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Interactive comment on "Investigation of the β-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR" *by* Martin Kaminski et al.

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We thank the reviewer for his/her comments. Here are our responses to the specific comments.

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:

Comment

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.

Response

As explained in chapter 3.4.3 there is a discrepancy between the OH concentration

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measured directly by LIF and DOAS and the OH concentration as calculated from the measured decay of b-pinene which we cannot explain. However, with any OH dataset the OH production rate corresponds the measured OH destruction rate with in the uncertainty of the instruments. The OH budget is closed. Also, when the measured HO2 concentration in the model is constraint with measured HO2 data, the difference between measured and modelled OH is small. For most of the experiment, the modelled OH concentration is higher than the OH concentration inferred from the VOC measurements and lower than the directly measured data. Therefore, the discrepancy of OH data from direct measurements and OH data inferred from the VOC data is not of importance for the key findings of the paper.

Comment

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.

Response

The interference of the HO2 data for RO2 radicals has been determined prior to the monoterpene degradation campaign in lab experiments. A sensitivity study (see supporting material) showed that even a doubling the interference would not be enough to explain the measured HO2 values. We agree that the measured HO2* values do not change significantly before and after the VOC injections. A similar time series of HO2* was observed in all b -pinene experiments, but not in limonene and a-pinene experiments which were conducted in the same time period. Therefore this HO2 time series is chemistry related and not caused by artefacts of the instrument. The measured photolysis frequency of formaldehyde J(HCHO) had maximum values between 10:00 AM and 1:30 PM as the measured HO2, but this would be expected from the model, if a photolytic source of HO2 is assumed: In standard experiments HO2* agrees within 15% with the modelled values. Also we did not observed indications for impurities being injected together with the b-pinene. The compound was specified with a purity of 99%, and contaminants were detected neither by PTRMS nor by GC/MS.

Comment

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.

Response

NOx is changed to NO in the text

Comment

L18: Factor of 3 low or high?

Response

Nopinone concentration is three times higher than measured. The sentence is rephrased.

Changed text:

Old: The measured OH and HO2 concentrations were underestimated by up to a factor of two whereas the total OH reactivity was slightly overestimated because of the poor reproduction of the measured nopinone by the model by up to a factor of three

New: The measured OH and HO2 concentrations were underestimated by up to a factor of two whereas the total OH reactivity was slightly overestimated because the model predicted a nopinone mixing ratio which was three times higher than measured.

Comment

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

Response

The study is added to the text.

Changed text:

The newly discovered mechanisms for isoprene and methacrolein, however, can explain only part of the observed high OH concentrations. Another possible reason could be OH interferences in the low pressure laser-induced fluorescence (LIF) instruments that were applied in the above field studies. Artificial OH production was discovered in two similar LIF instruments applying a newly developed chemical modulation technique for OH detection (Mao et al., 2012; Hens et al., 2014; 5 Novelli et al., 2014; Feiner et al., 2016). The interference seems to be related to organic compounds, but the underlying OH formation mechanism is not known. Experimental tests with other type of LIF instruments have not found such interference (Fuchs et al., 2012, 2016; Griffith et al., 2013; Tan et al., 2017), yet it is difficult to draw firm conclusions for past campaigns as long as the reported artefacts (Mao et al., 2012) are not fully understood.

Comment

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

Response

The chamber strength of HONO, formaldehyde and acetone can be calculated with good precision from the measured photolysis frequency of NO2 (JNO2), the relative humidity and the temperature using a scaling factor. Prior to each experiment a zero experiment was conducted to determine the scaling factor needed to explain the observed values of these trace compounds. While both the scaling factors for the HONO source and the acetone source did not vary by more than 20% from day to day over the one month period, the scaling factor for formaldehyde increased by a factor of three throughout the campaign.

Comment

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

Response

Figure numbering is changed.

Comment

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.

Response

20% to 30% of the total acetone formed in the b-pinene experiment was due to emissions production of the chamber wall.

Changed text:

Old: The assumed acetone source strength was typically 70 ppth-1.

New: The assumed acetone source strength was typically 70 ppth-1 which was as large as 20 to 30 % of the total amount of acetone produced in the ß-pinene experiments.

Comment

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

RO2.

Response

This has been changed in the text

Changed text:

Old: In principle product yields of nonlinear degradation processes depend on multiple physical and chemical boundary conditions as pressure, temperature, H2O, O3 , VOC, HO2 and NO concentration.

New: In principle product yields of nonlinear degradation processes depend on the fate of RO2 which is governed by multiple physical and chemical boundary conditions such as pressure, temperature, H2O, O3 , VOC, HO2 and NO concentration.

Comment

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

Response

The product yields were determined from a linear fit of b-pinene consumed versus the amount of acetone produced. During the course of the experiment the yield of acetone increases due to the increased production from secondary products. Therefore, only the data of experiments were used for the yield determination when less than 70% of b-pinene was consumed, i.e. when the chemistry of secondary products is still minor relative to the b-pinene chemistry.

Comment

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.

