

Review of Bell et al ACP 2021

This paper presents a new set of chamber experiments exploring the condensed-phase dark aging of NO₃ + α -pinene SOA, which chemically speciated observations (EESI, FIGAERO-CIMS) illuminating the continued oxidation of the SOA. The analysis could be expanded to increase the impact of this paper, and I recommend additional analysis be included in the main body of the paper.

Major comments/suggestions:

- 1) The authors use the MCM model to determine the most likely RO₂ bimolecular reaction partner, and then note that the RO₂+RO₂ product channel is apparently more dominant based on observed products. Based on this empirical observation, could you use the model to infer what the RO₂+RO₂ rate constant must be, for these C₁₀ nitrate functionalized RO₂'s? It seems to me this is an opportunity your data give you that should be exploited! Suggest to include an additional section on modeling RO₂ fate.
- 2) I don't understand the claim that peroxy nitrates are controlled by RO₂ + NO₃ reactions. I think they would be controlled by nitrate-RO₂ + NO₂ reactions, which makes one of your ideas about oxidant sources less sound.
- 3) You discuss fragmentation as yielding only CH₂O as volatile fragments, but the loss of organonitrates that cannot be explained by hydrolysis to HNO₃ suggests that there must also be some fragmentation to high-volatility organonitrates. This would be good to elaborate upon. Would these be detectable in any of your gas-phase measurements?
- 4) Could semivolatiles be repartitioning differentially to the chamber walls? Your discussion of wall losses seems to assume a consistent loss rate for all species, but these rates could be species-dependent. Could the apparent loss of O₈ be due to greater wall repartitioning for that molecule than for higher-oxidized, heavier molecules? I suggest thinking about the speciated wall partitioning discussed in Krechmer et al. 2020 (<https://pubs.acs.org/doi/abs/10.1021/acs.est.0c03381>)
- 5) Sections 3.2 and 3.3 have the same title
- 6) Around line 155: can dimers also form in the EESI, in the reverse of the fragmentation you discuss?

Minor / technical points:

- 1) Line 11 "in or downwind of polluted"
- 2) Line 15: "in the absence of external stimuli" feels a bit vague to me -- what you really mean is aging in the dark, right? This phrase is also used later. Consider rewording? But this is a style choice, so just a suggestion to think about
- 3) Line 29: "Unlike isoprene, monoterpenes are emitted"
- 4) Line 30: "and NO₃) play an important"
- 5) Line 50: "still not well understood"
- 6) Line 59: "determine the absolute scale" is unclear to me. Perhaps something like "determine the magnitude of the effect"?

- 7) Section 2.1: find a place here to mention that these experiments were run in batch mode; also suggest to spell out EESI and FIGAERO here too (even though they came also in the abstract), since you spell out other acronyms in this section
- 8) Line 67: which instrument is the thermo-denuder in front of?
- 9) Line 75: indicate the approximate concentration of the cresol contaminant?
- 10) Line 83: "cresol contamination constitute ~1-2%"
- 11) Line 86: "experiments 1 - 3, ~100 ppb"
- 12) Table 1 caption: I suggest to add some rate constant modeling info to this caption:
"based on a fit to the VOC decay, assuming XXX as the NO₃ + apin rate constant at XX C"
- 13) Eq 1 formatting: need a space between equation and label
- 14) Line 117: "sampling the aerosol at 1 L min⁻¹"
- 15) Line 122 "ion guides and were separated" -- in general, check for verb tense consistency: most are past tense, but some a present tense.
- 16) Lin 127: "subtracting the background filter periods from the adjacent chamber sampling periods. A filtering"
- 17) Around line 132: this equation needs a number. There is some repeated text before and after "Avogardo's number and a conversion factor..." - remove one
- 18) Line 135 "including particle size,"
- 19) Line 140: "and had low sensitivity"
- 20) Line 143: give formula for acetonitrile at its first instance, to help reader interpret later clusters you mention
- 21) Line 146; " for all C₂₀H₃₂N₂O_x molecules" -- if this is in fact what you mean?
- 22) Line 175: "Tofware"
- 23) Line 177: "For the first filter in Exp. 2, due to a software failure, the filter was stored wrapped in aluminum foil for ~7 H after ... was done prior to desorption."
- 24) Line 178: " were similar to other experiments."
- 25) Line 187: "consumed, because the injection of N₂O₅ was less"
- 26) Line 199: " observations (Takeuchi and Ng, 2019), and with RO₂+ RO₂ reactions."
- 27) Line 201: "dimers over monomers"
- 28) Around line 206: I don't understand how peroxy nitrates would be formed from RO₂ + NO₃ reactions. WOuldn't they be formed by nitrate-RO₂ + NO₂ reactions?
- 29) Lines 222-224: The first sentence of this section doesn't make sense to me, sharpen / reword / make more specific?
- 30) Line 226; "larger SOA yields were observed under an RO₂ + RO₂ dominant"
- 31) Rest of section: make every instance consistently "RO₂ + X" - currently some have the + sign and some have long dashes --
- 32) Line 236: "HO₂ is not an important RO₂ reaction partner since there"
- 33) Line 240:" peroxy linkage. This molecule is the dominant dimer"
- 34) Around line 257: See comment above about expanding interpretation of RO₂ + RO₂ rate constant based on your observations.
- 35) Line 261; "and the FIGAERO-CIMS, were used to"
- 36) Line 265 spelling FIGAERO

- 37) Line 282: units “ag s-1 h-1” don’t make sense to me. Per second and per hour? (on next line too)
- 38) Line 312: spurious comma at the end of the line
- 39) Line 331: reorder confusing sentence: “Approximately half of the total depletion observed arises from an increase in oxidation, with the remainder coming from evaporative losses.”
- 40) Line 343-345: this last line of the paragraph, about no specific loss of -ONO₂ groups, is confusing to me.
- 41) Line 361: “initiated from the scission of O-O bonds in organic peroxides”
- 42) Next line: as mentioned above, I don’t see why PANs concentration would be drive by [NO₃] (rather, I would expect a dependence on [NO₂])
- 43) Around line 371-372: could the same N₂O₅ measurement be an artefact / wall background?
- 44) Line 373: “phase or organic peroxides could be”
- 45) Line 380: remove “making up the difference”
- 46) Line 384: “in the gas phase, dimers will”
- 47) Around linke 387: doesn’t this say fragmentation isn’t just CH₂O?
- 48) Line 389: ‘organic peroxides or from”
- 49) Line 390: “presented here, along with...), demonstrate that”
- 50) Line 397: “Overall, particle-phase ... regime, since .. is always an important sink of RO₂”
- 51) Line 405: suggest to start new paragraph with this sentence and edit to:” The atmospheric consequence of these results is that we will typically over-predict...”
- 52) Figure 1: what are the numbers after the experiment numbers in panel B caption?
- 53) Figure 2 caption references to panels a and b are confusing, reorder text?
- 54) Figure 4 notation about #O is confusing. What about “#O(non-NO₃) = #O(total) - 3*#N”?