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Interactive comment on "Effects of NO_x and seed aerosol on highly oxygenated organic molecules (HOM) from cyclohexene ozonolysis" *by* Meri Räty et al.

Anonymous Referee #1

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This manuscript presents gas-phase measurements of highly oxygenated organic molecules (HOMs) derived from cyclohexene ozonolysis, made using a nitrate chemical ionization mass spectrometer (NO3-CIMS), as a function of initial NOx mixing ratio and ammonium bisulfate (ABS) seed concentration. Comparison of mass spectra for experiments with and without NO addition reveals a general decrease in the abundance of C11–12H16–22O7–16 dimers, varied responses for C3–6H4–12O3–10 monomers, and increases in both N-containing monomers (C5–6H7–11NO4–10) and dimers (C11–12H17–20NO9–14). Based on the observed uptake of compounds to the ABS seed, the authors propose that condensation is primarily controlled by the number of oxygen atoms present in each molecule. The measured gas-phase losses of monomers, dimers, and N-containing compounds due to condensation are also compared to those predicted by two models designed to estimate volatilities of atmospheric oxidation products.

In many respects, this work is a replication of the recent study by Peräkylä et al. (2020), focusing on HOMs derived from ozonolysis of cyclohexene rather than a-pinene. Atmospheric interest in cyclohexene ozonolysis is as a surrogate for a-pinene, given the potential to derive generalizable mechanistic insight from its comparatively simpler symmetric structure. Although this manuscript has the potential to complement and extend the findings of Peräkylä et al. (2020), in its current form it presents few novel results and the discussion is lacking. In particular, molecular-level interpretation of the observed effects of NOx on the abundance and distribution of cyclohexene-derived HOMs is limited and often overlooks key findings from recent papers by co-author Matti Rissanen on HOMs formation in the cyclohexene ozonolysis system. For these reasons, I recommend that publication be considered only after the comments detailed below are addressed.

Specific Comments

1. Line 207: Dependence of $C_6H_8O_7$ and $C_6H_8O_9$ on NOx. Given that Rissanen et al. (2014) proposes structures and formation mechanisms for these HOMs based on quantum chemical calculations and experiments with isotopic labeling, “speculating the reason for this difference is difficult. . .” is a rather unsatisfying interpretation. A discussion that specifically addresses whether the observed NOx trends are consistent with the Rissanen et al. (2014) structures/mechanisms would strengthen this section considerably. Notably, Rissanen et al. (2014) states that “it seems more likely that $C_6H_8O_7$ product is formed through bimolecular reactions of the intermediate peroxy radials (i.e., by RO_2 + RO_2 reactions),” which is consistent with the observed decrease in the $C_6H_8O_7$ signal with increasing NO. Additionally, Rissanen et al. (2018) states that “at a low addition level, NO aids the $C_6H_8O_8$ HOM product formation by reactive alkoxy radical (RO) formation and illustrates the oxidation enhancing influence of gen-

erating highly reactive RO radicals." A similar role of RO reactions in the formation of the $C_6H_8O_9$ HOM may account for the observed increase in signal with increasing NO.

2. Line 184: Role of NO_2. Despite the statement that "only NO mainly has an impact on the radical chemistry," NO_2 should also exert a considerable influence in this system via reaction with acylperoxy radicals [$RC(O)O_2$]. Rissanen et al. (2014) proposes that acylperoxy radicals ($C_6H_9O_6$ and $C_6H_9O_8$) are key intermediates in the formation of the major $C_6H_8O_7$ and $C_6H_8O_9$ HOMs, while Rissanen et al. (2018) implicates acylperoxy radicals in the production of C12 dimers: "these observations imply the special importance of acylperoxy radicals in directing autoxidation phenomena." Given the reported NO/NOx ratio of ~3%, the role of NO_2 should be accounted for.

3. Kinetic Modeling. Interpretation of the observed NOx dependences would greatly benefit from a kinetic box model, parameterized with known rate constants where available, calculated rate constants from Rissanen et al. (2014), and structure-activity relationships from Jenkin et al. (2019). For example, as a function of the initial NO mixing ratio: What fraction of O_3 reacts with C_6H_{10} vs. NO? What fraction of the initially formed $C_6H_9O_4$-RO_2 undergoes unimolecular isomerization vs. reaction with NO or other RO_2? How much NO_3 is formed? What fraction of the C_6H_{10} decay is due to reaction with NO_3 vs. O_3 vs. OH? What fraction of OH reacts with NO_2 vs. C_6H_{10}?

