

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-575

Anonymous Referee #1

Referee comment on "Biomass burning plume chemistry: OH-radical-initiated oxidation of 3-penten-2-one and its main oxidation product 2-hydroxypropanal" by Niklas Illmann et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-575-RC1>, 2021

In this work, the authors provide a kinetic and mechanistic study of the OH-initiated oxidation of 3-penten-2-one (3P2), and its by-product 2-hydroxy-propanal (2HPr), chemistry that is of potential importance in biomass burning plumes. Major outcomes of the work include a first-time determination of the products of the OH-initiated oxidation of the two species, and a determination of the rate coefficients for their OH reaction (each of which was the subject of one previous study).

It is my opinion that this is likely to be a publishable body of work, although I think there are a few quantitative issues that need to be resolved before publication is recommended.

My major comment has to do with the modeling work that is done. I think much more needs to be said about the details of this modeling (even though this is outlined in a recent paper by the same authors), to lend confidence in the key parameters that are derived from it (e.g., $k(\text{OH}+2\text{HPr})$, branching ratios for this reaction, 'corrected' yields of various products). First, the details of what is included in the model, how it is run, what parameters are varied, etc., needs to be included. Further, the sensitivity of the model output to the varied parameters needs to be shown (presumably graphically). As examples, how sensitive is the model to the OH/2HPr rate coefficient, to the branching ratios to the two channels in this reaction, etc. What does an 80:20 branching in the OH/2HPr reaction look like compared to 70:30 or 90:10? Etc...

More minor remarks:

How is the 3P2 introduced into the chamber and how is its initial concentration determined? In particular, if this calibration is volumetric or similar, how is the 85% purity of the purchased sample dealt with?

Page 6 – Did the authors determine a wall loss for the reference species used in the $k(\text{OH})$ determinations? If so, were they negligible? What fraction of the 3P2 loss is due to the walls compared to the loss due to OH reaction in a typical experiment?

Page 7 – The formation of acetaldehyde from the large Criegee radical formed in the 3B2OL / O₃ system is a bit surprising to me. A standard pathway for decomposition might be to form OH and methylglyoxal, rather than acetaldehyde? Can the authors provide any further ideas or speculation on its formation mechanism? (Any chance of impurities existing in the alcohol?).

Minor corrections, suggestions, etc.:

I don't know what an Euler-Cauchy model is. Please explain briefly.

Page 2, line 33, I suggest "Unsaturated ketones are of increasing interest as ..."

Page 2, line 43, I suggest "is believed to be a ..."

Page 2, line 48, I suggest "Some field measurements of BB plumes..."

Page 2, line 59, I suggest changing "Besides" to "In particular" (or something similar).

Page 2, line 59, Change "expand" to "expanding".

Page 6, line 167: Maybe "all of the experimental results" instead of "the whole..."

Page 7, line 184: 'coexist' instead of 'coexists'.

Page 12, line 290: Specify that this is from the OH + 3P2 reaction.

Page 14, line 360, also Page 16, line 392: The equivalent yields of the two products does not prove that they come from the same pathway. I suggest using different wording here.

'suggests' or 'consistent with'?

Page 17, top: Nitrates are quite strong absorbers in the IR. Was there any sign of their formation? Can any limit on their yield be obtained, using nitrate IR cross sections (which are reasonably transferable) from other works?

Page 17, line 413: Specify that it is 3P2 that you are referring to.

Page 17, line 419: While I agree that 3P2 (and by-products) are a source of PAN, the overall contribution to NO_x reservoirs will depend on the concentrations of 3P2 relative to other PAN sources. Perhaps 'soften' the language here?