

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

Anonymous Referee #2

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

Experimentally, the measured rates of production and loss of OH are found to balance, in contrast to previous studies of isoprene and methacrolein chamber oxidation. However, a model analysis found lower rates of production and destruction, and overall lower radical concentrations. Use of a more detailed model, and measured HO₂ concentrations, partially reduced the discrepancy, and sensitivity analyses showed that

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the measured data could be better represented by introducing an unidentified source of HO₂.

Overall, this is a good paper. The experiments and modeling are well described, and attention is paid to uncertainties in the system.

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.

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 . . .”

Line 115 Change “effects” to “affects”

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

Line 180. Delete “are”.

Line 221. Inferring should be Interfering?

Line 246. Delete one of the double parentheses.

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

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

Line 312. Change “then” to “than”.

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

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Line 425. "under low NO_x conditions". I realize this is somewhat a matter of semantics, and under much discussion at present, but be careful how you classify the NO_x environment. With 100 ppt of NO (measured) and up to 20 ppt of HO₂, >50% of the RO₂ radicals will still react with NO. So it is not strictly a low-NO_x environment.

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.

Line 427. Remove double parenthesis.

Lines 436-438, and 4447-450. 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 NO_x (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.

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

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

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

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very fast photolysis rates?

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

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