

Atmos. Chem. Phys. Discuss., author comment AC1
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Reply on RC1

Zhaofeng Tan et al.

Author comment on "Atmospheric photo-oxidation of myrcene: OH reaction rate constant, gas-phase oxidation products and radical budgets" by Zhaofeng Tan et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-556-AC1>, 2021

We thank the reviewer for his/her comments, which helped to improve the manuscript. Please find below our answers.

Comment: PG 3: Oxidation mechanism of myrcene: The SAR of Peeters 2007 has recently been used and updated in the protocol by Jenkin et al., 2018 on the "Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction". Have you looked at this to see if it gives different results to Peeters 2017? Never the less, the Jenkin et al., 2018 work should be cited here also.

Answer: Thanks for reminding us of the work by Jenkin et al.. The SAR used in Peeters et al. (2017) and Jenkin et al. (2018) give indeed similar predictions of the reaction rate constant of the reaction of myrcene with OH. We added in Line 415 "The reaction rate constants calculated from structure-activity relationship (SAR) by Peeters et al. (2007) and Jenkin et al. (2018) give similar results between 1.8 to $1.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Values are approximately 20 % lower than the experimentally derived reaction rate constants. However, differences are within the accuracy of SAR predictions." Reaction rate constants derived from Jenkin et al. (2018) are added in Table 4.

Comment: Could epoxide formation in this system (c.f. IEPOX from isoprene + OH) also be an important pathway in the myrcene mechanism, with important implications on SOA formation?

Answer: products are formed as a third-generation product and are not very reactive with OH. For potential SOA formation not investigated in these experiments, epoxide formation could be of importance. However, for the photochemistry experiments in this work the chemistry was dominated by the first oxidation step of myrcene. This was ensured by the re-injection of myrcene once it had reacted away. Therefore, the formation of third-generation products did not play a role for the gas-phase chemistry. Thus, we cannot draw any conclusions about potential formation of epoxide products from these experiments.

Comment: PG 3: Spelling: "epxperimental" and "Peters"

Answer: Corrected.

Comment: PG 4, line 111: Should "Fig 1" be "Fig 2"?

Answer: Corrected.

Comment: PG 5, line 129: "e.g." wrong place

Answer: Corrected.

Comment: PG 5, line 130: add the experiment RH values to Table 1

Answer: Added.

Comment: PG 5, line 131: define "medium" NO in the context of your experiments

Answer: We clarify in Line 131: "two of which were done at medium levels of nitric oxide (NO) ranging from 0.1 to 0.4 ppbv (18 August 2012..."

Comment: PG 5, line 140: "Approx 50 ppbv O3 added..." - therefore ozonolysis of myrcene will form products similar to the OH reaction, potentially interfering with the mechanistic results. This needs to be discussed further here, and you need to show evidence that interferences from ozonolysis is minimized in these experiments (which you discuss later).

Answer: We added in Line 140: "Products from the ozonolysis of myrcene are similar to the products formed from the reaction with OH. These could lead to systematic errors in the conclusions with respect to the OH oxidation scheme. Given the typical OH concentration in this study ($5 \times 10^6 \text{ cm}^{-3}$), the contribution of ozonolysis to the entire oxidation of myrcene is less than 20%. The potential interfering is minimized in the medium NO cases, where ozonolysis only contributes 10% of the myrcene oxidation."

Comment: PG 5, line 142 – 145: I am unsure how these concentrations discussed here map onto those given in Table 1, i.e. 2.3 ppbv for the first injection in the "medium" NO expts and 0.8 ppbv for the first injection in the lower NO experiments...?

Answer: We corrected the numbers in the text: "Injections were done 2 times (approximately 2 ppbv each) in experiments with medium NO and four injections with smaller concentrations (approximately 1 ppbv) were done in the other experiments."

Comment: PG 5, line 146 – 149: again, cross reference the concentration data with the data given in Table 1

Answer: We changed the numbers in Table 1.

Comment: PG 6, line 163: How do the different methods of measuring HCHO compare? (and show evidence they are comparable in the experiments here, or that they are comparable from other SAPHIR experiments)

Answer: We added in Line 163: "The HCHO concentrations measured by the different methods has been shown to agree within 10% in a series of experiments in the SAPHIR chamber, in which both instruments concurrently measured (Glowania et al. 2020)."

