

# ***Interactive comment on “Ozonolysis of $\alpha$ -phellandrene, Part 1: Gas- and particle-phase characterisation” by Felix A. Mackenzie-Rae et al.***

## **Anonymous Referee #1**

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## **General comments**

This paper presents experimental results on the formation of gaseous organic species, OH radicals and secondary organic aerosols (SOA) during  $\alpha$ -phellandrene ozonolysis. Various dark ozonolysis experiments were performed in an indoor smog chamber facility (with or without OH scavengers, Cl scavengers and NO<sub>x</sub>). Gas-phase species were monitored using a PTR-TOF-MS, SOA size distributions with a SMPS and aerosol compositions with an AMS. Measurements were used to calculate yields for a few gaseous organic species, OH yields from  $\alpha$ -phellandrene and its first-generation products, and rate coefficient of first-generation products. Aerosol yields and effective density of SOA are also provided. The reactivity of  $\alpha$ -phellandrene with ozone, as well as its impact on HO<sub>x</sub> and SOA formation has currently not been studied in the scientific community. This paper provides experimental data that are valuable to better understand the

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environmental impact of biogenic compound ozonolysis and could therefore be of interest to the scientific community. However, the manuscript suffers from a lack of clarity, precision and discussion in several places. In particular, the current knowledge on  $\alpha$ -phellandrene ozonolysis is not enough presented, the purpose of the selected type of experiments are not explained, the methodology used to calculate yields or kinetic constants should be clarified and conclusions reached by the author should be better justified by comparison with previous work. All of this make that even if the results may well be fully valid, an explanation of the methodologies and a justification of conclusions are needed to support the results. Major revisions are therefore required before publication in ACP.

### Specific comments

The chemical reactions expected to occur during  $\alpha$ -phellandrene ozonolysis according to the literature are never described rigorously in the manuscript. The discussion and the Figure in S4 should be presented before section 2 (and not in section 3 where it is difficult to make the difference between our knowledge, the coherence of the observations shown in this study and the novelty of the results). This figure should be used in section 3 to justify the detection of some species and could be coupled with in Fig. 7 to explain the formation of the "new" species detected in this study and with Fig. 6. The structure of  $\alpha$ -phellandrene can also be presented from this figure, allowing to remove Figure 1 which is not really useful.

The various experiments are listed but the objective of each different type as well as the expected impact on the chemical system should be discussed (why several O<sub>3</sub> injections, NO<sub>2</sub> addition? what is the expected impact of an OH and a Criegee intermediate (CI) scavenger on the chemistry? how much of the CI is expected to be scavenged by the used amount of formic acid?). The observed influences of OH and CI scavengers, NO<sub>2</sub> or the several O<sub>3</sub> additions are not enough shown or discussed, questioning the interest of including exp. 6, 7, 9 and 11 in the paper. Do the authors see expected or unexpected differences in gaseous secondary organic and OH yields,

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SOA formation...?

What is the typical volume of the chamber at the end of an experiment? (p.3 I.31)

Numerous figures and tables are discussed before or without being presented. Each Figure or Table should be clearly introduced in the text before being discussed.

The temporal evolution of the PTR-TOF-MS signals presented in Fig 2 should be described in the text at the beginning of the section 3.1.1. In particular, Why are all concentrations at around 35 min going to 0 except  $m/z = 42$  and 137? Why does the precursor's concentration decrease at the same time? The  $m/z = 42$  signal is not impacted. Why? Is the linear decrease of O<sub>3</sub> (after 70 min) due to wall loss?

In OH scavenged experiment, the reactivity of the system is expected to stop when the two  $\alpha$ -phellandrene double bonds have each been reacting with O<sub>3</sub>. PTR-TOF-MS measurements show an increase of all the  $m/z$  signals (also for small molecules), except for the  $m/z$  assigned to the precursor and the inert gas. Some of these  $m/z$  could be assigned to first generation products (and also maybe second generation?) expected to be formed during scavenged  $\alpha$ -phellandrene + O<sub>3</sub> experiments. These first and also second generation species are expected to stop growing when no double bond remain in the molecule considering the known chemistry. The authors claim at several places in the paper that the observed increase suggests that these compounds are second-generation or higher generation species (e.g. p.5 I.25, I.35 and below in the paper) or that this unique profile implies that they derived from a source secondary to ozonolysis, such as gas-phase accretion (e.g. p.7 I.35., table 2, S3...). The authors should be careful in drawing their conclusions. Why an increasing signal makes the species a second-generation compound? If this increasing signal comes from the formation of dimers, why is an increase also observed for the low  $m/z$  signals ( $m/z = 47, 59, 61...$ )? The hypothesis of some chamber wall artefacts is never discussed in the paper. Have the author already tested the impact of chamber teflon walls on the off-gassing of radical and/or organic species in the gas phase? Could it be a possible

explanation of the increasing m/z signals?

