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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.

Martin Kaminski et al.

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

Anonymous Referee #2

Received and published: 23 December 2016

This paper describes experiments conducted in the SAPHIR chamber in Julich designed to study the photooxidation of beta-pinene. The chamber is well equipped with instrumentation to measure both free radicals (OH, HO2 and RO2) and stable molecules. Consequently, the study focuses mostly on the radical budget, and investi-

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gates whether the OH and HO2 rates of production and loss can be determined.

Experimentally, the measured rates of production and loss of OH are found to balance, in contrast to previous studies of isoprene and methacrolein chamber oxidation. However, a model analysis found lower rates of production and destruction, and overall lower radical concentrations. Use of a more detailed model, and measured HO2 concentrations, partially reduced the discrepancy, and sensitivity analyses showed that the measured data could be better represented by introducing an unidentified source of HO2. Overall, this is a good paper. The experiments and modeling are well described, and attention is paid to uncertainties in the system.

Comment

I was a little surprised that only one experiment of the three was analysed in any detail. In fact, no data were shown from two of the experiments (just briefly in the Table). I think this is a serious omission, as these were “normal” experiments, with no added O3, and no extra additions of beta-pinene. Would it be possible to include some of these experiments to contrast the results? A wider variation of the NO concentration would be useful. Also, it is unfortunate that no product information is given other than for acetone and nopinone, despite the fact that a PTRMS was used for analysis.

Response:

In total we performed three b-pinene experiments in 2012 at NOx concentration lower than 1 ppb. Unfortunately, SAPHIR experiments with the complete set of instruments are quite elaborate, therefore we preferred to repeat experiments at low NO concentrations rather than conduct experiments at elevated NO level. The results of the experiments were similar. In all three experiments, the OH budget was closed, i.e. measured OH production rate was balanced with the measured OH destruction rate. The measured OH and HO2 concentration were higher than predicted from the MCM 3.2. The production of nopinone was underestimated by the MCM3.2 model. The experiment we presented is the only one where there is both OH DOAS and OH LIF data. The

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only products we could observe by GC/MS were indeed acetone and nopinone. We were also not able to quantify additional degradation products in PTR-TOFMS measurements, because the concentrations of multiple oxygenated compounds were lower than the detection limit of the PTR-TOFMS and we were lacking the authentic samples for quantification.

Comment

Other Comments Line 48. I think it would be better to say that results showed "an incomplete knowledge" rather than "a lack of knowledge". Line 104 (and elsewhere). Insert "such" before "as" i.e. "species such as: : :"

Response: This has been changed

Changed text:

The results showed an incomplete knowledge about photochemical oxidation processes under low NO conditions and high BVOC concentrations in these regions (Rohrer et al., 2014)

Comment

Line 115 Change "effects" to "affects"

Response: This has been changed

Comment

Line 167. MCM is a zero-D, or box model (1-D usually refers to a column model with vertical transport).

Response: This has been changed

Comment

Line 180. Delete "are".

Response: This has been changed

Comment

Line 221. Inferring should be Interfering?

Response: This has been changed

Comment

Line 246. Delete one of the double parentheses.

Response: This has been changed

Comment

Line 253. Change “Caused by” to “As a result of: : :”

Response: This has been changed

Comment

Line 295. Again, insert “such” before “as”.

Response: This has been changed

Comment

Line 312. Change “then” to “than”.

Response: This has been changed

Comment

Line 346. Clumsy sentence beginning “Caused by: : :”.

Response: This has been changed

Changed Sentence

Old: Caused by the photochemical reactions of the detected OVOCs plus the unknown

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species contributing to the background reactivity RO2 and HO2 radicals are produced in SAPHIR, visible in a rise of the RO2* and HO2* concentration.

New: RO2 and HO2 radicals are produced in SAPHIR by photochemical reactions of detected and undetected species visible in a rise of the RO2* and HO2* concentration.

Comment

Line 425. “under low NOx conditions”. I realize this is somewhat a matter of semantics, and under much discussion at present, but be careful how you classify the NOx environment. With 100 ppt of NO (measured) and up to 20 ppt of HO2, >50% of the RO2radicals will still react with NO. So it is not strictly a low-NOx environment.

Response:

Unfortunately, HONO is produced in the illuminated SAPHIR chamber. We reduced the NO mixing ratio by adding ozone to the chamber but we could not reduce the NO concentration to values lower than 100 ppt.

Comment

Line 425 or so. I know Vereecken and Peeters ruled this out on the basis of barrier heights, but could a chemically activated BPINAO radical decompose by ring opening, rather than formation of nopinone and CH2OH? It might help to explain the acetone/nopinone dilemma .

