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 HO_2, 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 HO_2 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 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 HO_2 concentration in the model is constraint with measured HO_2 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) HO_2* in Fig. 1 climbs steadily throughout the experiment and reaches a maximum around 1300 UTC; indeed, the trend before and after β-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 HO_2* 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 HO_2*, could the "photolytic source" from molecule "Z" match HO_2* if it were set to a constant value instead of being tied to β -pinene oxidation? Perhaps some long-lived contaminant is injected along with β -Pinene.

Response

The interference of the HO_2 data for RO_2 radicals has been determined prior to the monoterpene degradation campaign in lab experiments. A sensitivity study (Appendix A) showed that even a doubling the interference would not be enough to explain the measured HO_2 values. We agree that the measured HO_2* values do not change significantly before and after the VOC injections. A similar time series of HO_2* was observed in all β -pinene experiments, but not in limonene and α-pinene experiments which were conducted in the same time period. Therefore this HO_2 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 HO_2, but this would be expected from the model, if a photolytic source of HO_2 is assumed: In standard experiments HO_2* agrees within 15% with the modelled values.

Also we did not observed indications for impurities being injected together with the β-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 HO 2 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 β-pinene experiments.

Comment

L296: More generally, one could just say that the product yield depends on the fate of RO_2.

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, H_2O, O_3 , VOC, HO_2 and NO concentration.

New: In principle product yields of nonlinear degradation processes depend on the fate of RO_2 which is governed by multiple physical and chemical boundary conditions such as pressure, temperature, H_2O, O_3 , VOC, HO_2 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 HO_2* agree well?

Response

In standard experiments HO_2* 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 HO_2.

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 HO_2 source as the reason for the discrepancy between the measured and modeled HO_2 concentration.

New: Kim et al. postulated a missing photolytic HO_2 source as the reason for the discrepancy between the measured and modeled HO_2 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 HO_2 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 HO_2 source. Two molecules of HO_2 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 HO_2 molecules, the measured HO_2^* 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 HO_2 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 β-pinene presented in this paper we propose a missing photolytic HO_2 source as the reason for the underestimation of OH in the model. An additional sensitivity study trying to identify the nature of the HO_2 source for the β-pinene experiment showed that a formaldehyde like photolytic HO_2 source is not a reasonable option to explain the measured HO_2 and OH levels. Due to the absence of a sufficient amount of photodegradable first generation products at the beginning of the β-pinene oxidation a photolytic source is not able to produce enough HO_2 to explain the measured concentration. A second sensitivity study demonstrated that the addition of RO_2 rearrangement reactions releasing HO_2 to the model is not a reasonable option either. In case of the RO_2 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 HO_2 concentration because the reduction of the HO_2 loss is too small. Further studies demonstrated that an underestimation of the known RO_2 interference on the measurements of HO_2 can be excluded as the reason for the observed high HO_2 concentrations. None of the previously discussed changes in the mechanism as well as the RO_2 interference is able to solely explain the deviations between model and measurements.

In conclusion, it can be said that the study of the β-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 HO_2 source still remains uncertain. To further elucidate the degradation mechanism for β-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 HO_2 can also have an important influence on the modeled HO_2 and OH concentrations.

New:

In accordance with the results for β -pinene presented in this paper we propose an additional HO2 source linked to β -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.

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, HO_2 and RO_2) and stable molecules. Consequently, the study focuses mostly on the radical budget, and investigates whether the OH and HO_2 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 HO_2 concentrations, partially reduced the discrepancy, and sensitivity analyses showed that the measured data could be better represented by introducing an unidentified source of HO_2.

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 B-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 HO_2 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 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 species contributing to the background reactivity RO_2 and HO_2 radicals are produced in SAPHIR, visible in a rise of the RO_2* and HO_2* concentration.

New: RO_2 and HO_2 radicals are produced in SAPHIR by photochemical reactions of detected and undetected species visible in a rise of the RO_2* and HO_2* 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 HO_2, >50% of the RO_2radicals 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 β -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 β -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 HO_2 and dicarbonyl compound which can be photolyzed to produce another HO_2 molecule. If ROO6R2O would completely react via ROO6R8 half of the missing HO_2 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 -pinene.

New: l. In the MCM 3.2 mechanism the OH radicals initially add onto the double bonds of β-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 specific designation), which react to nopinone. Acetone is a product of a minor pathway in which the the four-membered ring of β-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: 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 HO_2 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

We performed an additional simulation to explain the missing HO_2 source. Two molecules of HO_2 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 HO_2 molecules, the measured HO_2^* 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

Investigation of the *β*-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR

List of relevant changes

M. Kaminski[1,*], H. Fuchs[1], I.-H. Acir[1,**], B. Bohn[1], T. Brauers[1,†], H.-P. Dorn[1], R. Häseler[1], A. Hofzumahaus[1], X. Li[1,***], A. Lutz[2], S. Nehr[1,****], F. Rohrer[1], R. Tillmann[1], L. Vereecken[1], R. Wegener[1], and A. Wahner[1]

Page1 line 20: A passage was added onto the abstract

Page 2 line 20- Page 3 line 30 A passage was added to the introduction to explain artificial OH production in LIF instruments

Page 4 line 20: Instrumentation 2.2.: The passage was changed to clarify radical detection in LIF systems

Page 12 line 14: Chapter 3.3. Experimental OH Budget analysis: The chapter was rephrased.

Page 13 line 28: The chapter 3.4.1 was rephrased to describe β-pinene oxidation in detail.

Page 17 line 29: The chapter 3.5.2 ‘Model sensitivity studies’ was shortened. The detailed sensitivity studies were moved to the supporting material.

Page 21 line 1: Chapter 3.5.3 was added to include new model studies which explain the HO_2 source.

Page 22 line 25: Within the conclusions the part with the sensitivity studies was shortened, a passage on the new model studies was added.

Page 23: The sensitivity study in the appendix was moved to the supporting material.

Figure 1: The reaction scheme is expanded.

Figure 4: Added to explain the additional HO_2 source

Figure 5: New model runs added.

Supporting material is added.

Investigation of the β-pinene photooxidation by OH in the atmosphere simulation chamber SAPHIR

M. Kaminski[1,*], H. Fuchs[1], I.-H. Acir[1,**], B. Bohn[1], T. Brauers[1,†], H.-P. Dorn[1], R. Häseler[1], A. Hofzumahaus[1], X. Li[1,***], A. Lutz[2], S. Nehr[1,****], F. Rohrer[1], R. Tillmann[1], L. Vereecken[1], R. Wegener[1], and A. Wahner[1]

[1]Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany
[2]Department of Chemistry and Molecular Biology, University of Gothenburg, Gothenburg, Sweden
[*]now at: Bundesamt für Verbraucherschutz, Abteilung 5 - Methodenstandardisierung, Referenzlaboratorien und Antibiotikaresistenz, Berlin, Germany
[**]now at: Institute of Nutrition and Food Sciences, Food Chemistry, University of Bonn, Bonn, Germany
[***]now at: State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing, China
[****]now at: Verein Deutscher Ingenieure e.V., Kommission Reinhaltung der Luft, Düsseldorf, Germany
[†]Deceased

Correspondence to: Robert Wegener (r.wegener@fz-juelich.de)

Abstract.

Beside isoprene, monoterpenes are the non-methane volatile organic compounds (VOC) with the highest global emission rates. Due to their high reactivity towards OH, monoterpenes can dominate the radical chemistry of the atmosphere in forested areas. In the present study the photochemical degradation mechanism of β-pinene was investigated in the ~~Jülich~~ Jülich atmosphere simulation chamber SAPHIR. ~~The~~ One focus of this study is on the OH budget in the degradation process. Therefore the SAPHIR chamber was equipped with instrumentation to measure radicals (OH, HO_2, RO_2), the total OH reactivity, important OH precursors (O_3, HONO, HCHO), the parent VOC β-pinene, its main oxidation products, acetone and nopinone, and photolysis frequencies. All experiments were carried out under low NO conditions ($\leq$ ~~2~~300 ppt) and at atmospheric β-pinene concentrations ($\leq$ 5 ppb) with and without addition of ozone. For the investigation of the OH budget, the OH production and destruction rates were calculated from measured quantities. Within the limits of accuracy of the instruments, the OH budget was balanced in all β-pinene oxidation experiments. However, even though the OH budget was closed, simulation results from the Master Chemical Mechanism 3.2 showed that the OH production and destruction rates were underestimated by the model. The measured OH and HO_2 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~~ the model predicted a nopinone mixing ratio which was three times higher than measured. A new, theory-derived first-generation product distribution by ~~Vereecken and Peeters~~ Vereecken and Peeters (2012) was able to reproduce the measured nopinone time series and the total OH reactivity. Nevertheless the measured OH and HO_2 concentrations remained underestimated by the numerical simulations. These observations together with the fact that the measured OH budget was closed suggest the existence of unaccounted sources of HO_2. Although the mechanism of additional HO_2 formation could not be resolved, our model studies suggest that an activated alkoxy radical intermediate proposed in the model of Vereecken and Peeters (2012) generates HO_2 in a new pathway, whose importance has been underestimated so far. The proposed reaction path involves unimolecular rearrangement and decomposition reactions and photolysis of dicarbonyl products, yielding additional HO_2 and CO. Further experiments and quantum chemical calculations have to be made to completely unravel the pathway of HO_2 formation.

1 Introduction

Thousands of different volatile organic compounds (VOCs) are emitted into the atmosphere (Goldstein and Galbally, 2007). The emissions of biogenic volatile organic compounds BVOCs exceed those of anthropogenic VOCs by a factor of ten (Piccot et al., 1992; Guenther et al., 1995, 2012). On a global scale, isoprene and monoterpenes are the BVOCs with the highest emission rates with the exception of methane. About 44 % of the global BVOC emissions can be attributed to isoprene and about 11 % to monoterpenes (Guenther et al., 1995). Isoprene and monoterpenes are unsaturated hydrocarbons. Hence, their main atmospheric sink is the addition of hydroxyl radicals (OH), nitrate radicals (NO_3) or ozone to the double bond (Calogirou et al., 1999; Atkinson and Arey, 2003). During daytime the reaction of isoprene and monoterpenes with the OH radical is the major sink for these VOC species. The subsequent addition of oxygen produces organic peroxy radicals (RO_2). In the presence of nitrogen oxides (NO_x), RO_2 is indirectly converted to hydroperoxy radicals (HO_2) through reaction with NO. HO_2 reacts further with NO~~in a second reaction step to OH~~, recyling the ~~consumed~~ OH ~~from~~ consumed in the initial reaction step and producing further NO_2. As a side effect, ozone is produced by NO_2 photolysis. The oxidation of VOCs in the presence of NO is the main photochemical source of ozone in the troposphere (Seinfeld and Pandis, 2006). Moreover, the oxidation processes of isoprene and monoterpenes mainly lead to the production of less reactive polar oxygenated volatile organic compounds (OVOCs) which are significantly involved in the formation of secondary organic aerosols ~~(SOA).~~ (Kanakidou et al., 2005; Goldstein and Galbally, 2007).

~~As trees have the largest contribution in~~ During the last decade, the research on the chemical degradation of BVOCs in the atmosphere has made significant progress through laboratory and atmospheric chamber experiments, and theoretical chemistry studies. It was discovered that RO_2 radicals from the reaction of biogenic VOCs with OH can undergo unimolecular reactions which influence the chemistry of HO_x and OVOCs. In case of the degradation of isoprene and methacrolein, RO_2 was found to regenerate efficiently HO_x by isomerization and decomposition reactions (Paulot et al., 2009; da Silva et al., 2010; Peeters and Müller, 201 RO_2 radicals from the oxidation of isoprene and some monoterpenes were found to produce low-volatility OVOCs, which contribute substantially to SOA formation in the atmosphere (Paulot et al., 2009; Ehn et al., 2014; Bates et al., 2014). The discovered chemistry is particularly important in forests, which contribute to the global non-methane BVOC emissions with an estimated share of 75 % ~~(Guenther et al., 1995), our understanding of VOC oxidation processes in forested regions is essential for the understanding of the BVOC oxidation processes on a global scale~~ (Guenther et al., 1995; Wiedinmyer et al., 2004; Guenther et al., 2012). ~~Therefore the BVOC degradation by~~ In forests, the unimolecular RO_2 reactions can effectively compete with the RO_2 + NO reaction, since anthropogenic NO emissions are generally missing.

The above mentioned studies of BVOC oxidation mechanisms were mostly inspired by field observations of unexplained high OH concentrations in isoprene-dominated forests, which have pointed to unknown NO-independent OH ~~radicals in forested regions has been investigated in numerous field campaigns (Lelieveld et al., 2008; Hofzumahaus et al., 2009; Kubistin et al., 2010; the last decades. The results showed a lack of knowledge about photochemical oxidation processes under low conditions and high BVOC concentrations in these regions (Rohrer et al., 2014). State of the art atmospheric chemistry models were largely underestimating the measured~~ recycling processes (Tan et al., 2001; Carslaw et al., 2001; Ren et al., 2008; Lelieveld et al., 2008; Hofzuma The newly discovered mechanisms for isoprene and methacrolein, however, can explain only part of the observed high OH concentrations. ~~These observations could be partially explained by the identification of new NO independent~~ Another possible reason could be OH ~~recycling pathways in the oxidation of isoprene through lab experiments and chamber studies in the following years (Paulot et al., 2009; ?; Peeters and Müller, 2010; Crounse et al., 2011, 2012; Wolfe et al., 2012; Crounse et al., 2013; Liu Since the field campaigns were mainly conducted in tropical forests, where VOC emissions are dominated by isoprene, most mechanistic investigations focused on isoprene. Regardless of the integration of new NO independent recycling pathways in the isoprene degradation mechanism , models could not completely explain the measured~~ interferences in the low-pressure laser-induced fluorescence (LIF) instruments that were applied in the above field studies. Artificial OH ~~concentrations~~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; 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.

Due to their ~~high~~ abundance and their structural similarity to isoprene, ~~monoterpenes~~ unknown monoterpene chemistry may contribute to ~~an underestimation of the~~ the underestimation of OH ~~concentration in the models~~ concentrations in forests as proposed by ~~? for open chain~~ da Silva et al. (2010) for open-chain monoterpenes like myrcene and ocimene. ~~Moreover, during~~ During a field campaign in Borneo, Whalley et al. (2011) observed that discrepancies between measured and modeled OH ~~also~~ occurred in the morning hours when VOC emissions were dominated by monoterpenes. ~~Recent studies in Finland (Hens et al., 2014) and~~ Moreover, field studies in Greece (Carslaw et al., 2001), in the U.S. (Kim et al., 2013) and in Finland (Hens et al., 2014) indicate that the radical chemistry in forested areas~~that~~, which are dominated by monoterpene and 2-methyl-3-buten-2-ol (MBO) emissions, is not well understood.

In this work we investigated the atmospheric degradation of monoterpenes in the ~~SAPHIR~~ atmosphere simulation chamber ~~in Jülich~~SAPHIR in Jülich. β-Pinene comprises 17 % of the estimated global monoterpene emission rate (Sindelarova et al., 2014) and was therefore chosen as a representative species for our investigations. To our knowledge it is the first chamber study investigating the β-pinene, or any monoterpene degradation in general, under natural concentration conditions (VOC less than 5 ppb). In comparison to other chamber studies which focused on the determination of products and SOA yields (Lee et al., 2006; Saathoff et al., 2009; Eddingsaas et al., 2012a, b; Zhao et al., 2015) our main goal was to investigate the radical budget of the monoterpene degradation. For that purpose all critical radical species (OH, HO_2, RO_2) were ~~quantified.~~ measured. In order to exclude possible measurement artefacts for OH, differential optical absorption spectroscopy (DOAS) was applied for OH measurements in addition to LIF.

2 Methods

2.1 SAPHIR atmosphere simulation chamber

The atmosphere simulation chamber SAPHIR (Simulation of Atmospheric PHotochemistry In a large Reaction Chamber) located in the Forschungszentrum ~~Jülich~~ Jülich (Germany) is a tool to investigate complex atmospheric mechanisms under nearly natural conditions. The chamber has a cylindric shape (18 m length, 5 m diameter, 270 m^3 volume) and consists of a double walled FEP Teflon foil attached to a steel frame. The Teflon foil guarantees a maximum of inertness of the chamber surface and leads to a minimization of wall effects. In SAPHIR natural sunlight is used as light source for photochemical reactions. About 85 % of the UV-A, UV-B and visible light is transmitted by the FEP foil. A shutter system allows to switch between illuminated and dark chamber conditions within 60s. To investigate photochemical degradation processes in the ppb and sub-ppb range SAPHIR is operated with ultra pure synthetic air (Linde, N_2 99.9999 %, O_2 99.9999 %). A slight overpressure of about 30 Pa in the inner chamber prevents diffusion of outside air into SAPHIR. Due to small leakages and consumption of air by instruments a replenishment flow has to be introduced into the chamber to keep up the pressure difference to the outside. During experimental operation this flow is in a range of 9-12 $m^3 h^{-1}$, leading to a dilution of trace gases at a rate of approximately 3-4 % h^{-1}. An installed ventilator guarantees well mixed conditions during the experiments. For more detailed information about the chamber and its properties the reader is referred to previous publications (Poppe et al., 2007; Schlosser et al., 2007, 2009; Wegener et al., 2007; Dorn et al., 2013).

2.2 Instrumentation

~~To investigate the radical budget during the β-pinene photooxidation, SAPHIR was equipped with a comprehensive set of analytical instruments.~~ OH, HO_2 and RO_2 concentrations were measured simultaneously by a laser-induced fluorescence (LIF) system, using three independent ~~measurement cells.~~ low-pressure detection cells. Each cell samples ambient air by gas expansion through an inlet nozzle, producing a fast gas flow through the cell. OH is detected by pulsed laser-excited resonance fluorescence at 308 nm (Holland et al., 1995). RO_2 and HO_2 are ~~both detected by~~ detected indirectly by chemical conversion with NO to OH~~and differentiated~~, followed by LIF detection of the formed OH (Fuchs et al., 2008, 2011). The peroxy radicals are distinguished from each other by their different conversion ~~efficiency with~~ efficiencies, which depend on the amount of added NO ~~. Because of the short residence time in the cell~~ and the reaction time between NO addition and OH detection~~,~~. In the low-pressure HO_x cell, the addition of NO leads to fast formation of OH in just one reaction step. In contrast, conversion of RO_2 to OH requires at least three reaction steps:

$$\mathrm{RO_2}\underline{species(e.g.acylperoxyradicals),whichrequireconversiontoalkoxyradicalswithsubsequentslowtransformationwith}+\mathrm{NO}$$

(R1)

$$\mathrm{RO} + \mathrm{O_2}\, to \rightarrow \mathrm{HO_2}\, radicalsbefore + \text{carbonyl compound} \quad \text{(R2)}$$

$$\mathrm{HO_2} + \mathrm{NO} \rightarrow \mathrm{OH}\, is formed, are assumed to be converted with very low + \mathrm{NO_2} \quad \text{(R3)}$$

For simple alkyl peroxy radicals, this reaction sequence is relatively slow (especially at reduced O_2 partial pressure) compared to the residence time in the HO_2 detection cell and results in a very low detection efficiency. However, β-hydroxy RO_2 species ~~as β-hydoxy alkyl peroxy radicals~~ produced by the reaction of alkenes with OH are converted by NO to highly reactive β~~-hydroxyalkoxy~~ -hydroxy alkoxy radicals. Instead of reacting with O_2 directly, β~~-hydroxyalkoxy~~ -hydroxy alkoxy radicals nearly exclusively decompose and then react rapidly with O_2 forming thereby HO_2 much faster than other ~~alkyl~~ alkoxy radicals. The fact that for β-hydroxy alkyl peroxy radicals the overall conversion to OH is ~~thereby much faster than for other alkyl peroxy radicals~~ very fast leads to an interference ~~of this subclass~~ in the HO_2 channel of the LIF instrument (Fuchs et al., 2011). The interference was carefully characterized for RO_2 species formed by the ~~initial~~ reaction of β-pinene with OH ~~by adding β-pinene to the gas of the / calibration cell. produced by water vapour photolysis reacts with β-pinene and produces first-generation radicals~~in laboratory experiments following the procedure described by Fuchs et al. (2011). About 25 % of these RO_2 species are detected as an additional signal in the HO_2 channel of the instrument. In the third measurement cell, the sum of atmospheric RO_2 and HO_2 is measured. In this case, RO_2 radicals are converted by NO in a pre-reactor to HO_2, which is then further converted together with atmospheric HO_2 to OH in the detection cell (Fuchs et al., 2008). Since the RO_2 concentration is calculated ~~from the~~ as the difference between the concentration of RO_x (RO_2 + HO_2) and measured HO_2~~concentration, the interfence also effects~~ , the interference in the HO_2 measurement also affects indirectly the RO_2 data.

On 27th of August 2012 OH was measured additionally by a differential optical absorption spectrometer (DOAS). In general both instruments showed a good agreement over the past 10 years (Schlosser et al., 2007, 2009; Fuchs et al., 2012). Also for the terpenoid campaign in 2012 on average no significant difference between LIF and DOAS instrument was observed. As the DOAS instrument is the only absolute method for the quantification of OH (Hofzumahaus and Heard, 2016), the DOAS OH data were used for the following evaluation of the OH budget analysis.

The OH reactivity k(OH) was measured by flash photolysis / laser induced fluorescence (FP/LIF) technique (Lou et al., 2010). The evaluation of the pseudo-first-order decays of OH gives a direct measure of the total rate coefficient of the OH loss.

Besides OH, HO_2, RO_2 and k(OH), ~~VOC (proton transfer reaction time of flight mass spectrometry PTR-TOF-MS, gas chromatography coupled with mass spectrometric and flame ionization detector (GC/MS/FID),~~ HCHO (Hantzsch reaction), HONO (long path absorption photometry, LOPAP), CO (reduction gas analysis, RGA), CO_2, CH_4, H_2O (cavity ring-down spectroscopy, CRDS), as well as NO, NO_2 and O_3 (chemiluminescence, CL) were determined by direct measurements. VOC were measured by a PTR-TOF-MS (proton transfer reaction time of flight mass spectrometer) and two gas chromatographs of the same type coupled with mass spectrometric and flame ionization detectors (GC/MS/FID). Moreover experimental boundary conditions including temperature (ultrasonic anemometer), pressure (capacitive gauge), replenishment flow rate (mass flow controller) and photolysis frequencies (spectroradiometer) were continuously recorded.

Table **??** provides an overview of the key instruments for this study and their specifications. For more detailed information on the analytical instrumentation of SAPHIR the reader is referred to previous publications ~~((Bohn and Zilken, 2005; Rohrer et al., 2005; Wege~~ and references therein.

2.3 Experimental procedure

Before every experiment day the chamber was flushed with dry ultra-pure synthetic air over night to purge contaminants of previous experiments under their detection limit. At the beginning of the experiment $20\,\mathrm{ppm}$ of $\mathrm{CO_2}$ were injected into SAPHIR as dilution tracer. After that the relative humidity was increased to $75\,\%$ by adding water vapour, generated by the vaporisation of ultra-pure water (Milli-Q), to the purge flow. As HONO photolysis is the main source of OH in the SAPHIR chamber it is impossible to conduct experiments in the complete absence of NO. To lower the NO level in the experiment on 27th August $50\,\mathrm{ppb}$ of ozone, produced from a silent discharge ozonizer (O3Onia), was injected after humidification. Shortly afterward the shutter system of SAPHIR was opened, exposing the chamber to sunlight.

In the following two hours of the experiments (so-called "zero air phase") no other trace gases were introduced into SAPHIR. During the zero air period HONO was formed from the chamber walls (Rohrer et al., 2005) depending on relative humidity and UV radiation. In addition to the OH production the photolysis of HONO leads to an increase in NO and $\mathrm{NO_2}$ concentration. In addition acetaldehyde, formaldehyde and acetone were formed in the chamber with a rate of $90-250\,\mathrm{ppt/h}$. The zero air phase ended with the injection of β-pinene while the SAPHIR chamber was exposed to light.. The injection was performed by introducing a high concentration gas mixture of β-pinene (about $50\,\mathrm{ppm}$) from a silcosteel canister (Restek) through a mass flow controller to the experimental flow. The β-pinene concentration of the mixture was previously determined by oxidizing a part of the β-pinene mixture on a platinum catalyst and quantifying the produced $\mathrm{CO_2}$. This absolute method makes it possible to calculate the VOC starting concentration of the experiment very accurately. During the following $6\,\mathrm{h}$ of the experiment, the so-called "VOC phase", β-pinene was degraded by OH in the illuminated chamber. In the experiment of 27th August β-pinene was injected for a second and third time into SAPHIR approximately two and four hours after the first VOC injection, respectively. Every experiment ended with closing the louver system of the chamber in the late evening of the experiment day. For all the chamber experiments the fan was running during the whole time ensuring homogeneous mixing of the chamber air.

Table **??** sums up the experimental conditions of the three β-pinene oxidation experiments.

2.4 Model calculations

The acquired time series of trace gases and radicals were compared to zero-dimensional box model simulations with the Master Chemical Mechanism (MCM). The MCM is a ~~state of the art 1-dimensional near explicit atmospheric box model~~ state-of-the-art chemical mechanism developed by Jenkin et al. (1997) and Saunders et al. (2003). For this publication the MCM version 3.2 was used (available at http://mcm.leeds.ac.uk/MCMv3.2/). For the application on modeling chamber experiments the model was extended by some chamber specific processes. As an alternative to the β-pinene chemistry in the MCM, we also applied the ~~kinetic model~~ reaction mechanism by Vereecken and Peeters (2012), which ~~replaces the β-pinene chemistry in the MCM~~ is based on theoretical-kinetic analyses of the reaction mechanism. The ~~current published mechanism~~ mechanism by Vereecken and Peeters (2012) only describes the first-generation product formation, i.e. the subsequent chemistry of the products formed in the first radical chain is not included in the model. ~~This could affect the predictions, in so far as these primary stable products contribute significantly to the reaction chemistry. The accumulated product yield of these~~ The accumulated yield of primary products in our model runs remains below 20 % compared to the sum of the residual concentration of β-pinene, and the concentrations of reactive primary products whose chemistry is fully described (~~nopinene, acetone, ...~~ e.g. nopinone and acetone). As such, it appears that omitting the secondary chemistry of these products does not have an overly large impact on the reaction fluxes, and ~~are~~ is therefore unlikely to be the main reason for any discrepancies relative to the measurements.

As mentioned in section 2.1 the required replenishment flow into SAPHIR leads to an additional dilution process for every model species. The applied dilution rate is thereby calculated from the measured CO_2 loss in the chamber. Previous characterization experiments showed that ozone had a shorter lifetime than CO_2 in the chamber (dilution corrected ozone lifetime approximately 30 h). This observation was included as additional loss term in the model. The chamber sources of HONO, HCHO and acetone are well known from routine reference experiments in SAPHIR and can be parametrized by empirical equations, depending on temperature, relative humidity and solar radiation in the chamber (Rohrer et al., 2005; Karl et al., 2006; Kaminski, 2014). The source strengths were adjusted to match the time series of NO_x, HCHO and acetone during the zero air phases of the experiments. The parametrization of the acetaldehyde source was less satisfactory and so the model was constrained by the measured acetaldehyde concentration.

In all experiments the summed contributions of known chamber sources to the OH reactivity measured in the zero air phase ($0.1 - 0.7\,\mathrm{s^{-1}}$) were not sufficient to explain the measured OH reactivity ($0.7 - 1.5\,\mathrm{s^{-1}}$). Analogous to the procedure applied by Fuchs et al. (2012, 2014) the unexplained part of the measured OH reactivity was modeled as a co-reactant Y, with constant OH reactivity in the model, where the concentration ~~time rate coefficient kOH~~ times rate coefficient [Y] $\cdot k_{\mathrm{OH+Y}}$ was set to reproduce the measured OH reactivity in the chamber after humidification. Analogous to CO the reaction of Y with OH is assumed to form one molecule of HO_2.

The parameters temperature, pressure, water vapor concentration, the calculated dilution rate and the photolysis frequencies for HONO, HCHO, O_3 and NO_2 were set as fixed boundary conditions in the model. Photolysis frequencies that were not measured were calculated for clear sky conditions by the function included in MCM 3.1 and then corrected for cloud cover and the transmission of the Teflon film by multiplying the clear sky value with the ratio of measured to modeled photolysis frequency of NO_2. Constrained parameters were re-initialized on a 1 min time grid. The injections of β-pinene and ozone in the chamber were modeled as sources which were only present during the time period of injection. The source strengths were adapted to match the measured ozone concentration and the OH reactivity at the point of injection. The subsequent time series of the concentrations were determined by the kinetic models described above.

Because of described instrumental interferences it is not possible to directly compare the modeled HO_2 concentration [HO_2] and the sum of the concentrations of the different RO_2 species [RO_2] against the measured time series of the LIF instrument, [HO_2^*] and [RO_2^*], for HO_2 and RO_2, respectively.

$$[\mathrm{HO}_2^*] = [\mathrm{HO}_2] + \sum \left(\alpha^i_{\mathrm{RO}_2} \cdot [\mathrm{RO}_2]_i\right) \tag{1}$$

$$[\mathrm{RO}_2^*] = [\mathrm{RO}_2] - \sum \left(\alpha^i_{\mathrm{RO}_2} \cdot [\mathrm{RO}_2]_i\right) \tag{2}$$

$\alpha^{\mathrm{i}}_{\mathrm{RO}_2}$: relative detection sensitivity for RO_2 species i (compared to HO_2 with $\alpha = 1$)

$\sum [\mathrm{RO}_2]_i$: interfering RO_2 radicals of β-pinene

$\sum \left(\alpha^{\mathrm{i}}_{\mathrm{RO}_2} \cdot [\mathrm{RO}_2]_{\mathrm{i}}\right)$: RO_2 interference

For a direct comparison of the measured ~~uncorrected signal~~ $[\mathrm{HO}_2^*]$ against the model, the modeled HO_2 plus an estimated RO_2 interference is combined to yield the model parameter HO_2^* (Lu et al., 2012). Depending on the experimental phase, up to 25 % of the modeled HO_2^* can be attributed to the interfering RO_2 species $[\mathrm{RO}_{2\mathrm{i}}]$. Moreover, note that the MCM and the modifications by Vereecken and Peeters yield different RO_2 species, which results in rather different contributions of RO_2 into the HO_2 signal.

RO_2 radicals are detected in the LIF instrument by a three step conversion of RO_2 to OH. Only species reacting with NO to RO and then decomposing or reacting with O_2 in a second reaction step to HO_2 can be detected with a sufficient sensitivity. Depending on the model used up to 70 % of the modeled RO_2 species of β-pinene are not detectable under these conditions. To account for this, the measured RO_2 signal $[\mathrm{RO}_2^*]$ is compared to the model parameter RO_2^*, which corresponds to the sum of the theoretically detectable RO_2 model species.

The model RO_2^* must be additionally corrected by the subtraction of the RO_2 species which are already included in the model parameter HO_2^*. This is again related to the operating conditions of the LIF instrument where in the RO_x cell the sum of detectable RO_2 plus HO_2 and in the HO_x cell HO_2 plus interfering RO_2 radicals are measured. As the RO_2 concentration is determined by subtracting the signal of the HO_x cell from the signal of the RO_x cell, an RO_2 interference in the HO_x cell automatically leads to an underestimation of the calculated RO_2 concentration.

3 Results and discussion

3.1 Determination of product yields

The formation yields of first-generation degradation products are important information for the understanding of the oxidation mechanism of β-pinene with OH (~~Figure~~Fig. 1)~~)~~. By correlating the concentration of the products with the concentration of the degraded β-pinene it is possible to determine the product yield. Because of the lack of suitable reference standards and the low concentration of β-pinene it was only possible to determine the yield of acetone and nopinone in the OH oxidation experiment. The concentrations of β-pinene and nopinone were determined by PTR-TOF-MS whereas interpolated GC/FID data of the acetone concentration were used for the yield determination. This was done to exclude any possible interferences on the quantifier ion of acetone in the PTR-TOF-MS.

~~Caused by the addition of ozone~~ As a result of ozone addition in the experiment on 27 Aug 2012 a part of the injected β-pinene was degraded by ozonolysis. The fraction of the ozonolysis in the total conversion of β-pinene was approximately 5 % and can be neglected.

The experiment duration of several hours necessitated the correction of the measured concentration time series to account for reactive losses of acetone and nopinone with OH and chamber effects like dilution (all species) and chamber sources (acetone). This was done using a recursive discrete time equation analogous to Galloway et al. (2011). The correction of the acetone concentration was done by scaling the assumed acetone chamber source to the measured values during the zero air phase of the experiments. The assumed acetone source strength was typically $70\,\mathrm{ppth}^{-1}$ which was as large as 20 to 30 % of the total amount of acetone produced in the β-pinene experiments. Equations 3 - 7 illustrate all applied corrections on the acetone concentration.

$$[\mathrm{CH_3COCH_3}]_{corr(i)} = [\mathrm{CH_3COCH_3}]_{corr(i-1)} + \Delta c_{\mathrm{CH_3COCH_3}} + \Delta c_{\underline{RL}\,\mathrm{RL}} + \Delta c_{\underline{DIL}\,\mathrm{DIL}} + \Delta c_{S_{\mathrm{CH_3COCH_3}}} \tag{3}$$

$$\Delta c_{\underline{RL}\,\mathrm{RL}} = [\mathrm{CH_3COCH_3}]_{(i-1)} \cdot [\mathrm{OH}]_{(i-1)} \cdot \Delta t \cdot k_{\mathrm{CH_3COCH_3+OH}} \tag{4}$$

$$\Delta c_{\underline{DIL}\,\mathrm{DIL}} = [\mathrm{CH_3COCH_3}]_{(i-1)} \cdot \Delta t \cdot k_{\underline{DIL}\,\mathrm{DIL}} \tag{5}$$

$$\Delta \underline{C} c_{S_{\mathrm{CH_3COCH_3}}} = S_{\mathrm{CH_3COCH_3}} \cdot \Delta t \tag{6}$$

$$S_{\mathrm{CH_3COCH_3}} = a_{\mathrm{CH_3COCH_3}} \cdot J_{\mathrm{NO_2}} \cdot (0.21 + 2.6 \cdot 10^{-2} \cdot RH) \cdot e^{(-2876/T)} \tag{7}$$

$[\mathrm{CH_3COCH_3}]_{\mathrm{corr}}$: corrected acetone concentration

~~Δc_{RL}~~Δc_{RL}: reactive loss

~~Δc_{DIL}~~Δc_{DIL}: dilution

~~$\Delta c_{\mathrm{S_{CH_3COCH_3}}}$~~$\Delta c_{\mathrm{S}_{\cancel{\mathrm{CH_3COCH_3}}}}$: chamber source

~~Δt~~Δt: time interval between between time i and (i-1)

~~$\mathrm{S}_{\mathrm{CH_3COCH_3}}$~~$S_{\mathrm{CH_3COCH_3}}$: source strength

~~$\mathrm{a}_{\mathrm{CH_3COCH_3}}$~~$a_{\mathrm{CH_3COCH_3}}$: scaling factor

~~RH~~RH: relative humidity

~~$\mathrm{J}_{\mathrm{NO_2}}$~~$J_{\mathrm{NO_2}}$: photolysis frequency $\mathrm{NO_2}$

The results of the yield determination are ~~summed up~~ listed in Table **??**. In principle product yields of nonlinear degradation processes depend on the fate of $\mathrm{RO_2}$ which is governed by multiple physical and chemical boundary conditions such as pressure, temperature, $\mathrm{H_2O}$, $\mathrm{O_3}$, VOC, $\mathrm{HO_2}$ and NO concentration. The discussed β-pinene experiment was conducted at ambient pressure in a temperature range of $298-304\,\mathrm{K}$. The relative humidity was about 50 % before the first VOC injection and decreased to 30 % over the course of the experiment, due to the warming of the chamber and the dilution of the chamber air by the replacement flow. It is known for many VOC species that the product yields depend on the VOC to NO ratio (Atkinson, 2000). This is why the two β-pinene experiments without and the β-pinene with the addition of $50\,\mathrm{ppb}$ ozone are handled separately. During the experiment on 27th August the nopinone yield as well as the acetone yield increased subsequently with the second and third β-pinene addition and are therefore denoted as range. The specified errors consider the errors of measurement of the correlated VOC concentrations as well as the errors originating from the correction of reactive losses, dilution and chamber sources. To reduce the influence of secondary product formation and to facilitate the comparability of the results ~~the yields were normalized to a conversion of~~ only the data of the experiment when less than 70 % of ~~the injected~~ β-pinene was used for the yield calculation. To our knowledge, these are the first acetone and nopinone yields measured for reaction mixtures with less than $5\,\mathrm{ppb}$ of β-pinene.

