

## **REVIEWER COMMENT #2:**

Summary and general comment:

Baker et al. present very interesting results obtained from laboratory experiments done at the SAPHIR STAR chamber based in Julich. In these experiments the authors have analysed the HOMs formation using  $\alpha$ -pinene as precursors and their impact on SOA. In these experiments they focus on two different main conditions: High and low HO<sub>2</sub>/RO<sub>2</sub> ratio. This study is very important because up to now most of the laboratory experiments have been done at relatively low HO<sub>2</sub>/RO<sub>2</sub> ratio however, if we want to mimic atmospheric daytime conditions, we need experiments also at high HO<sub>2</sub>/RO<sub>2</sub> ratio. In these experiments, they have found that at high ratio they observed a decrease of HOM-accretion products and several other changes. Basically, as the authors mentioned, the study showed that low HO<sub>2</sub>/RO<sub>2</sub> ratios can lead to an overestimation of SOA yields. Because of all these findings, I believe that this article is suitable for publication in ACP. Below I have added few minor comments.

### **Minor comments:**

Line 22-24 Rephrase the sentences: *The HO<sub>2</sub>/RO<sub>2</sub> ratio was increased by adding CO, while keeping the OH concentration constant. We determined the HOM's SOA formation potential, considering their fraction remaining in the gas phase after seeding with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aerosol.*”

I think that these sentences lack of details and probably don't belong in the abstract. I would either explain the details of how the experiments were done or simply mention the high and low ratio and remove them from the abstract.

### *Introduction*

The introduction is very well written, and it includes a nice set of references. My only minor comment here is related to the final sentences at line 79-80. The authors mentioned the used of mass spectrometry with chemical ionization (HR-TOF-CIMS). This is a very general term where these techniques can include a very large set of instruments and different ionization unit. Would be nice if the author can explain better with techniques they used and why.

### *Method*

The method part is also very clear. However, I have one main comment. I might have missed that but how many experiments and how many repetition were done? While reading the paper I had the feeling that there were not many repetitions for each experiment type. I am aware that those experiments requite lots of work and lots of data analysis. I was just wondering how representative they are and would be the impact on their conclusions.

### *Results and Discussions*

The authors include a vast description of their results. One comment here is about figure 4 and its discussion. I understand very well that the accretion products decrease. However, I would expect an increase in the monomers. The authors mentioned that shortly, but I believe more discussions is needed. For example, can it be due to the limited numbers of experiments and relatively low statistics? Is there any other explanation? Maybe is due to the normalization the authors used? As motioned above the rest of the discussions is very clear and full of details.

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## **ANSWER TO REVIEWER #2:**

We thank the referee for carefully reviewing our manuscript and for the constructive feedback. Please find our answers to the individual points below:

### Comment on Abstract:

We understand the principal concerns of the referee. However, we would like to mention that the results could be only gained by applying two relative new concepts:

1. Readjusting the OH concentration such that the primary turnover is nearly the same and effects arising from the different OH concentrations are suppressed.
2. We seed virtually the same evolved chemical system at steady state and use the fraction remaining to directly “measure” the SOA formation potential.

These “novelties” are conceptually inherent to our experiments and seemed important enough to be mentioned as a kind of a teaser in the abstract. However, the abstract would become lengthy when giving details beyond a teasing. They will be explained later in more detail.

### Comment on Introduction:

A sentence was added in Line 78-80 to highlight the use of NO<sub>3</sub>-CIMS due to its high selectivity for HOM compounds.

*L78-80: As the central analysis tool, we will use high resolution time of flight mass spectrometry with chemical ionization (HR-TOF-CIMS) with nitrate (NO<sub>3</sub><sup>-</sup>) reagent ions as this ionization scheme is selective towards HOM compounds (Hytinen et al., 2018).*

### Comment on Method:

Four experiments were performed, two unseeded experiments only investigating the gas phase and two experiments with addition of ammonium sulfate seed aerosol. Therefore, one repetition of each condition was conducted and a sentence clarifying this was added in Lines 251-252. The individual experiments as well as the average are represented in the bar graphs in the Results and Discussion section. The results for the individual experiments are represented by the markers, showing that the results were well reproduced between experiments. The same was observed for the experiments with seed compared to the unseeded experiments. We would like to mention that missing repetition is in parts compensated by multi-instrumental approach, which allows for consistency checks. Of course, more repetitions would give a better statistical basis.

*L251-252: Four experiments were performed in total, leading to one repetition of each studied condition.*

### Comment on Results and discussion:

As pointed out a decrease in accretion products should lead to an increase in monomers, as the HOM-RO<sub>2</sub> that terminated as accretion products at low HO<sub>2</sub>/RO<sub>2</sub> will terminate to monomer products (hydroperoxide termination group) with HO<sub>2</sub>.

However, we additionally observed a reduced steady state concentration of HOM-RO<sub>2</sub> themselves. This reduction can be due to a faster chemical sink at high HO<sub>2</sub>/RO<sub>2</sub>, but also a reduced production of HOM-RO<sub>2</sub>. As explained in Section 4.2 (Lines 438-443) a missing source term is expected for C<sub>10</sub>H<sub>15</sub>O<sub>x</sub> due to its formation pathways including alkoxy radical formation. This missing source term can explain that no overall increase in HOM-monomers was observed at high compared to low HO<sub>2</sub>/RO<sub>2</sub>.

A more in-depth explanation of the expected changes and shifts between product classes was added in Line 379-387:

*L379-387: Without changes in the rates and contributions of the different termination reactions, the observed reduction in the HOM-RO<sub>2</sub> precursors should lead to nearly the same reduction in HOM-Mon. However, the decrease of accretion product formation and fragmentation should lead to an increase in HOM-Mon. The presence of HO<sub>2</sub> could reduce the alkoxy formation, and thus fragmentation of HOM-RO<sub>2</sub>. This missing sink could lead to an additional HOM-Mon source compared to the low HO<sub>2</sub>/RO<sub>2</sub> case. However, the distribution of the product classes at low and high HO<sub>2</sub>/RO<sub>2</sub> (Fig. 5) shows that contributions are shifted from HOM-Acc to HOM-Mon, while the contribution of HOM-Frag remains constant. Each HOM-Acc is formed from one HOM-RO<sub>2</sub> (HOM-RO<sub>2</sub>+RO<sub>2</sub>) or potentially even two HOM-RO<sub>2</sub> (HOM-RO<sub>2</sub>+HOM-RO<sub>2</sub>) and therefore each HOM-Acc not formed will lead to at least one HOM-Mon.*