

Comment on acp-2021-347

Anonymous Referee #2

Referee comment on "Photolytically induced changes in composition and volatility of biogenic secondary organic aerosol from nitrate radical oxidation during night-to-day transition" by Cheng Wu et al., Atmos. Chem. Phys. Discuss.,
<https://doi.org/10.5194/acp-2021-347-RC2>, 2021

General Comments

This manuscript (which is a companion paper to one submitted by Bell et al.) describes results of a laboratory study of the effect of light on the mass and composition of SOA formed from the reaction of NO₃ radicals with three terpenes: isoprene, α-pinene, and β-caryophyllene. 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. Particle volatility was also estimated using a variety of SARs. Experimental evidence is presented indicating changes in the composition of the aerosol when the lights are on, with shifts from dimers to monomers, but with little corresponding evaporation. The observations are thoroughly discussed, and various possible explanations 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 mechanisms by which light might have altered the SOA. 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

- Since neither the EESI-TOF or the FIGAERO-CIMS signals have been calibrated, the authors cannot assume that all compounds have the same sensitivity. All discussion about "mass changes" or "mass fractions" should therefore be changed to "signal changes" of signal fractions". These problems with the MS methods may help to explain why the changes in mass measured by the SMPS (a real mass measurement) are so much smaller than the changes inferred from the MS signals.
- I find the plots in Figures 2 and 3 difficult to interpret. I would like to see similar plots

for samples collected a few minutes apart to see how well the subtraction approach works. For such a comparison the spectra should essentially cancel out, giving a reader more confidence that what is shown in Figures 2 and 3 is not just statistical noise.

- Similar to Comment 2, throughout the manuscript the authors discuss changes in signals on the order of 10% as if they are real. What evidence do they have for this? Have these experiments been replicated?
- Line 455: I do not understand why partitioning cannot be a significant part of the explanation for the observed changes. If many of the oligomers are formed and dissociate by reversible reactions then this seems quite possible.
- Line 480: Since the major sink for OH formed by photolysis in these experiments is reaction with NO₂, then a significant amount of HNO₃ is formed. Couldn't this HNO₃ catalyze the decomposition of dimers, helping to explain observed MS changes?

Technical Comments

None.