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Interactive comment on “A comparison of secondary organic aerosol (SOA) yields and composition from ozonolysis of monoterpenes at varying concentrations of NO₂” by D. C. Draper et al.

Anonymous Referee #2

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The authors reported results from a series of laboratory chamber experiments to evaluate the effect of added NO₂ (to ozonolysis experiments) on SOA formation, yields, and compositions for a series of BVOC. Experiments were conducted in a 400L flow through chamber. For α -pinene, the SOA mass appeared to decrease with increasing NO₂, possibly a result of increasing reaction between α -pinene and NO₃ radicals. The authors noted that β -pinene and carene retained similar mass yields with increasing NO₂, while limonene generated more SOA with increasing NO₂. Filter samplers were collected from these experiments, and higher molecular weight products were detected

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in experiments with more NO₃ oxidation, suggesting the importance of oligomerization reactions.

The research topic would be of interest to the research community and is certainly worthy of investigating. Unfortunately, there is a mismatch between the experimental design and set up and the goals of this study, which is a critical weakness of the study. The experiments were conducted by introducing BVOC into the chamber after the oxidant concentrations stabilized. The BVOC concentration was not measured during the experiments. Instead, the BVOC concentration from the flask containing it was measured before and after the experiments, and compared to estimates from a model. The modeled BVOC was then used to calculate yields ($Y = \text{delMo}/\text{delHC}$). As shown in Figure S4, the uncertainties associated with [BVOC] are very large. The authors did not specify the uncertainties, but from Figure S4 it appears that the uncertainties can be as large as +/- 50% and even a factor of 4 for limonene. With a lack of direct measurements of [BVOC] and such large uncertainties in the estimated [BVOC], the authors cannot attribute their observed yield differences to the effects of added NO₂ and subsequent NO₃ chemistry. Further, when taking such uncertainties into account, except for the α -pinene reactions, the data shown in Figure 4 for differing amount of added NO₂ are essentially the same within uncertainties. One cannot use the data from Figure 3 to draw any conclusions either. As the experiments have different NO₂ and BVOC concentrations, one cannot attribute the difference in SOA growth in Figure 3 to NO₂ only.

I have some serious concerns regarding the authors' interpretation of SOA yields. Many of the discussions reflect a lack of understanding of SOA yields. First and foremost, SOA yields should not be reported on their own, and be compared across different systems/experiments, without taking into account the corresponding delMo values. Even for the same BVOC reacting system, SOA yield is a function of delMo (Odum et al., 1996). Secondly, in performing chamber experiments in flow-through mode, one typically waits till the chamber achieves steady state and reports the yield (with the

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corresponding steady state delMo). However, here, it appears that the chamber did not reach steady state (base on info from the experimental schematic). With this, what do the “yields” reported in this study mean? It is some sort of time-dependent yield, but with the chamber not reaching state, the authors cannot simply compare these time-dependent yields between different experiments and make conclusions regarding the effects of added NO₂.

Overall, the experimental design and setup in this study do not allow for an accurate assessment of the effects of NO₂ concentration on SOA formation and yields. While the writing is clear, the data interpretation is questionable and the conclusions are not well justified. I do not think the manuscript is suitable for publication in ACP in its current form.

Specific comments.

1. Page 14929, line 1-5. The authors stated that the initial [VOC] was characterized directly from the flask using GC-FID before and after each experiment.

a. Why is the GC-FID measurement not performed during the experiment at chamber inlet/outlet? This would seem like the most logical way to greatly reduce the uncertainties in their yield calculations.

b. Figure S4 shows the average GC-FID measurements of BVOC source concentrations plotted against the BVOC source concentration range predicted by kinetics modeling for each experiment. This figure needs to be discussed extensively in the main text. As seen in Figure S4, the uncertainty in the modeled BVOC concentration is easily as high as +/-50%, and even can be a factor of ~4 for limonene. These are very large uncertainties. As SOA yield = delMo/delHC, the large uncertainties in [VOC] will directly translate to the uncertainties in yields, making it extremely difficult to compare the yields across different experiments and arrive at any concrete, well-supported conclusions.

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c. What is the relative importance of RO₂+RO₂ in the experiments? With the very high mixing ratios of VOC used in these experiments, one would imagine RO₂+RO₂ would dominate. Please comment on the atmospheric relevance of these experiments in this regard.

2. Page 14830, section 3.1. I think this section is misleading. One a first read, it looks like the authors are comparing the aerosol formation in each system systematically, as a function of NO₂ added. This would be fine if everything in the system is maintain constant, except for the amount of NO₂ added. However, this is not the case.

a. With the large uncertainties in [VOC] modeled, one can see from Table 1 that the [VOC] concentration can vary up to a factor of > 3 for the same VOC system. Therefore, the authors simply cannot discuss the trends in Figure 3 as a result of varying [NO₂] on SOA formation (because there is a large variation in [VOC] as well). For instance, if one looks at the results for b-pinene in Table 2, the ozonolysis experiment has [VOC] = 370 ppb, while the low [NO₂] experiment has [VOC] = 470 – 680 ppb. The authors argued that the addition of NO₂ enhanced SOA formation. However, given the large uncertainties in [VOC], one can argue that the higher SOA formation in the low [NO₂] experiment (as compared to the ozone-only) is a result of a larger amount of VOC reacted.

b. Are the “ozone-only” experiments truly ozone only? Is any OH scavenger added? This is not mentioned in the text so I assume no scavenger was added. Thus, in the ozone-only experiment, there can also be BVOC+OH reactions. If so, the different extent of BVOC+OH reactions in the “ozone-only” experiments and “NO₂ added” experiments can also contribute to the difference in the observed SOA loadings and yield. Thus, this could also alter the interpretation of the trends observed and the conclusions of the manuscript. Please comment.

c. All the [VOC] data in Table 2 should include uncertainties.

3. Page 14932 and onwards, discussion of SOA yields.

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a. These discussions reflect a lack of fundamental understand of SOA yields. SOA yield is a function of delMo (e.g., Pankow , 1994, Odum et al., 1996). The two product model governs that SOA yield will increase with delMo. In this regard, it is not meaningful to simply report SOA yields without providing the corresponding delMo data as well (Table 3, and page 14933, line 9, line 20, etc). One should never compare a “SOA yield” from one precursor to another (or from one experiment to another), without taking into the corresponding delMo values. (unless SOA yield is constant for all delMo values).

b. Page 14932, line 10. What are the “difficulties”? Do these reflect the uncertainties in the modeling framework? Please provide more information. Why were these “difficulties” only encountered for the high NO₂ experiments?

c. Page 14933, line 4. Is it possible that the “0 %” SOA yield from a-pinene is a result of the experimental deign and set up? (e.g., high a-pinene mixing ratio, higher contributions from RO₂+RO₂, mixing, etc?).

d. Page 14933, line 16. The authors noted that in the b-pinene experiments, aerosol size distribution grew out of range of SEMS. Did the size distribution grow out of range in other experiments? What are the implications of this on data interpretation and conclusions of the manuscript? Does this mean that the delMo data reported for b-pinene are underestimated (and the authors did not know the extent to which the underestimation is?), which would also affect the SOA yields?

4. Figure 4 and related discussions. The data shown in Figure 4 demonstrate the main weakness of the manuscript.

a. The main goal of the study is to evaluate the effect of added NO₂ on SOA formation and yields from various hydrocarbon precursors. As noted in the comments above, the uncertainties in [VOC] are very large (as large as +/- 50% and a factor of ~4 for limonene). If one takes these uncertainties into account, for each precursor (perhaps except for a-pinene), all the delMo vs. delHC plots shown in Figure 4 would essentially

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be the same within uncertainties. Thus, one cannot arrive at any conclusion regarding the effect of added NO₂ on SOA formation and yields. This is not to say such a study cannot be performed, but the experimental design and the uncertainties in [VOC] in this work is suitable to evaluate the effect of added NO₂ on SOA formation and yields.

b. When operating the chamber in steady state mode, one typically reports the yield at steady state. In this study, it appears that the chamber never reached steady state after BVOC was added, thus, the yields reported in this study are time-dependent yields. It is not clear what time-dependent yields in a flow-through chamber mean and how such data can be interpreted, as the results can be drastically affected by mixing, injection, etc. If one operates the chamber as a batch reactor, the time-dependent SOA yields can be similar or different from “final yields”. Here, without performing a series of experiments over a range of initial [BVOC] (for each BVOC) and wait till steady state, it is difficult to compare yields from these experiments and make conclusions regarding the effect of added NO₂.

c. If one still tries to calculate the time-dependent SOA yields from the data shown in Figure 4, another issue arises. Typically, SOA yield increases with reaction time, and may decrease towards the end of experiment due to particle wall loss being greater than SOA growth. However, the shape of the curves (convex shape) in Figure 4 indicates that in these experiments, the slope (and hence SOA yield) decrease with time. What caused such an atypical behavior? Please explain.

5. Page 14934, comparing yields from the current study to prior studies.

a. When taking delMo into account, one can compare the SOA yields between different studies. The SOA yields from the “ozone-only” experiments appear to be quite different from those in Griffin et al, for a delMo = 200 ug/m³. Does this reflect the limitation of the yields reported in the current study (i.e., yields are not steady state yields)?

b. In line 2, the authors noted that the “relative yield” for each monoterpene follow the same trend as in Fry et al. (2014). This research group has published multiple

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studies reporting SOA yields from various BVOC with nitrate radicals. However, when comparing SOA yields at similar delMo values for the same BVOC, it appears that the SOA yields are quite different between the different studies from the same group, and that there are no detailed discussions regarding why they are different. This makes it difficult for the readers to interpret their results. Of course, there are many factors affecting SOA yields, but it's important to ensure the results are consistent with their own prior studies, or other studies in literature, if the experiments are performed under similar conditions. If any yield differences can be a result of differing experimental design and conditions that should be pointed out clearly and discussed as well. In this case, the authors mentioned that their results are consistent with the trends in Fry et al. (2014), where it appears to be a flow-through chamber study as well. Fry et al. (2014) showed that the SOA yield for b-pinene at a delMo of ~ 30 $\mu\text{g}/\text{m}^3$ is ~ 0.5 . From Table 4 of the current study, the model predicted that a majority of the b-pinene in the med [NO₂] experiment should react with NO₃. However, if one converts the b-pinene med [NO₂] data shown in Figure 4 of the current study into a yield curve, it would be very different than the one shown in Fry et al. (2014). This is just one example. I encourage the authors to carefully compare and discuss their findings with their prior results/other results in literature, and justify any differences observed.

6. The composition data are quite interesting. There are several speculative chemical structures, could the authors provide some discussion (speculation) as how these large molecular weight compounds can be formed.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 14923, 2015.

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