Du et al. combined online FIGEROI-CIMS with offline LC-orbitrap MS to measure products from α-pinene oxidation. They compared the chemical composition measured by the two instruments, performed hierarchical clustering based on temporal behaviors, and compared volatility using CIMS partitioning measurements and structural information derived from LC-orbitrap MS. The combination of the two techniques provides insights into structures, isomer information, and uncertainties in vapor pressure estimations. The manuscript is generally well written with clear presentation of the results. I recommend publishing the manuscript after a minor revision.

We appreciate the reviewer for your time and effort in providing comments for our manuscript. we addressed each comment point by point. For clarity, we kept the reviewer’s comment in black. Our answers are marked in deep blue and changes to the manuscript are in deep blue and Italic. Line numbers in the responses refer to the revised manuscript.

My comments are listed below:

- It is unclear from the manuscript what OH source the authors used.
  
  The initial OH source was generated through the photolysis of the injected NO₂. During the experiment, photolysis of ozone and unsaturated VOC ozonolysis (or potentially via OH recycling) can also generate OH source. The irradiance for photolysis of both NO₂ and O₃ is provided by two 6 kW Xenon arc lamps and 5 rows of halogen lamps as described in Shao et al. (2022). This description has been added to the manuscript in L182th-186th.

- Did the authors report both iodide clustered species and de-clustered species? In Table S2-S4, there are some open-shell products. This makes the reviewer wonder if those open-shell products were formed in the chamber or just de-clustered species in the instrument.

  We reported that all species in the Table S2-S4 are iodide clustered species. In order to make it clearer. The sentence ‘All ions are reported as iodide clustered species.’ has been added in the caption of tables S2-S4.
There are a few open-shell products such as $C_{10}H_{15}O_5$ and $C_9H_{15}O_5$ which were reported by previous literature (Shilling et al., 2009). Those products are generated from the oxidation of a-pinene. However, their detection in our study is likely from either the formation via the chamber, clustering with I and being detected, or from being de-clustered species in the instrument. More work is needed to distinguish their specific source in future.

- Did the authors observe any delay of signals due to losses to tubing or IMR surface (especially for sticky compounds) in the onset period? Would the delay affect the shape of the time series and thus affect the hierarchical clustering?

There were delayed signals for some detected compounds in the gas and particle phases, respectively. In this study, we addressed this issue by subtracting the ‘instrumental background’ for the two phases. Also, the data processing method was validated by Voliotis et al. (2021). Although background correction for all ions was the same, the possible difference in the delayed signals for different compounds may affect the time evolution and thus affect the clustering to different degrees. We acknowledge the reviewer pointed this out and future work is needed to determine the magnitude of the effect. The detail about the background correction in gas and particle phases was shown below:

For the gas phase, we employed the fast background measurement (it was stated in the L220 ‘The instrument was flushed with ultra-high purity nitrogen (UHP, 99.999% purity, N$_2$) for 0.2 min every 2 min during each gas-phase measurement, which acted as the gas-phase instrumental background.’ The pure signal of detected compounds was obtained by the signal of 2 min measurement subtracting the signal from the 0.2 min instrumental background to remove the influence of delayed signals in the gas phase.

In the particle phase, there were delayed signals from the last gas-phase measurement at the beginning of the thermogram period. Thus, the signal in the first 60-90s regarded as the instrumental background was subtracted from the ion signals. As stated in the L246th-250th of the manuscript, ‘For the particle phase, the signal in the first 60 - 90s with relatively low and stable signals was considered as the instrumental background, enabling interference between the gas and particle mode switching to be removed (Voliotis et al. 2021).’

- What were the differences in mass loadings of materials collected on the FIGAERO filter vs on the LC filter due to the difference in collection time? Could any of the differences in composition (e.g., high carbon number compounds) be explained by a lower loading that is close to the detection limit in the CIMS?

The mass loadings of materials on the filters for FIGAERO-CIMS and LC-MS analysis were indeed different. The mass loading of the filter for FIGAERO-CIMS was around 1.55µg ((1slpm *30 min * $10^{-3}$/12 m$^3$) *620 µg; Note: 1slpm is the sampling flowrate; 30 min is the sampling time; 12 m$^3$ is the estimated final chamber volume; 620µg is the average mass of chamber from the SMPS measurement). For the LC-MS analysis, one-quarter of the filters collected at the end of experiments were used with the mass loading of ~166 µg (AS seeds + aerosols) from the SMPS measurement.

There are a number of factors that could result in the differences in the composition, including thermal desorption of SOA in the filters or the selectivity and sensitivity of
instrumental ionisation methods toward compounds (Stark et al., 2017; Mehra et al., 2020; Voliotis et al., 2021) and possibly differences in the limits of detection of the instruments as suggested by the reviewer. It is not possible to attribute the differences in composition to a specific cause in our experiments, but this should be the focus of future work.

- The reviewer suggests that the authors include a figure to show the time series of the precursor in the experiment. It will be useful to know the decay of the precursor along with the formation of products to understand first-gen vs later-gen products.
  The figure has been added to the supplementary information in Figure S3.

References:


