Review of "Investigation of the B-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR", Kaminski et al., ACP (2016)

Summary

This paper analyzes a set of chamber experiments focused on the chemistry of OH + B-pinene. Unlike previous studies, these experiments are done at relatively low VOC and NOx loading, thus better representing true atmospheric conditions. The chamber is also highly instrumented, allowing examination of both radical chemistry and product formation. Interpretation is aided by a box model. The authors find that formation of first-generation products is represented well by a recent theory-based mechanism, but not the MCM. They further identify a major discrepancy between modeled and observed HO2, which they ascribe to an unknown radical source.

The results of these experiments are interesting, novel, and worthy of publication in ACP. The English is verbose/awkward in places, but still understandable. The text is a little long and could be shortened in places. My primary concerns lie in the interpretation of the radical budgets, and in particular the potential for chamber or measurement-based artifacts. Publication is recommended after considering the following.

General Comments

The reviewer is not convinced that a missing HO2 source is the most reasonable hypothesis to fit the observations. Two specific concerns in this regard:

1) The decay of B-pinene is well described by the base model simulation, and any attempts to artificially increase model HOx degrade this agreement. This is discussed in Section 3.4.3, where it is stated that two independent measurements of both OH and B-pinene (decay) agree well with one another, therefore there seems to be no obvious explanation. One could argue, however, that observations of absolute OH concentration are susceptible to systematic errors, while the decay rate of a VOC is less likely to have such errors. Indeed, the observed decay rate of B-Pinene coupled with the uncertainty in the OH+BPIN rate constant should bracket the range of "reasonable" OH concentrations. The alternative is that an additional process is causing the B-Pinene decay to be artificially slow, but no explanation is given to that end.

2) HO2* in Fig. 1 climbs steadily throughout the experiment and reaches a maximum around 1300 UTC; indeed, the trend before and after B-pinene injection is fairly similar. No other species show this behavior. My concern is that this is a chamber wall or instrument artifact, related to either the build-up of oxidation products and/or insolation. It would be nice to see, for example, what the time-progression of J(HCHO) is over this experiment. Does it also show a maximum at ~1300 UTC? The mystery HO2* source reported by Wolfe et al. (2014) showed a marked dependence on solar radiation, so this would provide some support that the two phenomena (whatever their origin) are similar. If J(HCHO) does show

a similar trend to HO2*, could the “photolytic source” from molecule “Z” match HO2* if it were set to a constant value instead of being tied to B-pinene oxidation? Perhaps some long-lived contaminant is injected along with B-Pinene.

Specific Comments

L10: when referring to “low NOx” in this context, it is better to give NO than NOx mixing ratios since this determines the radical fate.

L18: Factor of 3 low or high?

L55: It should also be mentioned that we have since discovered substantial artifacts in some HOx instruments for some conditions (Mao et al., 2012).

L190: Do these source strengths vary significantly day-to-day? Just curious if this could indicate something about chamber wall aging.

L246: Suggest ensuring figures and tables are numbered to reflect the order they appear in the text (this may even by ACP policy).

L261: How does this 70 ppt/h compare to production rate of acetone from BPIN? From figures , it looks like it is relatively small, but it would add confidence to say so.

L296: More generally, one could just say that the product yield depends on the fate of RO2.

L307: “the yields were normalized to a conversion of 70% of the injected B-pinene.” I do not understand what this means; please clarify.

L316: Do either the MCM or Vereecken and Peeters mechanisms exhibit an NO dependence in the yield? This could be examined fairly easily with the box model, ramping NO between say 10 ppt and 1 ppb.

L418: In these experiments, do measured and modeled HO2* agree well?

L438: What is meant by “stable?”

Section 3.4.4: This section could be shortened significantly by removing details. It seems like a lot of text to present 3 sensitivity studies, none of which explain the missing HO2.

L555: Some caution is warranted when comparing to these field studies, as the VOC were quite different. For example, in the works of Kim and Wolfe, MBO was the dominant VOC.

L600: Z is produced from B-pinene oxidation with an arbitrary yield of 1, so the choice of an equally arbitrary HO2 yield of 6 doesn’t seem very unreasonable. There may also be multiple generations of chemistry that are being wrapped up into Z.

Section 4: First paragraph could be shortened a lot. Don't need to re-outline the whole paper, just highlight the key findings. Also in last paragraph, please be more specific about what types of experiments, or what measurements, are needed to pin down this missing HO2 source. SAPHIR is already pretty well-armed.

Technical Comments

L35: delete "to OH"

L180: delete "are"

L221: "interfering"

L436: "formation now depends"

L674: "comprehensively"

Figure 1: suggest changing the name of the "MCM mod" run to something like "VP2012." If I read the text right, this is not MCM at all (except for maybe the inorganic chemistry).

Figure 2: Suggest setting the y scale for the top plot to 0-2.

Figure 3: Please include a line for the base simulation for comparison.

References

Mao, J., Ren, X., Brune, W. H., Van Duin, D. M., Cohen, R. C., Park, J. H., Goldstein, A. H., Paulot, F., Beaver, M. R., Crounse, J. D., Wennberg, P. O., DiGangi, J. P., Henry, S. B., Keutsch, F. N., Park, C., Schade, G. W., Wolfe, G. M., and Thornton, J. A.: Insights into hydroxyl measurements and atmospheric oxidation in a California forest, Atmos. Chem. Phys., 12, 8009-8020, doi: 10.5194/acp-12-8009-2012, 2012.