Comment on acp-2021-379
Anonymous Referee #2

Referee comment on "Particle-phase processing of α-pinene NO₃ secondary organic aerosol in the dark" by David M. Bell et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-379-RC2, 2021

General Comments

This manuscript (which is a companion paper to one submitted by Wu et al.) describes results of a laboratory study of the effect of aging in the dark on the mass and composition of SOA formed from the reaction of NO₃ radicals with α-pinene for a few different concentrations of α-pinene and N₂O₅, which was the source of NO₃ radicals. Experiments were conducted in a Teflon chamber, SOA mass and size were monitored with an SMPS, and gas and particle composition were monitored with a FIGAERO-CIMS and EESI-TOF. The observations are thoroughly discussed, and various possible explanations, such as evaporation, oxidation, and monomer-dimer reactions are proposed. In general, however, given the complexity of the system, the lack of information on the molecular structures of the SOA components (only elemental formulas are available), and the non-quantitative MS analyses, it was not possible to draw convincing conclusions about the physical or chemical processes that might have altered the SOA in the dark. Nonetheless, the data set is interesting, and future studies may provide more detailed data that can help to explain the results. I think the manuscript can be published after the following comments are addressed.

Specific Comments

- Line 205: The reaction RO₂ + NO₃ forms RO + NO₂ + O₂, not peroxynitrates (ROONO₂). I assume you meant RO₂ + NO₂ -> ROONO₂.
- How do you propose that peroxynitrates are converted to nitrates? The only ROONO₂ reactions I am aware of are reversible formation of RO₂ + NO₂ and decomposition to R(O) + HNO₃. It seems more likely that the additional nitrates observed in the excess N₂O₅ experiments 1 and 3 are formed by reactions of alcohols with N₂O₅: ROH + N₂O₅ -> RONO₂ + HNO₃, which is a well-known reaction that is used to synthesize organic nitrates from the corresponding alcohols.
- Line 255: Because the RO₂ + RO₂ and RO₂ + NO₃ reactions both lead to the same alkoxy radicals, and these can go on to form monomers that then form dimers in particles, an alternative explanation for the similarity in SOA dimer composition in the two radical regimes is that most of the dimers are formed in the particles and that gas-phase dimers are minor. Since these MS methods are not quantitative, it is not possible to draw conclusions on the importance of gas-phase dimers.
Line 329: Since the EESI is not calibrated, how can you measure a mass flux?

Since neither the EESI-TOF or the FIGAERO-CIMS signals have been calibrated, the authors cannot assume that all compounds have the same sensitivity. This makes it difficult to draw conclusions from the changes observed in MS signals over time. For example, if reversible (non-oxidative) monomer exchange reactions were occurring in the particles to form dimers with different structures and detection sensitivities, then this could appear as oxidation when it is not. One can imagine a variety of such scenarios that confuse an interpretation of the MS observations.

Technical Comments

- Please define ag s−1.