Within the calculated error the determined nopinone yield in this work agrees well with every literature value except the published yield of Hatakeyama et al. (1991). ~~He is the only author reporting~~ These authors report nopinone yields a factor of three higher ~~then~~ than every other literature value. Vereecken and Peeters (2012) pointed out that Hatakeyama et al. (1991) measured the nopinone yield by using FTIR absorption at $1740\,\mathrm{cm}^{-1}$, which includes the absorption of other carbonyl compounds. Taking recent literature and our results into account it seems that the nopinone yield of β-pinene oxidation with OH has no strong dependence on the NO level (see Table **??**). The slight increase of the nopinone yield over the three β-pinene injections in the experiment of 27th Aug 2012 can be related to a change of boundary conditions as well as a secondary nopinone source. For example, the MCM 3.2 contains nopinone formation pathways from the degradation of the related hydroperoxides and organic nitrates.

The determined acetone yield is in agreement with the reported literature values of Wisthaler et al. (2001), Librando and Tringali (2005) and Larsen et al. (2001). All reported literature values are smaller than the determined acetone yields in SAPHIR and show a wide range. Similar to nopinone there is no clear evidence of a NO dependence of the acetone yield. Due to the long reaction time the increase of the acetone yield in the experiment of 27 Aug 2012 is most likely related to secondary acetone production. Since the yields in the literature were determined under various boundary conditions (e.g. light source, OH source, relative humidity) it is not possible to determine the reasons for the discrepancy. It could be related to different boundary conditions or measurement errors.

3.2 Comparison of ~~the time series of trace gas concentrations~~ trace-gas measurements with ~~the~~ MCM 3.2 model calculations

In this section the measured ~~time series~~ trace gas concentrations of the β-pinene experiment from 27th August are compared to the base model using the unmodified MCM 3.2 (see ~~Figure~~Fig. **??**). ~~The comparatively low concentration allowed for the first time the intercomparison of modeled radical concentrations with parallel direct measurements of , and .~~ From the moment the roof of the SAPHIR chamber was opened, HONO was formed at the chamber walls. Due to the photolysis of HONO, OH and NO were produced in the chamber, leading to a rise in the OH as well as the NO concentration. The parametrized HONO source sufficiently describes the measured nitrogen oxides in the zero air phase. The rise in the NO and NO_2 concentration is well captured. The modeled OH concentration also agreed well with the measurements.

Beside HONO, also formaldehyde, acetaldehyde and acetone were formed or released from the chamber walls, as can be seen in the case of acetone ~~in slight a~~ as a slight concentration rise. These oxygenated VOC species (OVOCs) contributed to the increase of the measured background OH reactivity of $1.5\,\mathrm{s}^{-1}$ during the zero air phase of the experiment. As the sum of the measured OH reactants was not sufficient to explain the measured OH reactivity ($0.7\,\mathrm{s}^{-1}$ unexplained), the modeled OH reactivity was adjusted by a constant source of a species Y, assumed to react like CO, i.e. with similar rate coefficient and HO_2 formation. Under the assumption of a constant concentration of $120\,\mathrm{ppb}$ Y the measured background reactivity is well reproduced by the model. ~~Caused by the photochemical reactions of the detected plus the unknown species contributing to the background reactivity and radicals are produced in SAPHIR, visible in a rise of the and~~ The concentration of OH is well reproduced by MCM in the zero air phase, while HO_2^* ~~concentration. The model underestimates the measured~~ is slightly overestimated and RO_2^* ~~concentration~~ is underestimated by 25 %~~whereas is overestimated by about a similar order of magnitude. In general the measured time series of radicals are less well captured by the MCM during the zero air phases of the experiments. The two main reasons for this are firstly that the~~ , each. These deviations are probably caused by the chemistry of the unknown species, which contribute about half of the OH reactivity ~~is influenced by unknown species and secondly that radical sources and sinks are not well defined~~before β-pinene is injected.

With the beginning of the VOC phase of experiments, the OH reactivity is dominated by ~~well-known~~ known reactants, and ~~much better model to measurement~~ good model-to-measurement agreement is expected ~~. For well-investigated reactants like~~ for the radical concentrations, if the chemistry of the reactants is well understood. The reactants CO and CH_4, ~~agreements~~ for example, give agreement better than 15 % ~~are typical~~ for experiments in the SAPHIR chamber (Fuchs et al., 2013).

For the current case, the addition of β-pinene led to a sharp increase in the measured OH reactivity. Directly after the β-pinene injection the increase of the modelled OH reactivity, calculated from the canister injection, corresponded well with the measured $k(\mathrm{OH})$ increase. The β-pinene concentration measured by PTR-TOF-MS was about 15 % lower than ~~then~~ the calculated injection, but still agreed with the canister injection within the instrumental uncertainty. Over the course of the VOC phase, and thereby the consumption of β-pinene, the measured OH reactivity was increasingly overestimated by the model. During this time period nopinone has the highest proportion of ~~modelled~~ modeled OH reactivity beside β-pinene. However the measured nopinone concentration was overestimated by a factor of three by MCM 3.2 whereas the acetone ~~concentration was~~ and CO concentration were underestimated by a factor of two. In general the MCM gives a poor description of the first-generation β-pinene degradation products. Simultaneously with the increase of the OH reactivity a sharp decrease of OH radical concentration was observed. At the time of β-pinene injection model and measurement agreed well, but over the course of the experiment OH was increasingly underestimated by the model (30-50 %). The modeled concentration of theoretically measurable RO_2 radicals RO_2^* exceeded the measured concentration by about 40 %. Similar to OH, the modeled HO_2^* concentration initially agreed well with the measurements directly after β-pinene injection but was increasingly underestimated by the MCM in the latter part of the experiment. The measured time series of ozone was well captured by the MCM 3.2, whereas from the moment β-pinene was injected the model slightly overestimated the measured concentrations of HCHO, NO and NO_2~~concentration~~.

3.3 Experimental OH budget analysis

~~A complete model independent analysis of the radical chemistry taking place during the β-pinene oxidation is the analysis of the budget.~~ In the OH budget analysis~~the measured~~, the total OH production rate ~~$\mathrm{P_{OH}}$~~ P_{OH} is compared to the ~~measured~~ OH destruction rate ~~$\mathrm{D_{OH}}$. Thereby $\mathrm{P_{OH}}$ is defined as~~ (D_{OH}). Both rates (P_{OH} and D_{OH}) were calculated from measurements performed during the experiments. P_{OH} is the sum of production rates of all known OH ~~production terms, in this case: the three primary production terms in SAPHIR(and photolysis~~ sources in the β-pinene experiments in SAPHIR: the photolysis of ozone and HONO, VOC ozonolysis, ~~ozonolysis)~~ plus the OH production by the reaction of HO_2 with NO and O_3. Where $j_{\mathrm{O(^1D)}}$ and j_{HONO} are the measured photolysis frequencies of O_3 and HONO, f_{OH} is the fraction of $\mathrm{O(^1D)}$ reacting with water to OH and α defines the OH yield of β-pinene ozonolysis. The OH destruction ~~$\mathrm{D_{OH}}$~~ D_{OH} is given by the product of the measured OH reactivity and the measured OH concentration. As ~~$\mathrm{D_{OH}}$~~ the short-lived OH is in steady-state, D_{OH} should be balanced by ~~$\mathrm{P_{OH}}$ during the whole experiment a discrepancy in the budget gives a strong hint on possible missing~~ the calculated P_{OH}, if all relevant OH ~~production terms~~ source terms are included in P_{OH}.

$$\mathrm{P_{OH}}P_{OH} = j_{\mathrm{O(^1D)}}[\mathrm{O_3}]\cdot 2f_{OH} + j_{\mathrm{HONO}}[\mathrm{HONO}] + \alpha k_1[\mathrm{VOC}][\mathrm{O_3}] + k_2[\mathrm{HO_2}][\mathrm{NO}] + k_3[\mathrm{HO_2}][\mathrm{O_3}] \tag{8}$$

$$\mathrm{D_{OH}}D_{OH} = k(\mathrm{OH})\cdot[\mathrm{OH}] \tag{9}$$

$$\mathrm{P_{OH}} = \mathrm{D_{OH}} \tag{10}$$

Figure **??** displays the measured OH budget of the β-pinene experiment on 27th August 2012. The lower panel of the plot shows the time series of the calculated OH turnover rates. The OH destruction rate ~~$\mathrm{D_{OH}}$~~ D_{OH} is given as black line. The OH production rate ~~$\mathrm{P_{OH}}$~~ P_{OH} is shown by the sum of the colored areas. Because of the higher instrumental accuracy the OH concentration measured by the DOAS instrument was used to calculate ~~D_{OH}. For P_{OH}~~ D_{OH}. For P_{OH} the OH recycling reaction of HO_2 with NO is the dominant OH production term followed by the photolysis of HONO. The OH production by the ozonolysis reaction of β-pinene is of minor importance. As mentioned in the previous section HO_2 measurements include an interference from specific RO_2. For the calculation of the measured OH budget HO_2 data were not corrected for an RO_2 interference, as additional sensitivity studies showed that the results of the budget analysis are not affected by an assumed RO_2 cross sensitivity of 25 %, because the derived HO_2 concentration would be lowered by less than 10 %. The upper panel of ~~figure~~Fig. **??** shows the time series of the ratio of ~~D_{OH}/P_{OH}~~ D_{OH}/P_{OH} (red line). The maximum systematic error of ~~D_{OH}/P_{OH}~~ D_{OH}/P_{OH} is indicated by the grey area. Over the course of the experiment the measured OH destruction rate is balanced by the sum of the quantifiable OH production terms within the maximum systematic error as calculated from the sum of the uncertainties of the individual measurements. Therefore the existence of ~~large missing~~ a significant unknown OH ~~production terms~~ source can be excluded in the degradation of β-pinene under the experimental conditions. ~~The largest observed gap between P_{OH} and D_{OH} is in the order of 0.5 .~~ This result is different to previous studies ~~conducted by Fuchs et al. (2013, 2014) in the SAPHIR chamber, who, for~~ of the photooxidation of isoprene and methacrolein ~~, showed that significant missing production terms could be identified in SAPHIRexperiments. There, the measured destruction rate was about a factor of two higher than the sum of the quantifiable production terms. For the purpose of comparison the β-pinene study was conducted with the~~ in SAPHIR, where the same experimental setup and ~~under comparable experimental conditions . The high relative uncertainty of D_{OH}/P_{OH} during the zero air phase of the experiment is caused by the high uncertainty of the~~ similar experimental conditions were applied as in the β-pinene experiments. In case of isoprene and methacrolein, the OH ~~reactivity in that phase (uncertainty 0.5 at a reactivity of 1-1.5)~~budget analysis revealed significant additional OH sources (Fuchs et al., 2013, 2014), which were linked to OH regeneration by unimolecular reactions of RO_2 and contributed as much OH as the other OH production mechanisms together. To assure the ~~instrument data quality for~~ quality of the measured data used for the evaluation of the ~~budget analysis the~~ OH budget~~of well investigated reference systems (~~, test experiments were performed in SAPHIR with CO or CH_4 ~~oxidation) was evaluated~~ as main OH reactants. These experiments were performed before and after the β-pinene ~~campaign. Also in these experimentsthe measured destruction rate is balanced by the sum of the quantifiable production terms indicating that all major production terms in SAPHIR are covered by the instrumental setup~~ experiments, and showed a balance between P_{OH} (Eq. 8) and D_{OH} (Eq. 9) as is expected for the well-known CO and CH_4 chemistry.

