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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Relative Humidity Effect on the Formation of Highly Oxidized Molecules and New Particles during Monoterpene Oxidation" *by* Xiaoxiao Li et al.

Anonymous Referee #2

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This study examines the influence of relative humidity (RH) on the formation of HOM and aerosol from the ozonolysis of three different monoterpenes. HOM have been shown to be central for particle formation over the last years, and therefore knowing their yields under different atmospherically relevant conditions is important. The influence of RH has clearly not been addressed in earlier studies, making this work timely and appropriate.

The paper is well-written and the presentation of results is clear and straight-forward. The strength of the paper lies in the finding that HOM yields do not change as a function of RH, and this analysis by itself makes the manuscript worthy of publishing in ACP. The

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results and subsequent discussion on number and mass formation seem much more speculative. Overall, I have several comments that the authors need to address before potential publication.

Major comments:

1. RH control. In section 2.1, the authors describe that the RH in the flowtube was achieved by mixing a humidified and a dry flow. The humidified flow was 6.5 LPM while the total in the flow tube was 8.5 LPM. Assuming these flows were at the same temperature (which one would hope) when entering the flow tube, then even if the humidified flow was fully saturated at RH=100%, then the maximum achievable RH should be 6.5/8.5 = 76%. However, the authors state that RH was probed up to 92%. I do not see how this is possible, unless the humidified flow indeed was several degrees warmer when entering the flow tube. If this were the case, it would not be surprising that particle number formation decreased, as nucleation is an extremely temperature sensitive process.

2. In Figure 6b, when RH is 0, the mass concentration is steadily increasing over the course of nearly one hour. This is very surprising considering that the residence time in the flow tube is 1 minute. Clearly there is some memory effect, and this is not currently discussed at all in the manuscript. Accumulation of semi-volatile material on walls is a common phenomenon, and can perhaps explain this behavior. Whatever the reason, it puts very high uncertainties on the results, considering that RH may influence the rate of (re-)evaporation from the walls. Are the measured SOA mass changes really significant when considering this?

3. Particle number concentration was in excess of 1e6 cmˆ-3. At such high concentrations, couldn’t nucleation “shut down” at a certain point just because the condensation sink starts to overwhelm the collisions between nucleating agents? Alternatively, the ultimately measured particle number might mainly be limited by coagulation between newly nucleated clusters/particles. While I am not an expert on nucleation, the ex-

treme particle number concentrations raise many questions about how far the absolute values can be compared directly, as done by the authors.

4. Related to the previous point, the authors state that since the aerosol surface area is so much lower than the flow tube wall area, the dominant loss term for HOM will be wall loss. This statement seems completely illogical. How are the particles even formed in the flow tube if all ELVOC or LVOC would condense on the walls? The authors need to calculate the actual condensation sink (CS) produced by the particles and I think they will find that the lifetime of HOM due to CS is on the order of seconds, while wall loss will be a slower process. Calculating a coagulation sink in addition might also help address my earlier comment nr 3.

5. Section 3.6 discusses volatility estimates of HOM. However, it seems the authors are not aware of the work by Kurtén et al. (2016), entitled "α-Pinene Autoxidation Products May Not Have Extremely Low Saturation Vapor Pressures Despite High O:C Ratios". This work certainly needs to be discussed in conjunction with this section, as it raises considerable doubts about the applicability of SIMPOL to vapor pressure estimates of HOM. Using SIMPOL in this work is still completely appropriate, but the large uncertainties should be noted. Also other parts of section 3.6 are questionable, but primarily the authors need to revisit the discussion about oxidation state OS_C. The formula they utilize (2*O:C-H:C) is not applicable in the case that molecules contain (hydro)peroxide functionalities. And according to Table S1, the authors assume this is the case for every molecule under discussion. This will require rewriting all parts where OS_C is discussed.

Minor comments

6. Section 2.1 describes the flow tube setup, but the description is in many places unclear or ambiguous. For the flows, 0.5 LPM is diluted by 6.5 LPM and then mixed with 2.5 LPM. This adds up to 9.5 LPM, but the total flow was apparently 8.5 LPM? There also seems to be different types of zero air used, although they are named the

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same. Is some of it bottled synthetic air? Finally, the authors should clarify “Gas inlets to the flow tube were made from Teflon tubing that were capped and drilled with small holes” better, since as written, it remains unclear to me exactly how this part of the setup looked.

7. There is variability in earlier literature about how to write the plural of HOM. In some cases also the plural is “HOM”, while in other studies they are “HOMs”. However, the usage in many places in this work seems questionable. “HOMs dimers”, “HOMs volatility”, “HOMs production”, etc, sound incorrect to me, and HOM should not be in plural form in these cases.

8. In the conclusions, lines 378-383 present various ways through which water could affect HOM formation, but then this is followed by a sentence saying that none of them actually take place. Are those lines then really needed, or are they just more likely to confuse a reader?

9. Line 139, the inlet flow to the mass spectrometer is given as 0.5 LPM, but is it not closer to 0.7 LPM? This is given in some earlier studies, and is closer to the theoretical value for a 0.3 mm orifice.

10. Line 304. This is not a very clear sentence, but if I understand it correctly, the hydroperoxide should be an alcohol?

11. Figure 3. The legend says “upstram".

12. Figure 4 needs larger axis labels.

13. Figure 6c. The legend for the lines is incorrect. O3 radicals are given twice, as are OH monomers. They should be mixed.

14. Figure 9. The molecule in blue in the top-most box: Is the keto form not more commonly depicted than the enol form given here?

15. There are references to “Kurten et al (2012)” and “Kuerten et al (2016)”. As these,

to my understanding, are the same person, they should be spelled the same.

16. While the likelihood of misunderstandings about what particles are studied here is low, the word “aerosol” is not used before in section 2.3. I suggest to include it at least once at a much earlier stage.

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