

Response to Reviewer #2

General comment

Understanding the molecular level of aerosol formation has been a long-standing challenge, especially concerning the detailed chemical composition of organic aerosols. Zhao et al. used a new VIA-nitrate-CIMS technique to measure the detailed chemical composition of SOA produced by ozonolysis of α -pinene and provided some interesting new insights. They found the detected HOM molecules in the aerosol phase are significantly different from the “condensed” phase, especially in the dimer range, and indicated that the aerosol phase reactions influenced the aging processes. The manuscript is overall well organized. And more importantly, this is an encouraging attempt and can be an important step in understanding organic molecules in the aerosol phase. I recommend it can be published after a minor revision.

We thank the reviewer for the positive and insightful comments, and we answer the specific comments point-by-point below. The reviewer’s comments are in **blue**, and our answers are in **black**.

Specific comments

Comment #1:

The main findings from this work are, to some extent, similar of Pospisilova et al., 2020. Both studies suggest that aerosol phase reaction plays important role in the aging processes, and the decay of C_{20} and C_{19} HOM dimers was likely the source of C_{17} dimers in the aerosol phase. I suggest that the authors can discuss more on the difference from Pospisilova et al., 2020.

Response:

The gas- and particle-phase HOM measurements in Pospisilova et al., (2020) were conducted with different ionization methods. In this work, we used a nitrate chemical ionization inlet for both the gas and particle phase HOM measurements to minimize the uncertainty during comparisons. In addition, we introduced CO or NO_x into the α -pinene ozonolysis reaction system to change the distribution of gas-phase HOM products and investigated the impacts on both phases.

Based on the suggestion of the reviewer, we have now modified/extended the discussion concerning the comparison of our VIA system to the EESI system to emphasize the difference between this work and Pospisilova et al., 2020, in line 357: *“Furthermore, particle phase decomposition of more carbon-containing HOM compounds (e.g. C_{10} in the monomer range and C_{20} in the dimer range) was proposed as an important decay pathway of α -pinene SOA (Pospisilova et al., 2020), which could largely explain the relative enhancement of C_{16} - C_{19} compared to C_{20} compounds. However, the lifetime of SOA particles is different between the two studies. For example, C_{16} - C_{17} signals peak after ~ 2 hours of the α -pinene ozonolysis in their batch-mode experiments, whereas the residence time is ~ 1 hour for the continuous-mode experiments conducted in this work. Nevertheless, about half of the compounds were proposed to have half-lives of less than one hour (Pospisilova et al., 2020). If the thermal energy supplied during the evaporation of SOA within the VIA can promote this decay process, then the observed particle-phase HOM distribution would be expected to shift to lower C numbers.”*

And we modified the sentence in line 380: *“In order to understand this “dimer enhancement” better and to extend the results from α -pinene ozonolysis system (Pospisilova et al., 2020) to various conditions, we conducted experiments where we tried to modify the dimer/monomer (D/M) ratios of HOM in the gas phase, by adding CO or NO to the system (as discussed in the following sections), to investigate the effects of the corresponding D/M ratios in the particles.”*

Comment #2:

My biggest concern is still how much we can trust the VIA measurement. Is it possible the heating in the inlet speed up the decay of condensed HOM dimers? The authors suggested some possible reactions that should be responsible for the particle phase processes, e.g., the Baeyer-Villiger reactions. Does the heating process have the potential to influence the Baeyer-Villiger reactions?

Response:

The largest uncertainty of the current VIA inlet is indeed the inherent limitations of the thermal desorption techniques itself, i.e. thermal decomposition, especially when we care about the chemical composition of the evaporated vapors. Another method would be extraction if one wants to avoid thermal decomposition. However, the solvent used (e.g. water or some organic compound) may be selective towards some specific functionalities and may introduce a matrix effect. That is partly why the thermal evaporation method is still one of the widely used techniques since no perfect technique exists for now.

Nevertheless, we found that with the much shorter residence time (~0.2 s) in the VIA desorption tubing, less thermal decomposition seems to take place (which looks like very promising) compared to, e.g. the FIGAERO measurements (Lopez-Hilfiker et al., 2014; Lopez-Hilfiker et al., 2015). If thermal decomposition did play an important role in this VIA-NO₃-CIMS system, we would expect more decomposition of dimers (labile RO-OR compounds) than monomers, and in particular at the highest temperature. However, we observed the opposite, i.e. high dimer/monomer ratios in the particle phase. Although the measurements at 230 °C may falsely “increase” dimers but “lose” monomers compared to the measurements at 170 °C (Figure 2), it is still far from enough to explain the enhancement of dimers in the particle phase (Figure 8b). Concerning the opposite effect, as the reviewer might have been suggesting, that the heating would enhance accretion product formation, we would expect that this effect would be much stronger in systems like the FIGAERO where the particles spend much longer periods at the elevated temperatures. The short heating period in the VIA should minimize the probability of such reactions.

It remains an open question if (and to what extent) the thermal decomposition of SOA happens under different temperatures and if the thermal desorption techniques could promote particle-phase reactions. In order to understand more on this topic, we are making a more detailed characterization of the VIA-NO₃-CIMS system, trying to understand the temperature-dependent sensitivity (including evaporation and transmission efficiencies) for different types of organic molecules. This will at least narrow down part of the above uncertainties the reviewer asked about.

Comment #3:

Please provide the NO concentration for all the NO_x runs

Response:

In the NO runs, photolysis of NO₂ was used to introduce NO into the chamber. Thus, only the initial concentrations of NO₂ were provided in Table 1. After the reaction system reached a steady state, the NO concentrations ([NO]_{ss}) were measured and summarized in Table 1.

Comment #4:

Although I understand this is no longer possible in this work, it would be interesting to compare the three technologies, EESI, VIA, and FIGAERO in an experiment together.

Response:

We fully agree that it would be very interesting to have the currently widely used FIGAERO and EESI systems in parallel with the VIA-NO₃-CIMS for experiments, testing e.g. various reaction conditions. But unfortunately, we did not have an EESI or a FIGAERO available during the experiments. We hope that we can contribute to such an intercomparison in the future.

Reference:

Pospisilova, V., Lopez-Hilfiker, F. D., Bell, D. M., El Haddad, I., Mohr, C., Huang, W., Heikkinen, L., Xiao, M., Dommen, J., Prevot, A. S. H., Baltensperger, U., and Slowik, J. G.: On the fate of oxygenated organic molecules in atmospheric aerosol particles, *Science Advances*, 6, eaax8922, doi:10.1126/sciadv.aax8922, 2020.

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmos. Meas. Tech.*, 7, 983-1001, 10.5194/amt-7-983-2014, 2014.

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Carrasquillo, A. J., Daumit, K. E., Hunter, J. F., Kroll, J. H., Worsnop, D. R., and Thornton, J. A.: Phase partitioning and volatility of secondary organic aerosol components formed from α -pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds, *Atmos. Chem. Phys.*, 15, 7765-7776, 10.5194/acp-15-7765-2015, 2015.