3.4 Modifications of the β-pinene oxidation mechanism

3.4.1 ~~Modified~~ The β-pinene oxidation mechanism by Vereecken and Peeters

As discussed in sections 3.1 (see table **??**) and ~~**??**~~ 3.2 the primary product yields of acetone and nopinone, calculated by the MCM 3.2, are not in agreement with the determined product yields under low NO conditions in SAPHIR as well as with yields reported in the literature. For further evaluation of radical chemistry processes a good reproduction of the first-generation β-pinene products is essential. ~~An alternative model (Figure~~In the MCM 3.2 mechanism the OH radicals initially add onto the double bonds of β-pinene (Reactions a, b and c in Fig. 1)~~) was published by Vereecken and Peeters (2012), including~~

~~efforts to bring nopinoneand acetone model yields in agreement with experimental data. Based on quantum chemical and theoretical kinetic calculations Vereecken and Peeters proposed a fast ring opening reaction for the intermediate formed by~~ . About 85 % of the molecules are transformed into the tertiary radicals BPINAO1. These radicals add oxygen and form peroxy radicals BPINAO2 (MCM specific designation), which react to nopinone. Acetone is a product of a minor pathway in which the four-membered ring of β-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 ~~to the double bond of β-pinene~~OH to the external carbon of the double bond forming BPINO1$*$ is the main reaction. But in contrast to MCM3.2 Vereecken and Peeters (2012) proposed a fast ring opening of BPINAO1$*$ based on quantum chemical and theoretical kinetic calculations. This adjustment reduces the formation of the stabilized alkyl peroxy radical BPINAO2~~(MCM specific designation)~~, the main precursor in the MCM model for ~~the~~ nopinone formation, by about 70 %. Instead of BPINAO2 ~~, the formed after ring opening~~as in the MCM 3.2 mechanism, BPINCO2, is the dominant alkyl peroxy radical~~produced by the oxidation of β-pinene~~. With BPINCO2 as a starting point Vereecken and Peeters developed a new degradation scheme for this branch of the β-pinene oxidation. ~~In contrast to the original MCM 3.2 the primary acetone formation is now depending on two channels, leading to~~ This leads to an increase of acetone formation ~~under low conditions, whereas the acetone yield in the~~ at low NO concentrations compared to the MCM 3.2 ~~is fairly stable. More details about the mechanism can be found in Vereecken and Peeters (2012). Their model~~ while the yield of nopinone is predicted to be lower in the model by Vereecken and Peeters (2012). The model of Vereecken and Peeters (2012) was used without further changes except for the rate constant of β-pinene with OH which was set to the MCM 3.2 value to facilitate model intercomparison. The original rate constant in the Vereecken and Peeters model refers to the published rate constant of Gill and Hites (2002) which is approximately 10 % lower. In the following, the MCM with the revised β-pinene mechanism of Vereecken and Peeters (2012)) is denoted VP2012. The result of the model calculation is shown in ~~Figure~~Fig. **??** as blue line. In comparison to the MCM 3.2 the alternative β-pinene degradation scheme describes the measured time series of k(OH) better, assuming β-pinene products with a lower OH reactivity. The time behaviour of the nopinone concentration is reproduced well by Vereecken and Peeters model. The acetone formation which was slightly underestimated by MCM 3.2 is now overestimated by nearly the same amount. It should be noted that the acetone formation in the model by Vereecken and Peeters ~~explicitly marks~~ 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 ~~calibrate the acetone yield coming from a specific chemically-activated competition between different reaction channels available to alkoxy radical intermediate~~ verify this branching ratio. The current implementation assumes 100 % acetone formation; a more balanced value of 65 % would bring the acetone yield in agreement with the experiments.

Table **??** further illustrates the difference of the product yields for acetone and nopinone calculated by the measured and modeled time series. To enable an intercomparison the product yields calculated by modeled time series were also normalized to a β-pinene conversion of 70 %. All the corrections applied to the measured time series were applied in the same way to the modeled data. The measured nopinone yield of the first β-pinene injection is about 20 % lower ~~then~~ than the nopinone yield observed for the 2nd and 3rd injection. This feature is well captured by the MCM model even if the total nopinone yield is approximately a factor of 2 too high. The reason for the increase in the nopinone model yield is the secondary nopinone production by the degradation of previously formed hydroperoxides and organic nitrates originating from the same $\mathrm{RO_2}$ radical which is also responsible for nopinone formation. In contrast to the MCM 3.2 the model of Vereecken and Peeters predicts a more stable nopinone yield. However, it does not include all secondary chemistry.

Over the three injections the measured acetone yield increased from 20 to 36 %, showing a clear evidence for secondary acetone production. The MCM 3.2 as well as Vereecken and Peeters model also show an increasing acetone yield over time. In the MCM 3.2 the acetone yield is much too low compared to the measurements, but increases by a factor of three during the course of the experiment due to secondary acetone formations. The acetone yield calculated by Vereecken and Peeters model for the first injection is 70 % higher ~~then~~ than the measured value. In contrast to the time behaviour of the measured values the acetone yield is only slightly rising over the three injections, again possibly due to omitted secondary chemistry.

Concerning the agreement between measured and modeled radical concentrations the application of Vereecken and Peeters model does not lead to an improvement (see ~~Figure~~Fig. **??**). The measured OH and $\mathrm{HO_2^*}$ concentrations are still underestimated in the VOC phase of the experiment. For $\mathrm{HO_2^*}$ the decrease after the first β-pinene injection is even more pronounced. The reason for that is the $\mathrm{RO_2}$ interference included in the modeled $\mathrm{HO_2^*}$ data. In Vereecken and Peeters model less first-generation $\mathrm{RO_2}$ radicals, formed by the oxidation of β-pinene by OH, can be theoretically detected by the LIF system. That's why directly after the first β-pinene injection the modeled observable $\mathrm{RO_2}$ concentration by Vereecken and Peeters model is lower than in MCM 3.2. Simultaneously this also means that the modeled $\mathrm{RO_2}$ interference on the $\mathrm{HO_2^*}$ time series is reduced. Compared to the measured time series of $\mathrm{RO_2^*}$ Vereecken and Peeters model still overestimates the measured $\mathrm{RO_2^*}$ concentration. ~~Similar~~ The behaviour of modeled NO, $\mathrm{NO_2}$, CO and $\mathrm{O_3}$ is similar to the MCM 3.2~~the measured~~: NO and $\mathrm{NO_2}$ ~~concentration is~~ concentrations are slightly overestimated by the model, ~~whereas the timeseries of ozone is captured well~~ CO is increasingly underestimated over time, and ozone is well captured.

In summary~~therefore~~, it can be said that the alternative β-pinene degradation mechanism of Vereecken and Peeters is able to describe the measured time series of nopinone, the measured OH reactivity and with that the OH losses during the experiment much better than the MCM 3.2. However, these improvements do not lead to a satisfying description of the measured radical concentrations by the model, OH and $\mathrm{HO_2^*}$ are still underestimated.

The good reproduction of the total OH loss together with the underestimation of OH and $\mathrm{HO_2^*}$ by the model implies the need for an additional radical source to increase the modeled OH and $\mathrm{HO_2}$ concentration. On the other hand the OH budget analysis clearly showed that the measurable OH sources were able to balance the measured total OH loss in the experiment. With this additional information of the previous OH budget analysis , indicating no significant missing OH source, there is the arising question how the radical production can be increased without overbalancing the OH budget. One option for that is the addition of an $\mathrm{HO_2}$ source.

3.4.2 Oxidation mechanism by Vereecken and Peeters with measured HO_2^* as model input

To investigate the influence of an additional HO_2 source~~on the modeled time series of all key species a primary source was introduced in the model, taking~~, another model run was performed using the VP2012 mechanism and the measured HO_2^* taken data as model input. The known RO_2 interference in the measured HO_2^* data was taken into account and corrected in the HO_2 model input. The result of the model run is displayed by the green curve in ~~Figure~~Fig. **??**. Applying an additional HO_2 source to the model improves the agreement of the modeled OH concentration with the measured values. In general the modeled OH increases by about 50 %. The higher OH level leads to an increase of chemical conversion over time, visible in a stronger decrease of β-pinene, nopinone and $k(\mathrm{OH})$ as well as in an increase of the modeled RO_2^* concentration. Measured β-pinene, nopinone and $k(\mathrm{OH})$ are now underestimated by the model. A reason for that can be an underestimated RO_2 interference assumed for the HO_2 data, leading to a too strong HO_2 source in the model. In the case of the OH reactivity there is the additional uncertainty of the OH rate constants for the assumed β-pinene oxidation products beside nopinone, causing potentially a disagreement of modeled and measured $k(\mathrm{OH})$. For the overestimation of the measured RO_2^* concentration one also has to take into account that the displayed time series of modeled RO_2^* reflects the maximum RO_2 concentration which is theoretically detectable by LIF. An overestimation of the measured RO_2^* concentration by the model might be related to an overestimation of the theoretically detectable RO_2 species in model or an incomplete conversion of β-pinene derived RO_2 radicals in the RO_x cell of the LIF system. In addition the increase of the modeled HO_2^* concentration leads to an improved description of the measured NO and NO_2 time series. Especially in the second half of the VOC phase the modeled NO and NO_2 concentration is reduced. Also the time series of HCHO is improved, whereas CO remains unchanged and is still underpredicted by the model.As in any other model run there is no influence on the modeled ozone time series.

By the application of an HO_2 source to the model it was shown that the agreement between model and measurement could be improved for important key species like OH, NO and NO_2. Discrepancies in the OH lifetime and the RO_2^* concentration could be attributed to uncertainties of the model. Therefore~~the evidence of~~, a missing source of HO_2 in the degradation mechanism of β-pinene seems to be a reasonable hypothesis.

3.4.3 Uncertainties in the measured OH concentration

As stated in the previous section the input of the measured HO_2 concentration led to a satisfactory description of the measured OH concentration by the model. On the other hand the elevated OH concentration also resulted in an overestimated decrease of the β-pinene concentration measured by PTR-TOF-MS. ~~The reason for that is that the concentration calculated from the~~From the decay of β-pinene~~decay~~, an OH concentration can be calculated using a reaction rate coefficient of 7.95 x $10^{-11}\ \mathrm{cm^3 s^{-1}}$ (MCM v3.2) and taking dilution in the chamber into account. The calculated OH concentration is about 31 % lower than measured by the LIF and 24 % lower than measured by the DOAS instrument. Since both direct OH measurements agree well with each other and on the other hand the decay of β-pinene measured by PTR-TOF-MS agrees well with the decay measured by GC/MS/FID there is no clear indication for an instrumental failure or interference which would lead to an exclusion of one or the other dataset. Because this contradiction cannot be solved the implications of a potentially lower OH concentration on the previously discussed results should be elucidated. For the OH budget analysis a 24 % lower OH concentration would lead to a decrease of the calculated OH destruction ~~$\mathrm{D_{OH}}$~~ (D_{OH}) by an equal percentage. ~~$\mathrm{D_{OH}}$~~ D_{OH} would be overbalanced by ~~$\mathrm{P_{OH}}$ in a way that the quotient $\mathrm{D_{OH}}$~~P_{OH}, but the mean ratio D_{OH}/ ~~$\mathrm{P_{OH}}$ (0.76) would still be not~~ P_{OH} would still not be significantly different from ~~1.~~ unity, as can be seen from its experimental error (see Fig. ??, upper panel). As reported by Nehr et al. (2014) for OH budgets during SAPHIR chamber experiments investigating CO as reference system uncertainties of ± 20 % for ~~$\mathrm{D_{OH}}$~~D_{OH}/ ~~$\mathrm{P_{OH}}$~~ P_{OH} are common. For the comparison of the measured OH concentration with the model calculations, a 24 % lower measured OH concentration would result in a reduced underestimation of the measured OH concentration by the models ~~(now~~ of only 5-25 %~~)~~, whereas HO_2^* would still be underestimated by a factor of two. ~~Consequentially~~ Consequently, taking the corrected HO_2 concentration as model input would result in an overestimation of the OH concentration by the model up to 50 %. The influence of a 24 % lower measured OH concentration on the determined product yields would be negligible because the corrections were small anyways.

3.5 Possible reasons for the underestimation of HO_2^*

3.5.1 ~~Model studies to identify the reasons for the underestimation of~~ Field observations

The model simulations in the previous section demonstrated that an unaccounted source of HO_2 is a probable explanation for the disagreement of measured and modeled HO_x concentrations. A comparison of the acquired results from the SAPHIR experiments with recent field campaigns shows qualitatively the same results as in field studies which were conducted in forested areas dominated by monoterpene emissions. Kim et al. (2013) reported a mismatch of the observed HO_2 concentration and model calculations. As in the SAPHIR experiments the OH budget was nearly balanced. Kim et al. postulated a missing photolytic HO_2 source as the reason for the discrepancy between the measured and modeled HO_2 concentration in a 2-methyl-3-buten-2-ol (MBO) dominated environment. Further investigations of the radical budget by Wolfe et al. (2014) came to the same result. Additionally to the missing HO_2 source previously postulated by Kim et al., Wolfe et al. also suggested a second peroxy radical source, being a photolytical independent source of RO_2 radicals produced by the ozonolysis of unidentified VOC species. Similar to Wolfe et al. and Kim et al. also Hens et al. (2014) ~~.~~ reported that they found an unaccounted primary HO_2 source, when they were comparing the measured time series of OH and HO_2 with model calculations. Under conditions of moderate observed OH reactivity and high actinic flux, an additional RO_2 source was needed to close the radical budget. Again also in the case of Hens et al. the measured OH budget was nearly balanced. In general it seems that the radical chemistry in a monoterpene dominated biogenic atmosphere in field campaigns or chamber studies recent atmospheric models underpredict the HO_2 production.