Response

As proposed, NO was ramped in the model from 10 to 1000 ppt NO. The MCM model suggests an increase from 0.44 at 10 ppt to 0.7 at 1 ppb. The Vereecken model predicts only an increase from 0.21 at 10 ppt NO to 0.26 at 1 ppb.

Comment

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

Response

In standard experiments HO2* agrees within 15% with the modelled values.

Comment

L438: What is meant by “stable?”

Response

The sentence has been changed.

Changed text:

Old: In contrast to the original MCM 3.2 the primary acetone formation is now depending on two channels, leading to an increase of acetone formation under low NOX conditions, whereas the acetone yield in the MCM 3.2 is fairly stable. More details about the mechanism can be found in Vereecken and Peeters (2012).

New: This leads to an increase of acetone formation at low NO concentrations compared to the MCM 3.2 while the yield of nopinone is predicted to be lower in the model by Vereecken and Peeters (2012).

Comment

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.

Response

This section has been shortened. The sensitivity studies are only mentioned now. The detailed description of the sensitivity studies have been moved to the separate supporting information paper.

Comment

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.

Response

This is now mentioned in the text.

Changed text:

Old: Kim et al. postulated a missing photolytic HO2 source as the reason for the discrepancy between the measured and modeled HO2 concentration.

New: Kim et al. postulated a missing photolytic HO2 source as the reason for the discrepancy between the measured and modeled HO2 concentration in a 2-methyl-3-buten-2-ol (MBO) dominated environment.

Comment

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.

Response

We performed an additional simulation to explain the missing HO2 source. Two molecules of HO2 are supposed to be produced from a reactive intermediate together with a dicarbonyl compound. If the photolytical cleavage of the dicarbonyl compound produces two additional HO2 molecules, the measured HO2* time series can be reproduced by the model. This is now described in detail in chapter 3.5.3.

Comment

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.

Response

The section has been shortened and possible additional experiments are now included.

Changed Text

Old:In accordance with the results for ß-pinene presented in this paper we propose a missing photolytic HO2 source as the reason for the underestimation of OH in the model. An additional sensitivity study trying to identify the nature of the HO2 source for the ß-pinene experiment showed that a formaldehyde like photolytic HO2 source is not a reasonable option to explain the measured HO2 and OH levels. Due to the absence of a sufficient amount of photodegradable first generation products at the beginning of the ß-pinene oxidation a photolytic source is not able to produce enough HO2 to explain the measured concentration. A second sensitivity study demonstrated that the addition of RO2 rearrangement reactions releasing HO2 to the model is not a reasonable option either. In case of the RO2 rearrangement reactions the added reaction path competes with the formation of organic nitrates in the model and is thereby causing a strong overestimation of the measured nitrogen oxide concentrations by the model. Additionally a third model run showed that an overestimated yield of organic hydroperoxides can be excluded as the reason for the underestimation of the measured HO2 concentration because the reduction of the HO2 loss is too small. Further studies demonstrated that an underestimation of the known RO2 interference on the measurements of HO2 can be excluded as the reason for the observed high HO2 concentrations. None of the previously discussed changes in the mechanism as well as the RO2 interference is able to solely explain the deviations between model and measurements. In conclusion, it can be said that the study of the ß-pinene oxidation in SAPHIR as well as several field campaigns showed the lack of understanding of the radical chemistry involved in the OH oxidation of monoterpenes. The identity of the proposed missing HO2 source still remains uncertain. To further elucidate the degradation mechanism for ß-pinene and other monoterpenes more efforts have to be made to quantify degradation products like organic nitrates, hydroperoxides, aldehydes and ketones. Based on this knowledge proceeding investigations determining properties like photolysis rates can be carried out. Potentially the yield of hydroperoxide formation, a sink for HO2 can also have an important influence on the modeled HO2 and OH concentrations.

New: In accordance with the results for ß -pinene presented in this paper we propose an additional HO2 source linked to ß -pinene oxidation products as the reason for the underestimation of OH and HO2 in the model. With additional sensitivity studies it was possible to rule out photolytical processes or rearrangement reactions of RO2 as sole HO2 sources. Also a possible overestimation of the yield of organic hydroperoxides as well an underestimation of the known RO2 interference on the HO2 measurements were excluded as explanations for underestimating HO2 in the model. The gap between measured and modeled HO2* concentration can significantly be reduced modifying the mechanism of Vereecken and Peeters such that the radical intermediate ROO6R2O rearranges rather than being cleaved. The resulting acyl radical produces HO2, CO and a dicarbonyl compound which itself is a photolytical source of HO2 and CO. Still, the exact HO2 formation mechanism remains uncertain. Additional experiments and quantum chemical calculations have to be made to completely unravel the pathway of HO2 formation.

Comment

Technical Comments

L35: delete “to OH”

L180: delete “are”

L221: “interfering”

L436: “formation now depends”

L674: “comprehensively”

Response:

The typos are corrected.

Comment

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).

Response:

The name has been changed.

Comment

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

Response:

The y scaling has been changed.

Comment

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

Response:

The typos are corrected. A base simulation is included in Figure 5. Base simulation charts have been inserted.

Comment

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.

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