The Reviewer comments are in black, the replies are provided in blue, and the changed text in the manuscript are shown in orange.

Review of Bell et al ACP 2021

This paper presents a new set of chamber experiments exploring the condensed-phase dark aging of NO3 + a-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.

We would like to thank reviewer for their constructive comments and questions.

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.

We believe that the data here although useful, is not the whole story needed to be able to constrain the values for RO2+RO2 rate constants. In order to better constrain these rate constants, measurements about radical concentrations and well-calibrated gas-phase measurements would be required.

2) I don't understand the claim that peroxynitrates are controlled by RO2 + NO3 reactions. I think they would be controlled by nitrato-RO2 + NO2 reactions, which makes one of your ideas about oxidant sources less sound.

We would like to thank the reviewer for this comment. We should have said RO2 + NO2 reactions, as RO2 + NO3 will react to form an alkoxy (RO) radical. Whenever we have large concentrations of NO3 there are corresponding large concentrations of NO2 to go along with it.

This was changed on line 208 to say with the highlighted changes in orange: "Monomer dinitrates likely form via an RO_2 + **NO_2** reaction to form peroxynitrate functional groups (Chan et al., 2010), which is speculated to form monomer trinitrates in the isoprene + NO_3 system (Zhao et al., 2020). The lack of their formation in experiment 2 agrees with the smaller concentrations of N_2O_5 injected, and corresponding smaller amount of NO_2 present."

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?

Thank you for this comment. In the gas-phase, we observed a few species that increased more than 25% during the course of dark aging, which would be an indicator for the formation and subsequent evaporation of high volatility organo-nitrates. The molecules increasing include: $C_2H_4O_3$, $C_3H_6O_3$, $C_4H_8O_3$, $C_3H_5NO_5$, $C_4H_7NO_5$, $C_5H_9NO_5$. The use of CH2O was an example because the loss of a single carbon containing molecules is the most significant loss pathway.

We added the following on line 365:

"We should note, we do observe a few molecules increasing more than 25% in the gas-phase consistent with fragmentation reactions, including: C2H4O3, C3H6O3, C4H8O3, C3H5NO5, C4H7NO5, C5H9NO5"

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)

Although the loss of organo-nitrates doesn't necessarily mean there must be a fragmentation pathway to form high-volatility organo-nitrates, we agree with the reviewer suggestion that it could result from semi-volatile repartitioning to the chamber walls (Krechmer et al. 2020 and (Bertrand et al., 2018)). These molecules are generally thought to be non-volatile in nature (Mohr et al., 2019). However, when performing isothermal evaporation experiments in the atmospheric simulation chamber both the $C_{20}H_{32}N_2O_{8,9}$ are susceptible to repartitioning, giving credence to the idea these molecules are repartitioning directly.

Figure S8 was added to the Supplement:
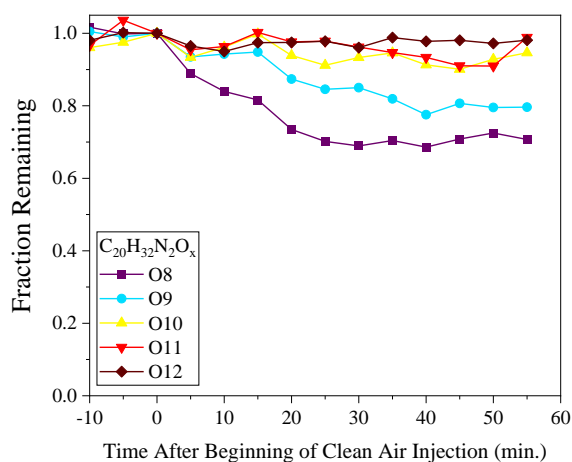
Figure S8: After experiment 3, clean air was injected into the chamber at 100 L min^{-1} for 60 min. The time traces here correspond to the EESI-ToF intensity relative to the time at the beginning of the injection of clean air into the chamber for the series of $C_{20}H_{32}N_2O_{8-12}$.

