Review of Tan et al.
Anonymous Referee #2

Referee 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-RC2, 2021

This paper presents measurements of the oxidation of myrcene in the SAPHIR chamber that are used to test a proposed OH-initiated oxidation mechanism. This is one of the first detailed experimental investigation of the myrcene oxidation mechanism. The authors include rapid RO2 interconversion steps through reversible oxygen addition as well as H-shift isomerization reactions similar to that in the oxidation of isoprene with estimated rate constants based on structure activity relationships (SAR). To test the mechanism, the authors measure OH, HO2, and RO2 radicals and several products during oxidation experiments at different mixing ratios of NO. In addition to measuring the rate constant for the OH + myrcene reaction, the authors measured the product yields of acetone and formaldehyde as well as the yield of organic nitrates and compared their results to previous measurements and SAR predictions. A radical budget analysis using the measured concentrations of radicals and their sources and sinks revealed that the total radical production and loss could only be balanced if the rate constant for the HO2 + myrcene RO2 termination reaction was approximately 40% lower than that predicted by the SAR or if this reaction significantly regenerated HOx radicals. Overall, the measurements suggest that the myrcene oxidation mechanism is complex and likely involves RO2 interconversion and isomerization reactions.

The paper is well written and provides new information regarding the myrcene oxidation mechanism and will be suitable for publication after the authors have addressed the following minor comments.

Page 6, line 170: While it does appear that a calibration error may be responsible for the discrepancy between the LIF and DOAS measurements of OH on 22 August given that the LIF and DOAS measurements agree during the 2013 measurements, the authors should comment on whether an unknown interference similar to that observed by Fuchs et al. (AMT, 9, 1431–1447, 2016) might be responsible for the discrepancy.

Page 14, lines 399 and 401: The authors should clarify the “?” reference referred to in this section.

Page 16, line 496 and Figure 10: The authors should clarify the adjustments made to the
MyO2+HO2 reaction to bring the radical loss into balance with production with the actual factor used to (between 0.4 and 0.7) in the text and in the caption to Fig. 10, perhaps also including the uncorrected loss rates for comparison.

Pages 17-18, lines 528-530: The authors provide a sensitivity study to show the impact of additional MyO2 isomerization reactions on the production and loss of RO2 radicals in Figs. 11 and 12, producing one HOx radical for each isomerization reaction (line 529). How does the addition HOx production impact the OH and HO2 radical budgets in Figs. 11 and 12? Does it improve the radical balance or make it worse?