Experimental results are used to provide various yields. The yields are however not always clearly defined in the paper. For secondary organic species (SOC), Y would be usually defined as:  $Y = \Delta [\text{SOC}] / \Delta [\text{COV}]$ . Here Y is calculated from the amount of O<sub>3</sub> that has reacted as  $Y = \Delta [\text{SOC}] / \Delta [\text{O}_3]$ . Has the  $\Delta [\text{O}_3]$  to be divided by a factor of 2 to correspond to the  $\Delta [\text{COV}]$  or not? Has this method been used previously? How do you deal with experiments without OH scavenger or with various additions of O<sub>3</sub>? The initial concentration of O<sub>3</sub> is not known. Does this have an impact on the calculated yields? Looking at Fig. 3, no data is used at the beginning of the experiment when the system is the most reactive, i.e. before  $\Delta [\text{O}_3]=40$  ppb. Why? The intercept of the regression lines is different of 0. Why? The all length of the experiment is used to optimize regression lines and therefore to get the yield. 4/5 of these measured data correspond to a decrease of O<sub>3</sub> concentration due to wall loss and an increase of secondary organic species which is difficult to understand. Is that not an issue to keep these points for the optimization?

Two OH yields are calculated, one for a-phellandrene and another one for its first-generation products using the methodology presented in Herrmann et al. (2010). The methodology used here should be presented using the Herrmann et al. (2010) reference with the two reactions p.8 l.34, before the presentation of the OH yield results. How do you define the end of the a-phellandrene dominated zone (Fig. 4)? Why is the intercept of the regression line different of 0 in Fig 5.a.? The intercept could be 0 with a good correlation coefficient if the end of the a-phellandrene dominated zone stops before. How do you define the end of the product dominated zone (Fig. 4)? Is that not when the observations are difficult to understand and when we do not look at ozonolysis? In Fig 5.b, shouldn't the OH and O<sub>3</sub> concentration variations be looked starting from the beginning of the product dominated zone (and not from the beginning of the experiment) and why is the intercept of the regression line far from 0 ?

The kinetic constant for the reaction of the secondary products with O<sub>3</sub> was optimized

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giving again most of the weight to the to the part of the experiment we do not understand. Is that not an issue?

What is the objective of all the section 3.2? No particle phase chemistry was studied in the paper. Please, change the title 3.2. Most of the sentences in section 3.2 are generalities, figures are listed but poorly discussed and the selected figures do not justify the reached conclusions. The writing of this section has to be largely improved with clear objectives and appropriated figures, discussion of the results and comparisons with literature.

Why are the activity coefficients needed (p.11 l.20)?

In the two product parameterization,  $a_1=a_2$  and  $K_{om1}=K_{om2}$ . What optimization method has been used? Does this mean that one product is enough to parameterized SOA formation? How can this be explained?

### Technical corrections

- p.2 l.32: change " $\mu$  g m<sup>3</sup>" into " $\mu$  g m<sup>-3</sup>"
- p.3 l.9: I don't see a link between this study and the "theoretical foundation" you are talking about. I would remove "theoretical foundation".
- p.3 l.27: "formic acid was added to experiment 6 and 7 to ascertain the role of SCI". What do you mean by "ascertain the role of SCI"? Are you talking about the role of CI?
- p.7 l.9: change "acetaldehyde" into "acetaldehyde"
- p.8 l.15: this part of the sentence "So whilst the complete product distribution will likely consist of a myriad of species (Aumont et al., 2005)" is off-topic.
- p.36 Fig.10: in the legend, " $\mu$  g m<sup>-3</sup>" has to be changed in a concentration in volume.
- p.31 Fig.5:  $\Delta[\text{OH}]$  on the y axis?
- check that the concentrations and the variation of the concentration are written as [X]

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and not X

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