We have added the following section to address the evaporation of semi-volatile dimers on line 373:

"Figure 1b shows that the SOA evaporates during aging in the chamber. Evaporative loss of dinitrate dimers is possible, though not common considering dimers typically have very low volatility. However, when performing isothermal evaporation measurements in the atmospheric simulation chamber both the $C_{20}H_{32}N_2O_{8,9}$ are susceptible to repartitioning (Figure S8). Because these dimers are low-volatility to semi-volatile molecules they are in equilibrium between the particles, gas-phase, and the walls (Bertrand et al., 2018;Krechmer et al., 2020). Therefore, part of the loss of $C_{20}H_{32}N_2O_8$ (and O9?) is due to repartitioning and accounts for a significant fraction of the organonitrates lost from the particle phase observed by the EESI-ToF, and a significant fraction of the decreasing signal in the FIGAERO-CIMS.»

We have changed part of our conclusions (Line 417) section to:

"Although there are changes in the nitrogen content, they do not appear to be associated with hydrolysis of nitrate functional groups, but rather the repartitioning of low-volatility/semi-volatile highly nitrated molecules."

5) Sections 3.2 and 3.3 have the same title

Thank you for pointing this out, the title has been changed to: "Evolution in the Particle Phase Composition"

6) Around line 155: can dimers also form in the EESI, in the reverse of the fragmentation you discuss?

It is possible for dimers to form in the EESI, but this is typically the case when there are very high concentrations of specific individual species. For instance, when performing calibrations with levoglucosan, dimers (Na^+-Levoglucosan-levoglucosan) are observed with a relative intensity of 0.01 – 1% of the of the typical adduct Na^+-Levoglucosan under our ion-guide settings. Similar to the ACN clustering discussed, the prevalence of these "dimers" are highly dependent on the ion-guide settings. Overall, these "dimers" are highly non-linear with aerosol mass concentration, and generally are not significant.

Minor / technical points:

Thank you for the minor points, all of them have been addressed either by changing the main text with the suggested change (i.e. done) or through the above comments.

1) Line 11 "in or downwind of polluted" done

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 good point here, it was changed to "in the dark"

3) Line 29: ' Unlike isoprene, monoterpenes are emitted" done

4) Line 30: "and NO3) play an important" done

5) Line 50: "still not well understood" done

6) Line 59: "determine the absolute scale" is unclear to me. Perhaps something like "determine the magnitude of the effect"? done

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 done

Line 64: "A series of batch-mode chamber experiments (Table 1) investigating formation…"
And added the description of the acronyms.

8) Line 67: which instrument is the thermo-denuder in front of?
Line 69 ", a thermo-denuder coupled with an SMPS, …"

9) Line 75: indicate the approximate concentration of the cresol contaminant? done

10) Line 83: "cresol contamination constitute ~1-2%" done

11) Line 86: "experiments 1 - 3, ~100 ppb" done

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 + apinrate constant at XX C" done

13) Eq 1 formatting: need a space between equation and label done

14) Line 117: "sampling the aerosol at 1 L min-1" done

15) Line 122 "ion guides and were separated" -- in general, check for verb tense consistency: most are past tense, but some a present tense. done

16) Line 127: "subtracting the background filter periods from the adjacent chamber sampling periods. A filtering" done

17) Around line 132: this equation needs a number. There is some repeated text before and after "Avogadro's number and a conversion factor…" - remove one done

18) Line 135 "including particle size," done

19) Line 140: "and had low sensitivity" done

20) Line 143: give formula for acetonitrile at its first instance, to help reader interpret later clusters you mention done

21) Line 146; " for all C20H32N2Ox molecules" -- if this is in fact what you mean? Done, and yes

22) Line 175: "Tofware" done

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." Adapted this suggestion to: "For the first filter in Exp. 2, due to a software failure, the filter was stored wrapped in aluminum foil for ~7 h before being desorbed."