Comment: PG 7, line 197: VOC reactivity and RO₂ speciation in myrcene experiments – give a brief explanation of how $k'(OH)$ was measured here

Answer: We added after the first sentence of this paragraph: "Total OH reactivity was measured by LP-LIF while the speciated OH reactivity for individual species X was calculated from the products of concentrations of X and its reaction rate versus OH."

Comment: PG 11, line 313: you need to provide information on where the ozonolysis OH and RO₂ yields are derived from in Table 3. What about the ozonolysis yields of HO₂?

Answer: We added in Line 313: "The applied rate constants are listed in Table 3. The OH and RO₂ yields are taken from Deng et al. (2018)., In their work, the yield of HO₂ is zero."

Comment: PG 13, line 378: "reactivity"

Answer: Corrected.

Comment: PG 13, line 379: Why was the methane experiment, which is key to understanding the uncertainties of this analysis, not repeated with the DOAS OH measurements? (and ideally a different CH₄ measurement?) Could experiments on a simple, well known alkene + OH system (such as ethene or TME) also be useful here?

Answer: In other experiments, DOAS and LIF measurements well agreed as demonstrated in a number of publications. One example is shown in the work Novelli et al. (2020), in which isoprene oxidation experiments are analyzed. It is certainly useful and will also be done to repeat the experiment regularly and to use other systems. In this work, we want to demonstrate the concept of the analysis and to estimate the accuracy that can be achieved.

Comment: PG 13, line 386: Both JPL and IUPAC need to be referenced appropriately

Answer: We added the references.

Comment: PG 14, line 399 and 401: appropriately reference "?"

Answer: Corrected.

Comment: PG 14, line 415: Jenkin et al., 2018 gives an My + OH rate constant (298 K) of $1.88E-10 \text{ cm}^{-3} \text{ s}^{-1}$ (see earlier comment with respect to update to the Peeters 2007 SAR...)

Answer: We added the results from Jenkin et al., 2018 in the text and in Table 4.

Comment: PG 15, line 440: Derive the yields from Jenkin et al., 2018 as well. Could you not also use a simple model to show the impact of RO₂ isomerisation reactions on the carbonyl yields? Which instrument(s) was used to measure the HCHO yields in the different experiments here? How do the different methods compare?

Answer: We derived the yields from Jenkin et al. (2018) and changed the first sentence: "... the isoprenyl part (Peeters et al., 2007). In comparison, the SAR developed by Jenkin et al. (2018) predicts a branching ratio of 63:37 for the OH addition to the $-\text{CH}=\text{C}(\text{CH}_3)_2$ moiety and the isoprenyl part, consistent with values reported in Peeters et al. (2007)."

The calculation of the formaldehyde yield from measurements takes into account the sources and sinks, in order to derive the yield from the OH oxidation of myrcene. This is compared to numbers expected from the oxidation scheme. A chemical model essential would give the same answer. This is also the case for other carbonyl products.

The question about the formaldehyde measurements is answered above.

Comment: PG 17, line 499: "well agrees"

Answer: Corrected.

Comment: PG 18, line 534: "Sensitivity model runs" Explain how these models were built and run here. In fact, there was no "model run", but numbers were varied to calculate turnover rates of reactions.

Answer: We changed the sentence: "A sensitivity test shows that using a bulk isomerization reaction rate constant of 0.05 s^{-1} instead of 0.02 s^{-1} would be sufficient to balance the RO_2 production rate."

Comment: Table 2: "acetaldehyde" (spelling): How and why was this measured here?

Answer: We removed the information about acetaldehyde in the table as its photolysis only makes a negligible contribution to the radical production rate.

Comment: Table 3: R4 - ?

Answer: Corrected.

Comment: Table 4: Add the value derived from Jenkin et al., 2018 – $1.88\text{E}-10 \text{ cm}^3 \text{ s}^{-1}$

Answer: We added the value in Table 4.

Comment: Figure 8: This figure is a bit messy, and could be clearer. Separate into 2 Figures (i.e. Figure 8a and Figure 8b)

Answer: We changed the figure as suggested.

References

Jenkin, M. E., et al., Estimation of rate coefficients and branching ratios for gas-phase reactions of OH with aliphatic organic compounds for use in automated mechanism construction., *Atmos. Chem. Phys.*, **18**, 9297–9328, 2018
[.https://doi.org/10.5194/acp-18-9297-2018](https://doi.org/10.5194/acp-18-9297-2018)

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