

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 #1

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General comments

This manuscript describes laboratory experiments that aim to investigate the efficiency of nitrate hydrolysis reactions on secondary organic aerosol (SOA) in order to order to try to reconcile existing discrepancies between previous bulk laboratory experiments and laboratory experiments that directly study SOA. Specifically, the work uses both High Resolution Time-of-Flight Aerosol Mass Spectrometry (HR-ToF-AMS) and Filter Inlet for Gases and Aerosols/Chemical Ionization Mass Spectrometry (FIGAERO-CIMS) techniques in order to track the evolution of alpha- and beta-pinene-derived SOA

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under different hydrolysis reaction conditions. The main claim is that the hydrolysis kinetics are found to be fast, consistent with previous bulk studies. The reason for the previous findings on SOA that estimated much slower hydrolysis lifetimes is attributed to analysis issues, namely the choice of the proxy systems used to estimate the lifetimes. Because knowledge of SOA chemical transformation pathways is critical to the development of accurate SOA mechanistic models, this work will be of great interest to readers of Atmospheric Chemistry and Physics. However, I believe that a number of issues need to be clarified in a revised version of the manuscript.

Specific comments

Line 221: The supposition that autooxidation is occurring deserves more support. For example, the statement concerning “a few hydroxy radical reaction reactions” should be expanded into a formal kinetic argument concerning the low probability of multiple OH-initiated oxidation steps.

Line 228: Again, the actual kinetic argument should be explicitly given. I assume that, combined with a typical RO₂ + NO rate constant and 10 ppb NO, the predicted RO₂ + NO pseudo first order rate constant is a “a few per second.”

Line 348: Although this paragraph is making an appropriate detailed argument about the difference between the two proxies, I think it is important to point out very simply to the reader that the reason why the proxy NO₃-(org)/Org works better is because the common atmospheric chamber problem of wall loss effectively gets cancelled out with this proxy method.

Line 381: It is quite clear from previous work that iodide CIMS sensitivity varies greatly for moderately oxygenated organics. Therefore, it is also quite likely that these species are underestimated in the present work.

Line 385: This really supports the appropriateness of the “reconstructive” kinetics shown in Figure 3b and should be explicitly pointed out.

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Line 397: It should be added that bulk studies also found that these reactions did not require low pH to be fast.

Technical comments

Line 219 (Figure S1): I think there must be something wrong with the symbols (or legend) here, as I don't understand what is actually being plotted. For example, does any green series correspond to any H17 compound and not just O8H17 (green squares)?

Line 236: Replace "subtraction" with "abstraction"

Line 278 and beyond: Nitrate, sulfate, and ammonium ions must be indicated by their proper chemical formulas, NO_3^- , SO_4^{2-} , and NH_4^+ , respectively, rather than the shorthand NO_3 , SO_4 , and NH_4 used in the manuscript. This is potentially particularly confusing as neutral NO_3 radical reactions are important formation routes for organonitrates.

Line 298: This sentence is confusing. I suggest "...on hydrolysis on pON that partitions to the aerosol due to condensation rather than dissolution."

Line 314: This sentence is confusing. I suggest "... is a reaction in which liquid water is a reactant, it is ..."

Line 349: Typo: replace "rector" with "reactor"

Line 355: Typo: replace "technique" with "techniques"

Line 360: Isn't this a mass concentration? This should be clarified.

Line 394: Add "a" between "in" and "prior"

Line 395: Add "here" between "observed" and "between"

Line 401: Add "method" after "solution"

Line 445: Replace "several" with "a few"

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