24) Line 178: " were similar to other experiments." Done

25) Line 187: "consumed, because the injection of N2O5 was less" Done

26) Line 199: " observations (Takeuchi and Ng, 2019), and with RO2+ RO2 reactions." Done

27) Line 201: "dimers over monomers" done

28) Around line 206: I don't understand how peroxynitrates would be formed from RO2 +NO3 reactions. Wouldn't they be formed by nitrato-RO2 + NO2 reactions? This was changed in accordance with the major comment above.

29) Lines 222-224: The first sentence of this section doesn't make sense to me, sharpen / reword / make more specific?

"Because particle-phase reactions are not well understood, it is necessary to understand what radical pathways control the initial composition of the SOA."

30) Line 226; "larger SOA yields were observed under an RO2 + RO2 dominant" done

31)…. Rest of section: make every instance consistently "RO2 + X" - currently some have the + sign and some have long dashes – done

32) Line 236: "HO2 is not an important RO2 reaction partner since there" done

33) Line 240:" peroxy linkage. This molecule is the dominant dimer" done

34) Around line 257: See comment above about expanding interpretation of RO2 + RO2 rate constant based on your observations. Talked about this above.

35) Line 261; "and the FIGAERO-CIMS, were used to" done

36) Line 265 spelling FIGAERO done

37) Line 282: units "ag s-1 h-1" don't make sense to me. Per second and per hour? (on next line too)

we modelled the decay rate and fit the decay with an exponential fit and now report a decay rate of " 0.01 min^{-1} "

38) Line 312: spurious comma at the end of the line done

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." done

40) Line 343-345: this last line of the paragraph, about no specific loss of -ONO2 groups, is confusing to me. Removed this sentence since it was repeating the point of the next paragraph.

41) Line 361: "initiated from the scission of O-O bonds in organic peroxides" done

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]) changed this to NO2 in the text, in line with the comment above.

43) Around line 371-372: could the same N2O5 measurement be an artefact / wall background?

The FIGAERO-CIMS measured directly gas-phase N_2O_5 and semi-simultaneously particle-phase N2O5 via heating collected filter samples (details see Methods). The gas-phase N2O5 signal increased from a very low background with adding N2O5 into the chamber, and decreased very fast back to a very low level in a few minutes. Thus, gas-phase N2O5 wouldn't impact the further particle-phase measurement. The particle-phase N2O5 from the filters had thermograms consistent with those of other species during heating round. This included starting near zero at the beginning of heating and increasing with heating temperature, and had a maximal desorption temperature of 80-90°C, and decreased to almost zero at the end of the heating cycle. This indicates that the N2O5 signal was not an artefact from surfaces of the instrument.

44) Line 373: "phase or organic peroxides could be" done

45) Line 380: remove "making up the difference" done

46) Line 384: "in the gas phase, dimers will" done

47) Around line 387: doesn't this say fragmentation isn't just CH2O? addressed in above comment

48) Line 389: ' organic peroxides or from" done

49) Line 390: "presented here, along with…), demonstrate that" done

50) Line 397: "Overall, particle-phase … regime, since .. is always an important sink of RO2" done

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…" done

52) Figure 1: what are the numbers after the experiment numbers in panel B caption?
We added to the figure caption " with the organic aerosol mass concentration associated with each experiment."

53) Figure 2 caption references to panels a and b are confusing, reorder text?
We reordered the text to clarify the EESI is (a) and FIGAERO is (b)

54) Figure 4 notation about #O is confusing. What about "#O(non-NO3) = #O(total) - 3*#N"?

We changed the Figure caption accordingly.

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Mohr, C., Thornton, J. A., Heitto, A., Lopez-Hilfiker, F. D., Lutz, A., Riipinen, I., Hong, J., Donahue, N. M., Hallquist, M., Petäjä, T., Kulmala, M., and Yli-Juuti, T.: Molecular identification of organic vapors driving atmospheric nanoparticle growth, Nat. Commun., 10, 4442, 10.1038/s41467-019-12473-2, 2019.

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