3.5.2 Model sensitivity studies

From the present study, it is obvious that an unknown HO_2 source is linked to the oxidation of β-pinene. Further model studies were performed to identify possible mechanisms that could generate additional HO_2. In atmospheric chemistry, primary sources of HO_2 include the ~~decomposition of alkoxy radicals,~~ photolysis of aldehydes and ketones, and ozonolysis of VOCs~~and~~

. Furthermore, HO_2 is produced by the reaction of ~~CO, ozone~~CO, ozone, or formaldehyde with ~~OH, the photolysis of aldehydes and ketones and finally~~ OH. In the chemical degradation of VOCs, HO_2 ~~formation~~ can be formed by the decomposition of alkoxy radicals, and finally by unimolecular rearrangement reactions of alkyl peroxy radicals (Orlando and Tyndall, 2012).

~~We investigate here two possible~~ We have investigated two potential sources of HO_2 ~~(see Figure ??)~~in separate model runs: firstly, the formation of HO_2 by photolysis of β-pinene reaction products, in particular aldehydes and ketones, and secondly ~~by~~ additional conversion of RO_2 to HO_2 without the involvement of ~~NO. A third option to explain the discrepancy between modeled and measured is the existence of an overestimated sink of hydroperoxyl radicals instead of a missing source of . A permanent sink of in the β-pinene degradation mechanism is the formation of organic hydroperoxides () by the reaction of radicals with . Hence, the yield in the reactions was varied in the third model run.~~

~~As the interference of radicals in the measurements of is also a subject of discussions, the maximum influence of the assumed interference on the model results was estimated in a fourth model case (appendix A). The sensitivity study proved that the interference of the radicals on the measured time series is incapable to explain the observed deviations between modeled and measured . More than 50 % of the observed discrepancy cannot be explained by any known interference. For detailed information the reader is referred to additional information in the appendix.~~

~~For the addition of a primary photolytic sourcean artificial species Z was introduced in the model. Every~~ NO. In both cases, generic reactions were added to the chemical mechanism (see details in the Supplement). In case of the photolytical source, it was assumed that every reaction of β-pinene with OH produces one molecule of a carbonyl-type species Z additional to the related RO_2 species. ~~Equivalent to an aldehyde the photolysis of Z, which is the only sink of the molecule beside dilution, produces an equal amount of~~ It was further assumed that Z is photolysed with a rate like for formaldehyde and ~~. Not much is known about the photolysis of monoterpene degradation products. The only well investigated species is pinonaldehyde, a main degradation product of α-pinene. As stated by Jaoui and Kamens (2003) the photolytic loss of pinonaldehyde is an important part of its overall atmospheric chemistry, accounting for as much as the loss by the reaction with during daytime. Nevertheless the photolysis rate of pinonaldehyde is very similar to the photolysis rate of formaldehyde. With regard to recent literature (Moortgat et al. (2002); Wenger (2006)), in general straight chain aldehydes and formaldehyde all have very similar photolysis rates. In contrast to that α-branched aldehydes as well as aldehydes of substituted aromatics show significantly higher photolysis rates (factor of 3-20). As it is unlikely that degradation products of β-pinene form aromatic structures the photolysis rate of formaldehyde was considered as a good first estimate for the photolysis rate of monoterpene degradation products in general. Therefore the photolysis rate of Z is set to the photolysis frequency of the radical pathway of the photolysis of formaldehyde . To increase the source strength the number of and molecules produced per photolysis of one molecule of Z was increased stepwise. The red curve shows the model run assuming a production of~~ generates six HO_2 and CO molecules per molecule ~~Z~~ Z, which is in terms of chemical feasibility a rather unlikely~~assumption. Even if one takes into account the possibility of a photolytical cascade, a subsequent photolysis of the photolysis products, as proposed by Jaoui and Kamens (2003) for pinonaldehyde, a production of more than three molecules of per molecule of β-pinene is rather implausible. Nevertheless under this assumption the modeled~~ , but not impossible assumption (see Supplement). Based on these assumptions, agreement between measurement and model is found for HO_2^* ~~agrees well with the measurements for the~~

and OH in the second half of the VOC phase~~. At the beginning~~ , but in the first half of the VOC phase a strong underestimation of HO_2^* ~~is still strongly underestimated because during that experimental phases there is still an insufficient amount of Z being built up yet (see Figure ?? red curves). Therefore the~~ remains (Figure 1, Supplement). Compared to all previous model runs, the measured concentration of CO is now well matched by the model. The modeled ~~concentration rises later than in the modelrun, taking measured as input. Other modeled~~ time series ~~like~~ of RO_2, NO, NO_2, ozone and the β-pinene products formaldehyde, acetone and nopinone stay nearly unchanged in comparison to the model run using measured HO_2 as model input. ~~The temporal behavior of modeled and clearly shows that adding a~~ In conclusion, the assumed photolytical HO_2 source ~~cannot be a reasonable explanation for the missing~~ gives an improved model description of the observations, but is not capable to regenerate HO_2 ~~production in the model . Especially in the first half of the VOC phase the production is too low to explain the measured levels. Increasing the production directly after the~~ sufficiently fast in the first 1-2 hours after the first β-pinene ~~injection would require a further increase in the photolysis rate to unrealistically high values. Furthermore, the assumption that one molecule of Z has to produce six molecules of and to match the measured level at the end of the VOC phase demonstrates that a missing photolytical source cannot be the sole explanation for the disagreement between measured and modeled in the second half of the phase.~~ addition.

~~In the second model run, displayed in blue in Figure ??, the impact of some chemical sources of on the model are shown. To simulate the influence of unimolecular~~ Next, the possible influence of unimolecular rearrangement of RO_2 ~~rearrangements without changing the whole degradation mechanism a modification of the so called X-mechanism~~ yielding HO_2 was studied (see Supplement). For this purpose, the so called X-mechanism published by Hofzumahaus et al. (2009) was used. An NO like species ~~X~~ X is thereby reducing RO_2 radicals to RO radicals. The rate constants applied for these reactions are the same as the rate coefficients of NO with the corresponding RO_2 radical. Contrary to the ~~X-mechanism of Hofzumahaus et al.~~ X-mechanism of Hofzumahaus et al., in case of β-pinene~~X~~ , X is not reacting with HO_2 radicals. ~~For the model run, shown in Figure ?? a constant concentration of~~ With 300 ~~ppt of X was assumed during the VOC phase. The comparison of the modeled~~ pptv of X, the model gives a significantly improved description of HO_2^*~~time series with the measurements shows that both time series are much better in agreement now, the measured is underestimated less than~~ , but an underprediction of 25 % ~~. With the increase of modeled also the modeled concentration increases and so agrees better with the measurements. In parallel the introduction of the new loss pathway leads to~~ remains (Figure 1, Supplement). The introduction of X causes a substantial decrease of ~~the modeled~~ RO_2^* ~~concentration. The measured is now slightly underestimated by the model. Furthermore the new loss pathway has a strong influence on the modeled time series~~ and a significant overprediction of NO and NO_2 ~~. Both time series overestimate the measurements by up to 50 %. The reason for that is the reduction of organic nitrate formation. As the yield of organic nitrates is strongly depending on the carbon number (Koppmann, 2008) monoterpenes have relatively high nitrate yields, 18-26 % were reported for α-pinene (Nozière et al., 1999; Rindelaub et al., 2014). If one adds fast independent rearrangement reactions to the model these reactions compete with the reaction of radicals and thus with the organic nitrate formation. With the X-mechanism the organic nitrate formation is reduced by about a factor of two compared to the base model of Vereecken and Peeters. Another effect is a slightly increased nopinone formation in~~ by the ~~model. Again the comparison of the measured time series with the model shows the limited applicability of unimolecular~~ model. Also CO is greatly overestimated. In conclusion, additional

RO_2 ~~reactions acting as~~ to HO_2 ~~source. In contrast to a photolytic source fast unimolecular rearrangement reactions are able to partially explain the measured levels at the beginning of the phase, but their influence on the organic nitrate yield leads to inconsistencies with the measured nitrogen oxide data.~~ conversion (without NO) alone is also not capable to describe all observations consistently.

~~The third sensitivity study (see the green curves in Figure ??) investigates the models response on a lower organic hydroperoxide yield. In the MCM 3.2 and the modelof Vereecken and Peeters the formation is nearly exclusively determined by the rate constant KRO2HO2 which is applied to the majority of all~~ Two additional model sensitivity tests were carried out in order to investigate, if the HO_2^* underprediction is caused by too fast RO_2 + HO_2 ~~reactions. For the presented experiment KRO2HO2 was on average about 20.0 x . This value is in good agreement with rate coefficients for~~ reactions in the Vereecken and Peters model, and how the model measurement comparison is influenced by uncertainties of the RO_2 ~~+~~ interference in the HO_2 ~~reactions of hydroxy alkyl peroxy radicals generated from α-pinene, d-limonene and γ-terpinene. Boyd et al. (2003) reported k-values of 19.7 -21.1 x with an uncertainty of 7 - 20 %. For biogenic species in general Orlando and Tyndall (2012) proposed an average~~ measurements (see details in Supplement).

In accordance with a proposed uncertainty of a factor of two for the rate constants of biogenic RO_2 + HO_2 reactions ~~. In the present sensitivity study the rate constant was therefore~~ (Orlando and Tyndall, 2012), the rate constants for the formation of ROOH were reduced by 50 %. As a result the modeled HO_2 concentration increases by 30 %, but HO_2 is still underestimated by the model ~~. Similar to also the~~ (Figure 1, Supplement). The modeled OH concentration slightly increases ~~. The measured concentration is~~ and the measured RO_2 concentration becomes overestimated by a factor of two~~by the model. A reduction of the organic hydroperoxide formation pathway also leads to a good model description of the measured time series .~~. The measured concentrations of NO and NO_2 ~~. The reason for this is that a reduction of KRO2HO2 automatically yields in an increased production of organic nitrates which act as a temporary or permanent sink for nitrogen oxides. The influence of the reduced ROOH formation on other model species is small. Acetone formation is still over predicted~~ are well matched by the model~~by 20 %, nopinone formation is slightly overpredicted as well as the $k()$ decay. The measured time series of β-pinene and ozone are reproduced well. A .~~, but CO remains underestimated. In conclusion, a reduction of the ~~ROOH~~ ROOH production may help to reduce the discrepancy between the modeled and measured HO_2 concentration, but cannot solely explain the deviations between model and measurements.

~~Two model studies investigating the likelihood of two potential~~ As the interference of RO_2 radicals in the measurements of HO_2 ~~sources~~ is also a subject of discussions, the maximum influence of the assumed RO_2 interference on the model results was estimated in a fourth model case (see Supplement). The sensitivity study proved that the interference of the RO_2 radicals on the measured HO_2 time series is incapable to explain the ~~missing~~ observed deviations between modeled and measured HO_2~~production term demonstrated that each source taken separately cannot explain the measured level. Furthermore in the third study a reduction of the total hydroperoxide production rate by~~. More than 50 ~~% is not sufficient to explain the underestimation of the measured~~ % of the observed discrepancy cannot be explained by any known interference.

3.5.3 Modifications of the β-pinene oxidation mechanism by Vereecken and Peeters to explain the missing HO_2^* source

The major difference of the β-pinene oxidation mechanism by Vereecken and Peeters compared to the MCM 3.2 mechanism is the fast ring opening of the alkoxy radical $\mathrm{BPINO1}*$ which is transformed into the radical $\mathrm{BPINCO1}$ (see Fig. 1). At low NO concentrations the largest fraction of these molecules are expected to react to $\mathrm{ROO6R2O}$. The formation of $\mathrm{ROO6R2O}$ is exothermic and the reaction sequence can either proceed via elimination of acetone (path e in Fig. 1 and Fig. **??**) or via 1,5-H-migration of the hydrogen at α position of the aldehyde (path f in Fig. 1 and in Fig. **??**).

The branching ratio of path b and path a significantly influences the amount of HO_2 produced. After acetone is eliminated $\mathrm{ROO6R8}$ radicals add two oxygen molecules. The emerged radical cleaves an OH radical and forms a peracid. No additional HO_2 radicals are supposed to be produced if degradation of the radical $\mathrm{ROO6R2O}$ proceeds via the acetone elimination channel.

