario when oxidized by NO₃. The current discussion focuses more on differences between OH and NO₃ oxidation and very little on differences between the precursor VOCs. The authors do say on page 9, lines 195-197 that a more distinct difference is observed between different oxidation conditions than between different precursor VOCs, but I would expect, based on previous literature, that substantial differences in CHO and CHNO fractions would exist between alpha- and beta-pinene owing to the positions of their double bonds. Please elaborate.

(4) Page 10, line 236: I don’t quite understand this statement. Both OH and NO₃ can abstract hydrogens, but ultimately it depends on the degree of saturation, or? OH and

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NO₃ preferably add to carbon-carbon double bonds over hydrogen abstraction. Please rephrase.

(5) There is no mention of pH-dependent (i.e., acid-catalyzed) hydrolysis and the formation of organic sulfates (Liggio and Li, 2008; Rindelaub et al., 2016; Rindelaub et al., 2015). This is likely an important process affecting pON concentrations and the NO₃,Org/SO₄ ratio. Could you estimate what fraction of SO₄ is organic?

(6) Page 14, line 330: The difference between the changes in NO₃,Org/SO₄ due to aerosol water content and reactor humidity alone is not clear. Doesn't the reactor humidity affect aerosol water content and subsequently pON hydrolysis? Please clarify how "reactor humidity alone" and not water content affects NO₃,Org/SO₄.

(7) Figure 3b: The y-axis label is confusing "Exp.4/Exp.3", are you dividing results from Exp.4 by Exp.3? Please modify.

(8) Page 14, discussion on volatility: another interpretation of the NO₃,Org/Org and NO₃,Org/SO₄ decay curves is the organosulfate products that possibly form are sufficiently low volatility that they remain in the aerosol phase, but a fraction of the hydrolyzed ON that is not organosulfate is sufficiently volatile that it repartitions to the gas phase.

(9) Page 17, lines 394-395: If no difference in pON hydrolysis is observed between AS and SA+MS seed experiments, might it be that HNO₃ in the particles sufficiently decreases aerosol pH that both "neutral" AS seed experiments and "acidic" SA+MS seed experiments are essentially the same pH? Aerosol pH measurements, e.g., with pH paper as in Craig et al. (2018), or predictions via AIM or ISORROPIA would help with interpretation but may be beyond the scope of this study. (10) Page 17, line 415: Please include citation. Presumably, the authors refer to greater uptake of N₂O₅ at higher relative humidity due to changes in particle viscosity? A good example would be Grzanic et al. (2015).

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