

Response Letter to Referee #2

The authors thank the reviewer for the careful review of our manuscript and the helpful comments and suggestions. All the comments (in bold text) are addressed below point by point, with our response following in non-bold text and the corresponding revisions to the manuscript in blue. All updates to the original submission are tracked in the revised version.

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.

We thank the reviewer for the positive assessment of the manuscript.

Specific Comments

- 1. 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.**

Thank you for the comment. In the revised manuscript, all discussion about “mass changes” and “mass fractions” related to MS data is changed to “signal changes” and “signal fractions”: Lines 24 – 25 in the revised manuscript were revised as “Overall, 48 %, 44 %, and 60 % of the total signal for the isoprene, α -pinene, and β -caryophyllene BSOA_{NO₃} was sensitive to photolytic aging and exhibited decay”; Lines 378 – 379 were revised as “These compounds contributed 48 %, 44 % and 60 % to the total pre-photolysis signal for these three systems.”; Line 584 – 586 were revised as “Despite finding 0–12 % of the mass evaporating during photolysis, 48 %, 44 % and 60 % of the total signal of the isoprene, α -pinene, and β -caryophyllene SOA, respectively, is sensitive to photolytic aging, representing a majority of the pre-photolysis composition.”.

2. 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.

With the FIGAERO-CIMS set up to measure continuously during the experiments, sample collection (10 – 20 min for most of the filters) was directly followed by thermal desorption, and the heating cycle took about 50 min. A comparison of samples only a few minutes apart is therefore not possible. We have added Fig. S7 to the supplementary information (SI) of our manuscript, where we plot the mass spectra of three filters (Filter 2, Filter 3 and Filter 4) collected during the 2 – 4.5 h of the dark aging period, and of Filter 5 collected during the photolysis period in Exp.3 (α -pinene + NO_3) as an example. Filter 1 collected at the beginning of the experiment was excluded because most of the changes in chemical composition occur over the first 2 h of dark aging (Bell et al., 2021). The changes in chemical composition between the three filters during dark aging (Filter 2, Filter 3 and Filter 4) are much smaller compared to the changes between Filter 4 (Pre 2) and Filter 5 collected after photolysis (Post), thus the changes of the chemical composition during photolytic aging is not just statistical noise.

In the revised manuscript, in order to see the small changes during dark aging, we keep Fig. 3 as it is. We have added Fig. S7 to the SI and the following sentence to lines 360 – 361 of the revised manuscript: “Fig S7 in the SI shows the changes in absolute signal fraction for the filter samples pre and post photolysis for Exp. 3.”

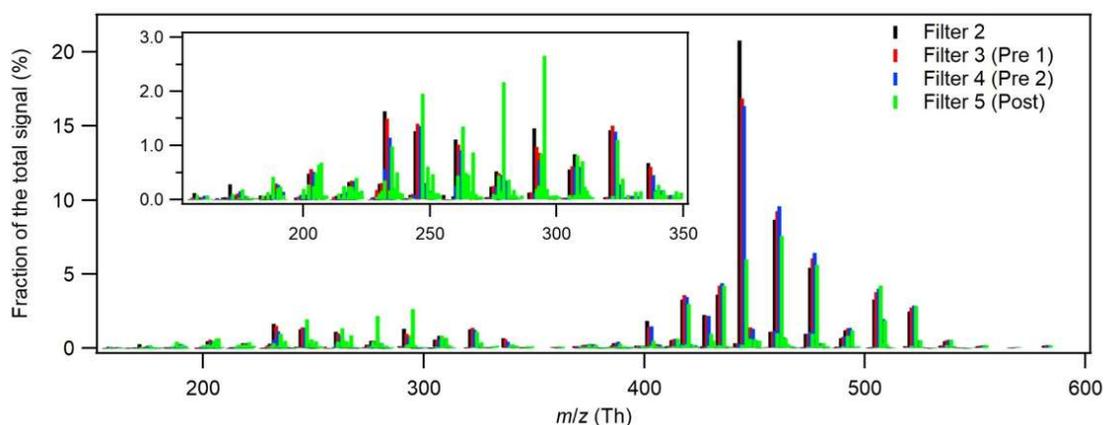


Fig. S7 Mass spectra of four filter samples collected during dark aging and photolysis in Exp.3.

3. 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?

In Fig. 3 and lines 362 – 370 of the revised manuscript, we report the changes in signal fraction of some major compounds in the three systems, with maximal changes in $\text{C}_{20}\text{H}_{32}\text{N}_2\text{O}_9$ (about 10 % decay in signal fraction). The changes in absolute signals of individual compounds were much larger. As mentioned in lines 374 – 378 of the revised manuscript, the average decay of the photolabile compounds in 1h was $44 \% \pm 20 \%$, $64 \% \pm 24 \%$, and $24 \% \pm 18 \%$ for the

isoprene, α -pinene and β -caryophyllene SOA, respectively. Take $C_{10}H_{17}N_3O_{13}$ from the isoprene + NO_3 system as an example, its change in signal fraction was only 2 %, but the absolute signal significantly decayed by about 50 % (Fig. S8 in the revised SI).

