Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2022-636-RC2, 2022

Comment on acp-2022-636

Anonymous Referee #2

Referee comment on "Large differences of highly oxygenated organic molecules (HOMs) and low-volatile species in secondary organic aerosols (SOAs) formed from ozonolysis of *β*-pinene and limonene" by Dandan Liu et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-636-RC2, 2022

The manuscript entitled "Large differences of highly oxygenated organic molecules (HOMs) and low volatile species in SOA formed from ozonolysis of β-pinene and limonene" reports chemical composition of SOA, particularly, HOM in particle-phase formed from ozonolysis of b-pinene and limonene. The SOA was formed in a flow tube with ~5 min reaction time. SOA composition was determined via filter collection followed by water extraction and analysis using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS). This study investigated the effect of ozone concentration and compared the difference of the chemical composition between SOA formed in b-pinene and limonene ozonolysis. It was found that for b-pinene ozonolysis, as O3 concentration increased, particle size, OS, relative abundance (intensity-based) of HOM, HOM dimer abundance, and the fraction of LVOC in HOM increased; the relative abundance (intensity-based) of HOM monomer kept almost invariant. For SOA formed in limonene ozonolysis, as O_3 increase, particle size increase, relative abundance of HOM stabilize, of HOM dimer, of HOM monomer remained generally stable; the fraction of LVOC OS, O/C, n(O), DBE, and MW first increased and then stabilized or slightly decreased with O3 increase. At the same O3 level, SOA formed in b-pinene ozonolysis had lower OS, MW, O/C, DBE, lower relative abundance of HOM, of HOM monomers, of HOM dimers, and more numbers of unique compounds (especially those with low OS_c) than SOA form limonene ozonolysis.

This study addresses the chemical composition SOA determined on molecular level, which is an important and challenging topic of atmospheric chemistry. The manuscript fits the scope of ACP. I have the following comments for the authors to consider before publication.

General comments

- Some formulations of the manuscript are not easy to follow (e.g. lines 18-19, 82-83, 214-216, 247-248, 295-297, 305-306). And there are a number of grammar mistakes. I suggest the authors to polish the language throughout the manuscript.

Specific comments

- Can the intensity-based abundance directly translate to concentration? (e.g. L220, Fig.3, and Fig.4).

In another word, do all compounds have same sensitivity in MS so that peak intensity is directly proportional to the concentration?

- How much are the organic aerosol concentrations for the various O3 levels? OA concentration can affect the partitioning of gas-phase species and thus interpretation of the dependence of chemical composition on O3 concentration.
- 7 vs. Fig. 9, why is there no ULVOC in HOMs?
- The foci of the abstract, conclusion, introduction is not exactly the same. . (extracted using water). only WSOC?
- L17, "5-13%" is not shown in the main text. How is this number obtained?
- L120, I suggest noting that the organic compounds are water soluble ones as only water is used for extraction.
- L192, why the standard of O/C<0.7 is used rather than n_O<7 for the classification of HOMs(Bianchi et al., 2019)?
- L200, "which may be due to the formation of high molecular weight and low-volatile dimers" such a statement is not supported by an evidence. I suggest either omitting this or citing the figures on dimers in this study.
- L207-208, "…tends to increase oxygen reaction" is not clear.
- L209, how the "abundance of organic peroxides" are obtained?
- L228-229, is it possible that dependence of composition on O_3 is related to the OH produced in ozonolysis as SOA formed via b-pinene ozonolysis likely does not contain C=C double bonds and thus can less likely react with O_3?
- L237, "as well as low H/C ratio organic molecules", I suggest citing Fig. 5 here. Otherwise, it is hard to follow.
- L259, what does the overoxidation mean? Also by dissociation, fragmentation might be a better word.
- L341, how the conclusion "β-pinene increases the possibility of carbonyl formation at high ozone concentrations" is not clear.
- L358, why it is attributed to "the particle-phase chemistry" rather gas-phase reactions?

Technical comments

- L24, "evolution mechanism of monoterpenes", do you mean evolution mechanism of monoterpene-derived SOA?
- L67, "The more abundant atmospheric β-pinene and limonene" is not clear?
- L205, this statement is for b-pinene.

- L261, the last “or” should be “and”.
- L274, a “of” is missed before “dimmer”.
- L316, many or more?
- L370-371, I think that these sentences are not directly relevant to the main findings of this study.
- L374, “with” is not correctly used here.
- 8, color bar is missed

Reference

- Bianchi, F., Kurten, T., Riva, M., Mohr, C., Rissanen, M. P., Roldin, P., Berndt, T., Crounse, J. D., Wennberg, P. O., Mentel, T. F., Wildt, J., Junninen, H., Jokinen, T., Kulmala, M., Worsnop, D. R., Thornton, J. A., Donahue, N., Kjaergaard, H. G., and Ehn, M.: Highly Oxygenated Organic Molecules (HOM) from Gas-Phase Autoxidation Involving Peroxy Radicals: A Key Contributor to Atmospheric Aerosol, Chem. Rev., 119, 3472-3509, 10.1021/acs.chemrev.8b00395, 2019.