



## Comment on acp-2021-575

Anonymous Referee #2

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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-RC2>, 2021

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This paper presents the results of a kinetic and product study of the reactions of 3-penten-2-one (3P2) with OH, which relevant to models of biomass burning plume chemistry. The results gave reasonably well characterized rate constants and product yield data, and should eventually be published. They also investigate the kinetics and mechanisms of its oxidation product 2-hydroxy propanal (2HPr) by modeling irradiations of reaction mixtures after it is formed in the experiments with 3P2. The results were used primarily as a means to correct the yield data in the 3P2 experiments for secondary reactions, but also provide a useful addition to the literature, though the results for 2HPr are more uncertain because they are obtained from modeling a complex system.

The use of modeling with a simplified mechanism to correct the yield data presents some uncertainties, most of which are discussed in the text. However, the approach seems reasonable though not well described (see below). Fortunately, the corrections do not have an excessively large effect on the reported yields (see Table 2), and the general conclusion that the 2HPr + acetyl peroxy route is about twice as important as the methyl glyoxal + acetaldehyde route is not affected. This is an interesting result in the context of SAR development, as well as for improving models for 3P2 reactions.

Although this paper makes a contribution to the literature and should eventually be published, it does have some problems that need to be addressed. Most of the problems with this paper were noted in the posted review of Anonymous Reviewer #1, which I have read prior to writing my comments (but after reading the paper), along with the response by the authors. I agree with the comments of this reviewer, and believe that for the most part (but see below) the authors propose changes that should adequately address these comments.

The major problem noted by Reviewer #1 is the inadequate description of the modeling method used to correct the data and obtain the yield parameters. As the reviewer noted, the reference to the "Euler-Cauchy" model to derive parameters or corrections to the data is unclear, since this refers to a general solver method that could be applied to any system. In response, the authors improved the text around line 120 to better describe how the corrected yields were derived. The new Table 2 is a valuable addition to the text.

However, the proposed changes to the reference of "Euler-Cauchy" in the abstract is not

totally adequate. In responding to the reviewer, they changed the sentence in the abstract from "Employing an Euler-Cauchy model to describe the temporal behaviour of the experiments, the further oxidation of 2HPr was shown ..." to "Employing a simple modeling tool describe the temporal behaviour of the experiments, the further oxidation of 2HPr was shown ...". However, the modeling tool did not describe the temporal behavior of the chemical system, their assumed mechanism (given on the new Table 2) did. A better change may be "Employing a simple chemical mechanism to analyze the temporal behaviour of the experiments, the further oxidation of 2HPr was shown ...". The modeling methodology need not be given in the abstract, since it is not newly developed in this study, and is presumably adequate.

Reviewer #1 also noted that reaction of the hydroxy-substitued Criegee intermediate shown on Figure 2, forming acetaldehyde. is not the expected pathway. In any case, Figure 2 doesn't show the whole mechanism for the CI decomposition, since not all atoms are accounted for. In response, the authors wrote that acetaldehyde formation was unexpected and may be due to experimental impurities, and that speculation of the CI mechanism was beyond the scope of this work. But at least they should give a complete proposed mechanism on Figure 2, or show a "?" and "+ other products" on the figure to indicate that they don't know the mechanism.

However, there is quite a reasonable explanation for acetaldehyde formation from this CI on Figure 2. The H on the -OH could move to the outer O on the intermediate via a 6-member ring transition state, which could then rearrange rapidly to form acetaldehyde + formaldehyde + OH. This may not be the only route (the other route forming methyl glyoxal as the reviewer noted could also occur), but it is possible acetaldehyde formation may occur at least part of the time (and maybe dominate). Perhaps add both routes to Figure 2 and state in the discussion that relative importance of each is uncertain and not further investigated in this work.

Reviewer #1 noted other problems with the paper, but it appears that the authors' responses were adequate, so I will not discuss them here. However, I have a few additional comments and suggestions. Other than these, I did not see major additional problems with the paper.

It was unclear whether the product concentrations plotted on Figure 4 have been corrected for secondary reactions when that figure was first introduced. Later (around line 314) it is implied that Figure 4 shows uncorrected data. It might be a good idea to show both corrected and uncorrected data on Figure 4, so one can get a feel of the size and effects of the corrections.

Around line 294 it was stated that yield plots of 2HPr showed "small but precise" curvature. However, the 2HPr data on Figure 4 don't look particularly curved. Are they referring to corrected data? If so, this is another reason to include corrected data on Figure 4.

The failure to observe the PAN analogue  $\text{CH}_3\text{-CH}(\text{OH})\text{-CO-OONO}_2$  shown in Figure 7 might be due to another rapid 1,4 H-shift reaction where the H on the -OH moves to the peroxy O next to  $\text{-NO}_2$ , forming  $\text{HNO}_3$  and (ultimately)  $\text{CO}_2$  and acetaldehyde. This could be potential source of acetaldehyde in the system that is not accounted for in their model (new Table 2). Would this affect the acetaldehyde yield from 3P2 that fit the data?