Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC3
https://doi.org/10.5194/acp-2021-575-RC3, 2021

Comment on acp-2021-575

Aparajeo Chattopadhyay (Referee)

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-RC3, 2021

General comments:

This study by Illmann et al. describes kinetics, products study, and reaction mechanism for the OH-initiated oxidation reaction of 3-penten-2-one which had been detected in biomass burning plumes. To understand biomass burning chemistry and its role on tropospheric ozone and SOA formation, the chemistry of individual chemical components of a biomass burning plume should be known. This study presents a comprehensive understanding of the atmospheric chemistry of 3-penten-2-one which could be important from biomass burning perspective. The authors also discussed OH reaction for 2-hydroxypropanal which is an oxidation product of 3-penten-2-one.

This work is of high scientific quality and is suitable for readers of Atmospheric Chemistry and Physics (ACP). However, in many cases, the detail about the measurements and the analysis is missing in the manuscript which could bring questions to the mind of the readers. Therefore, I recommend publishing this manuscript in ACP after addressing the issues mentioned below. Necessary modification to the manuscript should be done accordingly.

Specific comments:

1. Page 4, line 117: A polynomial function was used for CO_2 calibration. Any possible reason why a linear correlation was not observed?

2. Page 4, line 121: Describe Euler-Cauchy approach. At least some details are required for the readers of this manuscript who are not familiar with this method.

3. Page 5, line 147: The sample purity is low. Even a sample purity of 85% is not good in this kind of precise measurement and it could severely impact the product studies. It creates a lot of uncertainty if we don't know what is that 15% impurity and what chemistry it can bring here.

Did you try to distill the sample?

Given the fact that the IR cross-section of 3-penten-2-one was determined in the present study, it is not possible to check impurities using FTIR if you don't have reference spectra of the sample from other independent studies that used more pure samples.

FTIR itself is not sensitive enough to identify small impurities and a more sensitive method e.g., GCMS could have been used.

4. Page 6, line 154: Why is the loss rate of the sample about one order of magnitude larger in the chamber having higher volume? I expected an opposite trend as the S/V is expected to be less for the larger cell.

Please show representative first-order decay plots for wall loss in Supplement.

What are the S/V values for the two chambers?

What are the wall loss rates for the reference compounds?

5. Page 6: 3-penten-2-one + OH kinetic data looks satisfactory. For presentation purposes, the data points for individual experimental runs could be shown using different symbols/colors to highlight data quality for individual experimental runs.

Typically, how much corrections (in percentage) were made on individual data points to account for the 3-penten-2-one wall loss?

It was noted that a previous study from the same laboratory reported a rate coefficient that is slightly higher than the number obtained in the present study. It was noted that they agree within 20%, to my opinion this difference is rather large. Mesityl oxide was an impurity in the previous study, but this should not bias kinetic results in relative rate measurements if it does not interfere with your spectral subtraction. In fact, when I see kinetic data for Isoprene reference (Figure 1), there are some points (probably correspond to the last row of Table 1 i.e., Expt 3P2#6) that are bias low making the whole kinetic data scatter and the rate coefficient bias low. If only E2-butene data are considered, then the correspondence is much better ~ 10%.

6. Page 7: In situ generation of 2-hydroxypropanal – Determination of 2-hydroxypropanal (2HPr) infrared cross-section, which was used later for its yield determination, is based on the assumption Yield (2HPr) = 1 – Yield (HCHO). This assumption is valid if HCHO is formed only by pathway a (Figure 2) and 2HPr is formed only by pathway b and there are no other pathways for POZ decomposition. The authors did not discuss the total fate of corresponding CIs (from pathways a and b) which can complicate the analysis. For example, the CI for pathway b for 3B2OL is CH_2OO i.e., the simplest Criegee Intermediate. Bimolecular self-reaction of CH_2OO (whose rate is very fast) could form additional HCHO, then the above assumption would be invalid. Similarly, it was shown that the branching ratio for acetaldehyde formation from the CI that is produced from pathway a is 0.36, what is the fate of the rest of CI? If there is a bimolecular self-reaction, then it would produce additional 2HPr. Give proper evidence that these bimolecular self-reactions of CIs are not happening in your experimental condition.

The quoted uncertainty for OH absorption band cross-section is very high which would make the product yield data unreliable. The high uncertainly was chosen for the error on the HCHO yield and wall loss of 2HPr. Give more details on that.

Does the wall loss follow the first-order decay?

Did you also observe wall loss for 3B2OL and corrected it?

7. Page 11, line 266: If the loss of acetaldehyde and methylglyoxal by OH reaction is significant, should not you observe nonlinearity in their yield data (Figure 4) at longer times?

8. Figure 5: The fate of CH_3CO radical following reaction with O_2 and NO is shown to be the formation of CO_2 and HCHO. If HCHO is formed by CH_3OO reaction, then other products such as methanol are also expected.

9. Page 13, line 312: Describe the model that was used to correct 2HPr yield due to the 2HPr + OH reaction. Input/output could be provided as a Supplement.

10. Page 13, line 330: A rate coefficient for 2HPr + OH reaction is quoted but the details on how this number was obtained are not presented. Please provide the necessary details. The rate coefficient differs from a previously measured value by 30% which is not an excellent agreement.

11. Page 14, line 353: Again, the details of the model that was used to find the branching ratios, was not given. Provide necessary details here and Input/Output as a supplement.

Did you do any sensitivity analysis?

12. Page 17, line 416: The authors have concluded that OH reaction is the dominant degradation process since they did not observe measurable photolysis in their experiments. This is not true because UV light intensities and OH concentration in the chamber and in the real atmosphere are not the same. In general, aldehydes have photolysis lifetimes that are comparable with OH reaction lifetimes. A conclusion on this can only be made after evaluating its atmospheric photolysis lifetime from UV absorption cross-section and quantum yield values.

Minor technical correction:

1. Title: The word “main” could be omitted as there are other major oxidation products.

2. Page 9, line 229: Also add 2HPr.