Exp. 1 and Exp. 2 could serve as replicates. We observed similar chemical composition (Fig. 2a vs. Fig. S6) and also similar changes due to photolytic aging in these two experiments. 52 and 56 out of 359 compounds decreased significantly during photolysis, and they contributed 49.6 % and 47.2 % to the total pre-photolysis signal in Exp. 1 and Exp.2 respectively. The average decay of the photolabile compounds in 1h was $36 \% \pm 22 \%$ and $52 \% \pm 19 \%$ in Exp. 1 and Exp. 2 respectively.

4. 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.

We apologize we did not make this more clear in the text. By “repartitioning” here we mean evaporation of compounds from the particle phase to re-establish equilibrium that was disturbed due to photodegradation in the gas phase. Lines 465 – 469 were revised as “If gas-phase photo-degradation was the dominant cause for mass loss in all systems, then the largest decays in the particle phase would be expected from the most volatile species. Further, large non-volatile molecules (e.g. dimers in the β -caryophyllene SOA) should be non-responsive to such a pathway. Because there is a systematic degradation of dimers in all systems, it is unlikely that repartitioning derived from gas-phase photodegradation is driving the change in SOA composition during UV aging.”.

It is worth mentioning that dissociation of particle-phase dimers by reversible reactions independent of light conditions (if this is what the reviewer meant) is not an important reason for the changes in chemical composition during photolysis in our study. In Fig.3, we compared firstly the two filters during dark aging to check for reactions, including reversible dimerization, that are not necessarily associated with photolysis. The changes during dark aging were much smaller than the changes due to photolysis, and more importantly different compared to the changes due to photolysis. The signal fractions of smaller compounds decreased and that those of bigger compounds increased during dark aging, which is opposite to what happened during photolysis. Thus, we can exclude reversible dimerization independent of light conditions as a possible explanation.

5. Line 480: Since the major sink for OH formed by photolysis in these experiments is reaction with NO_2 , then a significant amount of HNO_3 is formed. Couldn't this HNO_3 catalyze the decomposition of dimers, helping to explain observed MS changes?

In our experiments, the gas-phase HNO_3 was very high even during dark aging, likely stemming from hydrolysis of N_2O_5 in our injection inlet or on chamber walls. Switching on the lights did not cause significant changes ($< 10 \%$ of pre-photolysis signal in all experiments) in the gas-phase HNO_3 signal (see an example Exp. 2 in Fig. R1). As mentioned above, during dark aging, the signal fractions of smaller compounds decreased and that those of bigger

compounds increased, thus decomposition of dimers catalysed by HNO_3 was unlikely important for the changes in chemical composition during dark aging. Therefore, it also cannot explain the changes we observed during photolysis. In the revised manuscript, we have added the following sentence to line 495: “However, we didn’t observe significant increase in the gas-phase HNO_3 signal.”

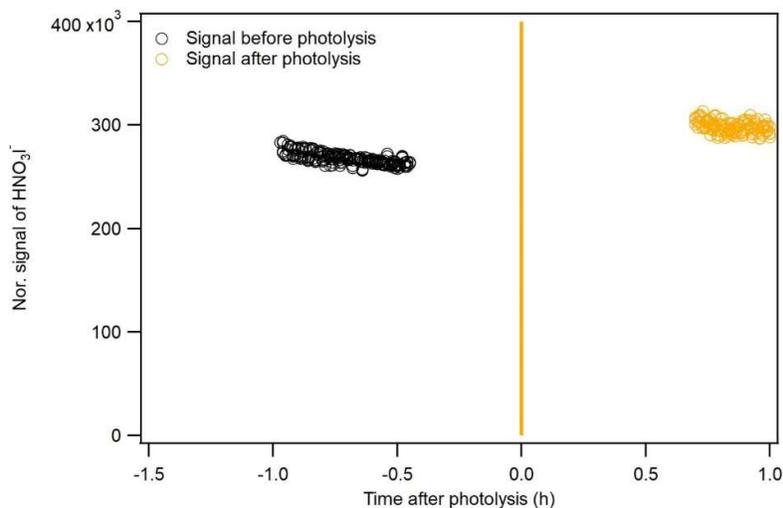


Fig. R1 Normalized signal of gas-phase HNO_3I^- before and after photolysis from Exp. 2 (isoprene + NO_3).

Technical Comments

None.

References

Bell, D. M., Wu, C., Bertrand, A., Graham, E., Schoonbaert, J., Giannoukos, S., Baltensperger, U., Prevot, A. S. H., Riipinen, I., El Haddad, I., and Mohr, C.: Particle-phase processing of α -pinene NO_3 secondary organic aerosol in the dark, *Atmos. Chem. Phys. Discuss.*, 2021, 1-28, 10.5194/acp-2021-379, 2021.