4. Figures 2 and 3. Molecular formulas should either be rotated 90 degrees and placed directly above the corresponding peaks or moved into the white space at the top of the figure and linked to peaks with arrows. The existing format is cluttered and difficult to interpret. Also, the y-axis should be labeled "normalized ion counts," given the normalization to the reagent ion signals.

5. Figure 4. The discussion of Figure 4 is sparse and does not provide any information beyond that presented in relation to Figure 5. However, there are some interesting nonlinear NOx dependences displayed in Figure 4. For example, the $C_{12}H_{19}NO_{11}$ signal decreases between 8 and 10 ppb NOx after increasing from 1 to 4 ppb NOx, presum-

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ably due to suppression of RO2 + RO2 at sufficiently high NO. Additionally, the traces for C6H8O7 and C12H20O9 are effectively superposable, suggesting similar formation pathways. The discussion of this figure should be expanded to include interpretation of these trends.

6. Figures 5 and 6. The use of a color scale in Figure 5 that incorporates opacity makes it very difficult to determine if the degree of marker transparency for a given compound is due to the fit factor, relative signal change, or a combination of the two. Instead of transparency, perhaps different marker symbols (e.g., square, triangle, circle, diamond) could be used to denote different fit factor ranges (e.g., <0, 0.1-0.4, 0.5-0.7, 0.8-1.0). For consistency, the use of symbols to indicate fit factor ranges should also be applied to Figure 6.

7. Line 223: Dimers from O3- and NO3-Derived RO2. The proposed formation of N-containing dimers via cross-reactions of O3- and NO3-derived RO2 is quite interesting and possibly the first account of such chemistry. Several recent studies (Zhao et al. 2018, Kenseth et al. 2018, and Li et al. 2019) report on the analogous formation of dimers from cross-reactions of O3- and OH-derived RO2. A discussion of the current work as it relates to these studies and the potential importance of multi-oxidant chemistry would be useful.

8. Line 259: Model Adaptation. Rather than shifting the fit between FR and log10(C*) reported for a-pinene in Peräkylä et al. (2020) by one unit to account for the difference in SOA concentration, which seems somewhat arbitrary, why not generate a new logistic fit using values for cyclohexene model compounds calculated by the ADCHAM model?

9. Line 282: Model-Measurement Agreement. Both models significantly overpredict the FR for compounds between m/z 250 and 300, including the major C6H8O7 and C6H8O9 HOMs. Was the FR overpredicted for all observed HOMs, suggesting an inability of the models to effectively capture HOMs volatilities? A more detailed discus-

sion of the potential causes of the model-measurement disagreement (e.g., ability to accurately model contributions of key HOMs functionalities, such as hydroperoxides, to volatility) would be beneficial.

10. Line 292: Scaling Experimental Data. What assumptions were made in scaling the data from Peräkylä et al. (2020) to facilitate comparison with the results obtained in this work under different experimental conditions? Such a comparison seems somewhat contrived and the utility is not immediately clear, however, beyond stating that the scaled data are included in Figure 9 they are not discussed. The authors should either include a comparison of the elemental composition vs. volatility trends for cyclohexene- and a-pinene-derived HOMs or remove the Peräkylä et al. (2020) data from Figure 9. As an example, Figure 6 in Peräkylä et al. (2020) suggests that m/z > 300 is required for the FR of non-N-containing a-pinene compounds to drop below 50%, whereas Figure 8 in this work shows that for non-N-containing cyclohexene compounds m/z > 250 corresponds to FR values below 50%. A discussion of such differences would be informative.

Minor Comments

1. Line 29. Sentence beginning with “Through oxidation…” is awkward. Consider rephrasing.

2. Line 76. What is the detection limit of the NOx analyzer?

3. Line 81. Sentence beginning with “Experiments with ammonium sulfate…” is unnecessary.

4. Figure 7. Why is there so much variability in the signal of the three species prior to ABS seed injection (~0.9-1.1)? What are the uncertainties in the measured signals of the detected species and their relative changes as a function of NOx mixing ratio and ABS seed concentration?

5. Line 244. How were the modeled values “scaled to the range of observed remaining

fractions”?

6. Line 250. A discussion of the suitability of using an activity coefficient of unity and the potential impacts of this assumption should be included.

7. Line 315. This sentence is contradictory. By definition, “increased termination of RO2 radicals by NO” does not lead “to more alkoxy radicals” but rather to closed-shell alkyl nitrates. Radical propagation via reaction of RO2 with NO will produce more RO radicals, which seems to be the intent of the sentence.

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