If instead the hydrogen atom on α position of the aldehyde of $\mathrm{ROO6R2O}$ migrates, $\mathrm{ROO6R8}$ is formed. This acyl radical is supposed to cleave CO, and after another 1,5-H-migration, also HO_2. The resulting molecule is the dicarbonyl compound $\mathrm{ROO6R9P}$ whose photolytical cleavage results in the additional production of one molecule CO and one molecule HO_2 (path f in Fig. **??**). Unfortunately, Vereecken and Peeters could not accurately predict the branching ratio of these two reaction channels due to large number of active conformers at higher energies. Instead, the 1,5-H-migration in path f was supposed to be outrun by acetone elimination in path e, and path e was omitted in the model of Vereecken and Peeters.

The effect of the branching ratio in Fig. **??** on the predicted HO_2^* concentration ~~by the model . A fourth study (see appendix A) investigating the influence of the interference on measured~~ can be evaluated if $\mathrm{ROO6R2O}$ is fixed in the model to react exclusively via path f. The respective model run (see the green curve in Fig. **??**) predicts a HO_2^* ~~time series also ruled out the assumption that the underestimation~~ concentration which is 30 % higher than forecasted by the original model of Vereecken and Peeters. Also, the predicted CO, RO_2^*, HCHO and nopinone concentration now coincide with the the measured data. Still, the measured HO_2^* is 20 % higher than prognosticated.

The gap between measured HO_2^* and modeled HO_2^* can be closed if the cleavage of a second HO_2 is incorporated into the model (see orange curve in Fig. **??**). The time series of HO_2^*, RO_2^* and OH are now captured by the model~~can be attributed to measurement interferences alone~~. Also the measured nopinone, CO and HCHO are well described. Only acetone is now underestimated by the model, because acetone is mainly formed via the pathway e in Fig. **??**. Although $\mathrm{ROO6R9P}$ can potentially cleave acetone, quantum chemical calculations are needed further to pin down the mechanism of acetone cleavage.

4 Summary and Conclusions

~~In this paper a~~ A set of three β-pinene oxidation experiments, conducted in the SAPHIR atmosphere simulation chamber, was ~~comprehensibly~~ comprehensively investigated with regard to the involved radical species during the OH oxidation. A special focus was placed on the identification of possible missing OH production terms in the degradation mechanism (Whalley et al., 2011). The experiments were conducted under nearly ambient β-pinene concentration (4.3-4.7 ppb VOC) and low NO conditions (100-300 ppt NO). The comparatively low VOC concentration allowed for the first time the investigation of the radical budget of β-pinene by parallel measurements of OH, HO_2, RO_2 and k(OH). In a first approach this comprehensive dataset was used for a model independent analysis of the OH budget. For this purpose the sum of the measurable OH production terms (HONO photolysis, O_3 photolysis, VOC ozonolysis, HO_2+NO, HO_2+O_3) was compared with the measured OH destruction rate (k(OH) x [OH]). Contrary to previous studies of isoprene and methacrolein in SAPHIR (Fuchs et al., 2013, 2014) the OH budget was balanced in the β-pinene oxidation experiments, giving no evidence for significant missing OH production terms. In a second approach the measured time series of the atmospheric key species were compared to ~~1-dimensional~~ zero-dimensional box model calculations to investigate whether the models are able to predict the β-pinene degradation well. The comparison of the measured time series with the MCM 3.2 revealed that the model was not able to reproduce the measured time series of OH, HO_2, k(OH) and nopinone. The modeled OH as well as the HO_2 concentration was underestimated by more than 50 %. At the same time the modeled OH reactivity was slightly overestimated. The reason for this disagreement is obviously a biased product distribution of the first-generation degradation products. The measured nopinone concentration was about a factor of three lower than predicted by the model. A comparison of the experimentally determined nopinone yield with recent literature showed a good agreement ~~with recent literature~~ but is a factor of two lower than in the MCM model. Hence, for further investigations an updated MCM mechanism published by Vereecken and Peeters (2012) was used. Their model was able to reproduce the measured time series of nopinone and k(OH) much better than the MCM 3.2, but still significantly underpredicted the measured OH and HO_2 concentration. As the previous analysis of the OH budget showed no evidence of a missing OH source, an additional HO_2 source was introduced into the model to improve the agreement for OH and HO_2. ~~The~~ A sensitivity study showed that taking the measured HO_2 time series as model input generally improves the overall agreement of the modeled time series with the measurements. OH is now well described by the model. These findings are qualitatively in agreement with recent field studies (Kim et al., 2013; Wolfe et al., 2014; Hens et al., 2014) reporting that in a monoterpene dominated biogenic atmosphere models were not able to describe OH and HO_2 levels well although the measured OH budget was balanced.

In accordance with the results for β-pinene presented in this paper we propose ~~a missing photolytic~~ an additional HO_2 source linked to b-pinene oxidation products as the reason for the underestimation of OH and HO_2 in the model. ~~An additional sensitivity study trying to identify the nature of the source for the β-pinene experiment showed that a formaldehyde like photolytic source is not a reasonable option to explain the measured and levels. Due to the absence of a sufficient amount of photodegradable first generation products at the beginning of the β-pinene oxidation a photolytic source is not able to produce enough to explain the measured concentration. A second sensitivity study demonstrated that the addition of rearrangement reactions releasing to the model is not a reasonable option either. In case of the~~ With additional sensitivity studies it was possible to rule out photolytical processes or rearrangement reactions of RO_2 ~~rearrangement reactions the added reaction path competes with the formation of organic nitrates in the model and is thereby causing a strong~~ as sole HO_2 sources. Also a possible 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 concentration because the reduction of the loss is too small. Further studies demonstrated that~~ as well an underestimation of the known RO_2 interference on the ~~measurements of~~ HO_2 ~~can be excluded as the reason for the observed high~~ measurements were excluded as explanations for underestimating HO_2 ~~concentrations. None of the previously discussed changes in the mechanism as well as the interference is able to solely explain the deviations between modeland measurements~~in the model.

~~In conclusion, it can be said that the study of the β-pinene oxidation in SAPHIR as well as several field campaigns showed the lack of understanding of the radical chemistry involved in the oxidation of monoterpenes. The identity of the proposed missing~~ The gap between measured and modeled HO_2^* 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 HO_2~~source still remains uncertain. To further elucidate the degradation mechanism for β-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~~, CO and a dicarbonyl compound which itself is a photolytical source of HO_2 ~~can also have an important influence on the modeled~~ and ~~concentrations.~~

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~~The interference of alkene-derived radicals on the~~ CO. Still, the exact HO_2 ~~measurements by LIF instruments is a well known measurement uncertainty in the determination of the~~ formation mechanism remains uncertain. Additional experiments and quantum chemical calculations have to be made to completely unravel the pathway of HO_2 ~~concentration (Fuchs et al., 2011; Whalley et al. Before the monoterpene measurement campaign the Jülich LIF instrument was carefully characterized with regard to this interference. There average interference of primary radicals formed by the reaction of monoterpenes with was determined to be 25 ± 10 % on average. This interference was incorporated in the displayed model curves for and in the modified MCM model (see the red curves). To exclude an impact of the interference on the proposed missing source a sensitivity study was carried out. For that the previously determined interference for primary s was doubled and applied on every species in the model. The result of this sensitivity study is displayed in the blue model curves in Figure **??** . As one can see the enhanced interference leads to 50 % increase in . But is still underestimated by 20-30 % in the model. Caused by the measurement principle of the LIF, determining the concentration by subtraction of the from the signal, an increase in the modeled leads necessarily to a decrease in the modeled concentration. In comparison to the base run of the model of Vereecken and Peeters the modeled level drops by 50 % and the model now underestimates the measured concentration~~formation.

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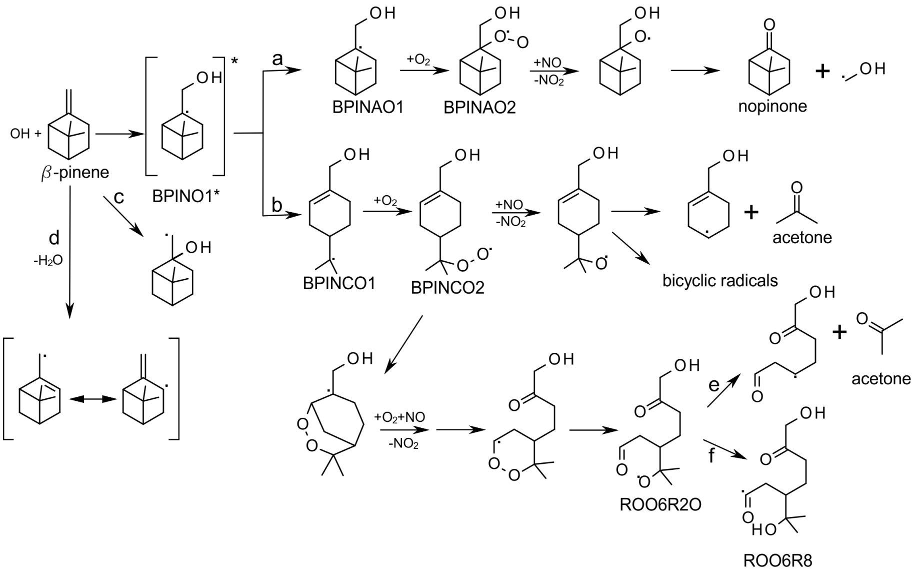


Figure 1. ~~Comparison of the measured~~ Acetone and ~~modeled time series of β-pinene, *k*(), , , , NO, , acetone and~~ nopinone ~~in the~~ formation from OH initiated β-pinene oxidation ~~experiment from 27August . Red: MCM 3.2 Blue: modified MCM model by~~ after Vereecken and Peeters (2012)~~with changed product yields Green: modified MCM model by Vereecken and Peeters (2012) constrained by~~. For simplification only the ~~measured concentration~~major reactions are shown

~~Comparison of the measured and modeled time series of β-pinene, , , , , NO, , acetone and nopinone in the β-pinene oxidation experiment from 27August. Red: modified MCM model by Vereecken and Peeters (2012) with additional photolytic source producing , Blue: modified MCM model with additional formation by independent rearrangement reactions, Green: modified MCM model with 50 % reduced yield of organic hydroperoxides~~

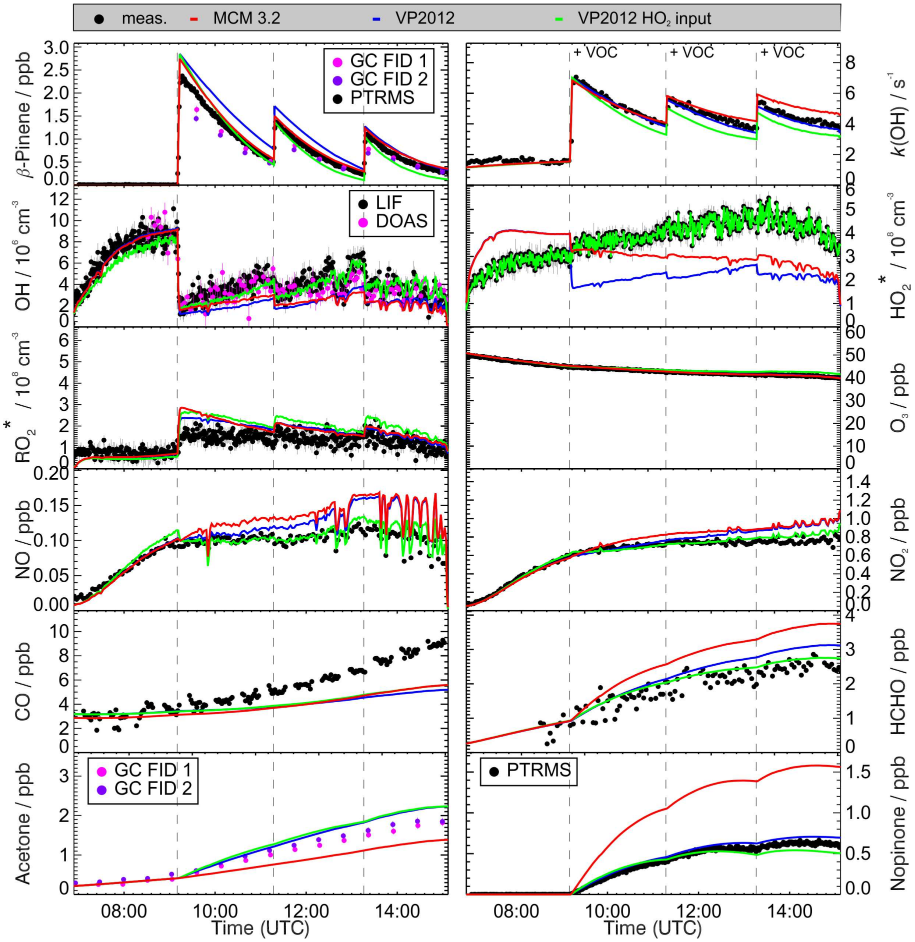


Figure 2. Comparison of the measured and modeled time series of β-pinene, k(OH), OH, HO_2^*, RO_2^*, NO, NO_2, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August . Red: MCM 3.2 Blue: modified MCM model by Vereecken and Peeters (2012) with changed product yields Green: modified MCM model by Vereecken and Peeters (2012) constrained by the measured HO_2 concentration