Response

The decomposition of activated BPINAO followed by ring opening has been proposed by Vereecken and Peeters and is discussed in section 3.4.1. The Vereecken and Peeters model, like the MCM, incorporates the opening of the 4-membered ring, but solves the acetone/nopinone dilemma using ring closure reactions in either the alkylperoxy or the alkoxy radical stage. This is supported by theoretical data, and modelling studies (such as the current work) on b-pinene oxidation. Barring new evidence, we feel the dilemma is resolved.

Comment

Line 427. Remove double parenthesis.

Response: This has been changed

Comment

Lines 436-438, and 447-450. I think a few more words of clarification might be useful here for people not familiar with the mechanism. As I understand it, the original (as in MCM) fate of BPINCO2 was to react with NO to make acetone predominantly. In the Vereecken and Peeters mechanism, this radical can isomerise under low NOx (to make a bicyclic peroxy radical, which then reacts with NO to make acetone, via a chemically activated alkoxy radical. However, this alkoxy radical can also isomerise (from the aldehyde group) to give different products. A few words describing this train of thought would be helpful. Particularly, be more specific about the radicals involved and how they are reacting.

Response

We realize that the description of b -pinene is rather short. We have expanded this section to make it clearer. On the other hand, the mechanism proposed by Vereecken et al. is much too complex to be presented in this paper in detail. The main difference between the MCM and the VP2012 mechanism is the ring closure reaction in the early stage of b-pinene oxidation which balances nopinone and acetone formation, whereas the MCM lacks these channels then thus forms either too much nopinone, or too much acetone. The resulting radical ROO6R2O in figure 1 is indeed highly activated. ROO6R2O can either release acetone or isomerize to an acyl radical which can release HO2 and dicarbonyl compound which can be photolyzed to produce another HO2 molecule. If ROO6R2O would completely react via ROO6R8 half of the missing HO2 source could be explained. A discussion on this reaction channel has been included in the section 3.4.4.

Changed Text

Old:

An alternative model (Figure 5) was published by Vereecken and Peeters (2012), including efforts to bring nopinone and acetone model yields in agreement with experimental data. Based on quantum chemical and theoretical kinetic calculations Vereecken and Peeters proposed a 430 fast ring opening reaction for the intermediate formed by the addition of OH to the double bond of b-pinene.

New:

In the MCM 3.2 mechanism the OH radicals initially add onto the double bonds of ß-pinene (Reactions a, b and c in Fig. 1). About 85 % of the molecules are transformed into the tertiary radicals BPINAO1. These radicals add oxygen and form peroxy radicals BPINAO2 (MCM speci?c designation), which react to nopinone. Acetone is a product of a minor pathway in which the the four-membered ring of ß-pinene is broken and BPINCO2 is formed (Reaction b in Fig. 1). An alternative model was published by Vereecken and Peeters (2012). Still, the addition of OH to the external carbon of the double bond forming BPINO1* is the main reaction. But in contrast to MCM3.2 Vereecken and Peeters proposed a fast ring opening of BPINAO1* based on quantum chemical and theoretical kinetic calculations.

Old:

It should be noted that the model by Vereecken and Peeters explicitly marks acetone formation in the current reaction conditions as a valuable metric to calibrate the acetone yield coming from a specific chemically-activated competition between different reaction channels available to alkoxy radical intermediate ROO6R2O.

New:

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It should be noted that the acetone formation in the model by Vereecken and Peeters depends on fate of the radical ROO6R2O. This radical can either release acetone or undergo a hydrogen shift to yield radical ROO6R8. Unfortunately,Vereecken and Peeters could not predict the branching of these reactions accurately and were only estimating that acetone cleavage is the dominant reaction. Still, Vereecken and Peeters explicitly mark acetone formation in the current reaction conditions as a valuable metric to verify this branching ratio.

Comment

So why should the acetone yield increase at low NOx (line 437), if the MCM predicts only acetone as a product?

Response

The dependence of the acetone yield in the Vereecken and Peeters mechanism depends more from the NOx level then the acetone yield in the MCM 3.2 model does. In the Vereecken and Peeters mechanism acetone is from produced from via BPINCO2 two pathways. At low NO concentrations the reaction via ROO6R2O producing acetone is the dominating pathway.

Comment

Again, a more detailed analysis of some experiments with varying NO concentrations would have been very useful to diagnose this.

Lines 596-600. As the authors agree, such a large source of HO2 from photolysis of a carbonyl is implausible. But is it? Presumably photolysis leads to the production of 2 radicals. So increasing the photolysis rate by a factor of 3 would work, rather than producing 6 radicals. Is it possible that it is a dicarbonyl similar to glyoxal, which have very fast photolysis rates?

Response

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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 process is now discussed in section 3.4.4.

Comment

Line 686. 1-dimensional should be zero-dimensional.

Response: This has been changed

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