(R4)

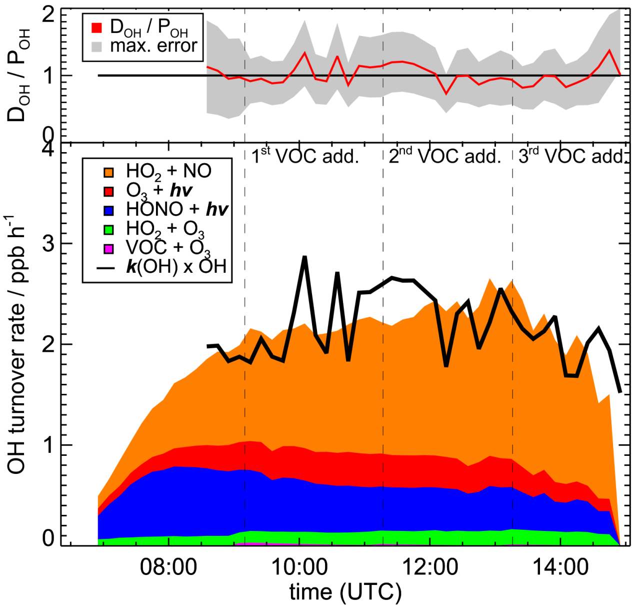


Figure 3. OH budget for the experiment on 27th August 2012. The OH destruction rate ~~D_{OH}~~ D_{OH} calculated from the measured OH reactivity k(OH) and the measured OH concentration (DOAS) is given as black line. The coloured areas display the OH production rate ~~P_{OH}~~ P_{OH} calculated from measurements. The upper panel of the diagram shows the ratio of ~~D_{OH}/P_{OH}~~ D_{OH}/P_{OH} as red line. The maximum systematic error of the ratio is indicated by the grey area. For reasons of clarity all data in the upper as well as the lower panel of the diagram are shown as 5 min average values. During the course of the experiment the OH destruction rate is balanced by the sum of the measurable OH production terms. The reaction of HO_2 with NO and the photolysis of HONO are the dominant OH production terms. HO_2 measurements were not corrected for the interference from specific RO_2 species.

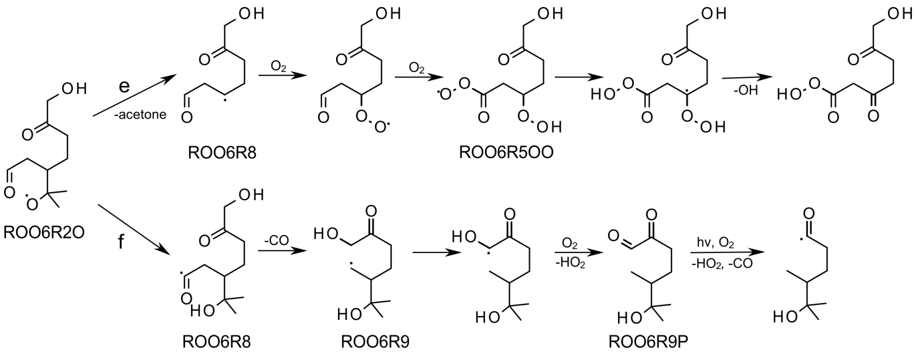
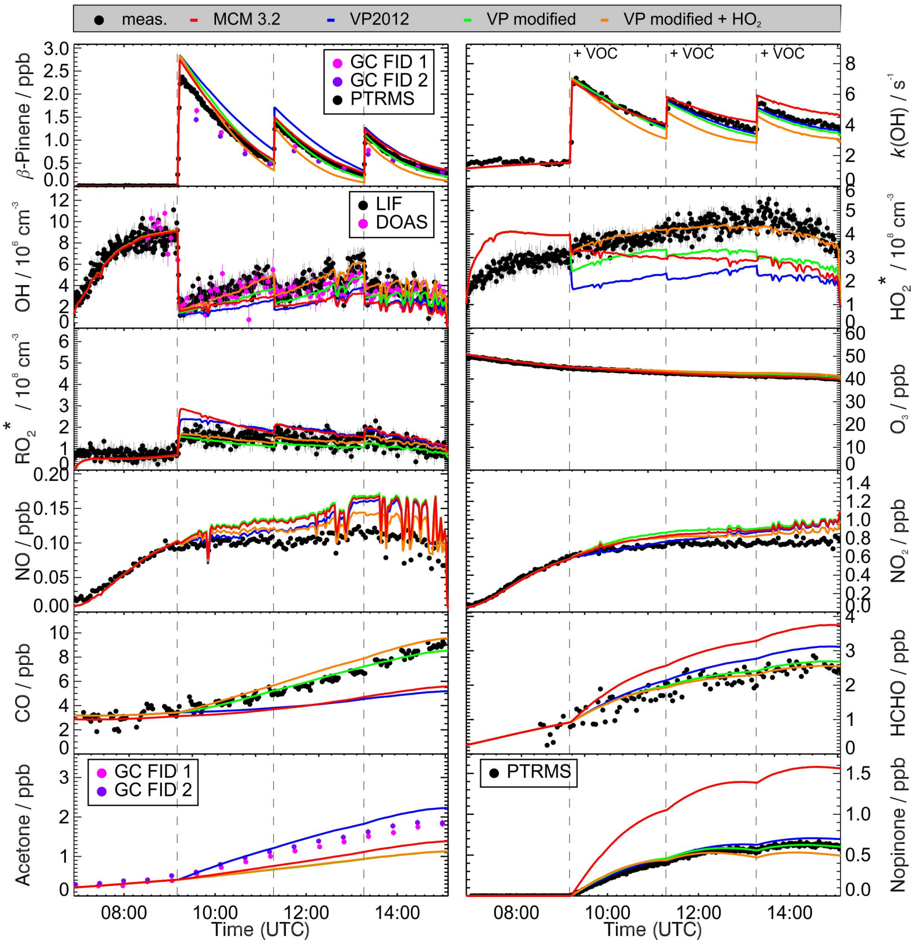


Figure 4. Possible HO_2 formation pathway in the oxidation of β-pinene modified after Vereecken and Peeters (2012)



~~Acetone~~ and ~~nopinone formation from OH initiated β-pinene oxidation after Vereecken and Peeters (2012)~~CO.~~For simplification only the major reactions are shown.~~

~~Acetone~~ and ~~nopinone formation from OH initiated β-pinene oxidation after Vereecken and Peeters (2012)~~CO.~~For simplification only the major reactions are shown.~~

Figure 5. Comparison of the measured and modeled time series of β-pinene, OH, OH, HO$_2^*$, RO$_2^*$, ~~NO~~NO, NO$_2$, CO, HCHO, acetone and nopinone in the β-pinene oxidation experiment from 27th August. Red: ~~modified~~ MCM 3.2, Blue: model by Vereecken and Peeters (2012), Green: model by Vereecken and Peeters (2012) with ~~changed product yields~~1,~~Blue~~5-H-migration of ROO6R2O, Orange: ~~modified MCM~~ Modified model ~~assuming an interference~~ by Vereecken and Peeters (2012) with 1,5-H-migration of ~~50 %~~ ROO6R2O and an additional production term for ~~the~~ one molecule of HO$_2$ ~~measurements~~

~~Acetone~~ and ~~nopinone formation from OH initiated β-pinene oxidation after Vereecken and Peeters (2012)~~CO.~~For simplification only the major reactions are shown.~~

Table 1. Instrumentation for radical and trace gas detection during the β-pinene oxidation experiments.

	Technique	Time Resolution	1σ Precision	1σ Accuracy
OH	DOAS[a] (Dorn et al., 1995; Hausmann et al., 1997; Schlosser et al., 2007)	205 s	0.8×10^6 cm^{-3}	6.5 %
OH	LIF[b] (Lu et al., 2012)	47 s	0.3×10^6 cm^{-3}	13 %
HO_2, RO_2	LIF[b] (Fuchs et al., 2011, 2008)	47 s	1.5×10^7 cm^{-3}	16 %
k(OH)	Laser-photolysis + LIF[b] (Lou et al., 2010)	180 s	0.3 s^{-1}	0.5 s^{-1}
NO	Chemiluminescence (Rohrer and Brüning, 1992)	180 s	4 pptv	5 %
NO_2	Chemiluminescence (Rohrer and Brüning, 1992)	180 s	2 pptv	5 %
O_3	Chemiluminescence (Ridley et al., 1992)	180 s	60 pptv	5 %
VOCs	PTR-TOF-MS[c] (Lindinger et al., 1998; Jordan et al., 2009)	30 s	15 pptv	14 %
	GC[d] (Kaminski, 2014)	30 min	4-8 %	5 %
CO	RGA[e] (Wegener et al., 2007)	3 min	4 %	10 %
HONO	LOPAP[f] (Häseler et al., 2009)	300 s	1.3 pptv	10 %
HCHO	BB-DOAS[g] (Brauers et al., 2007)	100 s	20 %	6 %
Photolysis frequencies	Spectroradiometer (Bohn and Zilken, 2005)	60 s	10 %	10 %

[a] Differential Optical Absorption Spectroscopy.

[b] Laser Induced Fluorescence.

[c] Proton-Transfer-Reaction Time-Of-Flight Mass-Spectrometry.

[d] Gas Chromatography.

[e] Reactive Gas Analyzer.

[f] LOng Path Absorption Photometer.

[g] Broadband Differential Optical Absorption Spectroscopy.

Table 2. Experimental conditions of the β-pinene oxidation experiments. Maximum values are given for β-pinene and averaged values for the part of the experiment, when β-pinene was present, for the other parameters.

β-pinene ppbv	OH $10^6\,\mathrm{cm}^{-3}$	NO_x ppbv	NO pptv	O_3 ppbv	RH %	$j(NO_2)$ $10^{-3}\,\mathrm{s}^{-1}$	T K	date
4.3	6.0	1.0	300	10	45	5	295	12 Aug 2012
4.3	4.5	0.9	200	10	45	4	299	15 Aug 2012
4.7	3.5	0.9	100	40	40	4.5	293	27 Aug 2012

Table 3. Product yields from the reaction of β-pinene with OH radicals under various NO and VOC concentrations

Product	Yield OH reaction	Reference	consumed VOC ppbv	NO ppbv
Nopinone	0.35 ±0.13	This work	3	0.4
	0.28-0.37 ±0.13		3	0.1
	0.79^{a} ±0.08	Hatakeyama et al. (1991)	700	1800
	0.30 ±0.045	Arey et al. (1990)	960	960
	0.27 ±0.04	Hakola et al. (1994)	1000	9600
	0.25 ±0.05	Larsen et al. (2001)	1300-1600	0
	0.25 ±0.03	Wisthaler et al. (2001)	1000-3000	1000-2000
	0.24	Librando and Tringali (2005)	4100-13200	0
Acetone	0.19 ±0.06	This work	3	0.4
	0.20-0.36 ±0.07		3	0.1
	0.13 ±0.02	Wisthaler et al. (2001)	1000-3000	1000-2000
	0.11 ±0.03	Larsen et al. (2001)	1300-1600	0
	0.03-0.06	Fantechi (1999)		
	0.02 ±0.002	Orlando et al. (2000)	1800-12000	800-8000
	0.085 ±0.018	Reissell et al. (1999)	880-920	9600
	0.14	Librando and Tringali (2005)	4100-13200	0

[a] Yield measured by FTIR absorption at 1740 cm^{-1}*, andissuspected7toincludeothercarbonylcompounds*

Table 4. Comparison of measured and modeled product yields from the reaction of β-pinene with OH radicals for the three β-pinene injections during the experiment on 27 th August 2012

Product	Injection	Yield measured	Yield MCM 3.2	Yield Vereecken and Peeters
Nopinone	1 st	0.28	0.53	0.27
	2 nd	0.37	0.61	0.28
	3 rd	0.35	0.65	0.30
Acetone	1 st	0.20	0.07	0.37
	2 nd	0.24	0.16	0.47
	3 rd	0.36	0.21	0.49