

Authors' responses to comments from Anonymous Reviewer #2 on: Illmann et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-575>

The original comments are shown in black and our responses are marked in blue. Changes made in the text are marked in red.

Comment 1a: 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.

Response: We thank the referee for the comments.

Comment 1b: 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.

Response: The sentence “Fortunately, the corrections do not have an excessively large effect on the reported yields” suggest the possibility of a misunderstanding. The secondary processes for which the corrections were made have a certain antagonistic effect on the net formation of a product, which is reflected in the modelled yield values.

Comment 1c: 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.

Response: We understand that the reviewer read the comments of Anonymous Reviewer #1 and our answers before making his own comments. We wonder if the purpose Reviewer #2 in mentioning this, was to avoid duplicating the issues raised by Reviewer #1. Sometimes he describes the comments of Reviewer #1 and the corresponding answers without making a clear statement. An example is: “I [...] believe that for the most part (but see below) the authors propose changes that should adequately address these comments“. Does the referee agree or not with the changes we made? If he disagrees, we would kindly ask him for a clear statement. Further, in our understanding “[...] changes that should adequately address these comments” does actually mean that they DO NOT adequately address these comments.

Comment 2: 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.

Response: The comment denotes a certain misunderstanding caused by the use of "model" and "method" in the original text. Reviewer #1 asked for more details on our approach, but he also asked what a "Euler-Cauchy-Approach" is (which has probably been a misunderstanding). On the other hand, what does "since this refers to a general solver method that could be applied to any system" mean? This is actually what has been done! Besides, we cite a previous work from our group where a description of the method is given.

Comment 3: 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.

Response: With all due respect, but the abstract should contain information on how the results were derived. The methodology is not given in the abstract, it is just said that branching ratios of the product were derived from modelling. Besides, since employing a simple chemical mechanism is exactly what we do with our simple modelling approach, the referee's suggestion would not change the content of this sentence. What does "presumably adequate" mean? The methodology can be either adequate or not. If not, the referee should provide a comment on that.

Comment 3: Reviewer #1 also noted that reaction of the hydroxy-substituted 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.

Response: Once again, the referee is summarising a comment of Reviewer #1 and our response. With due respect, this comment shows that RC2 possibly did not read carefully the RC1's comments nor the paper. We DID NOT say that acetaldehyde formation may be due to experimental impurities. This has been a suggestion from Reviewer #1 and we explained why this is very unlikely. Fig 2 does not show the whole mechanism. This has never been claimed and it is not necessary to do so. Fig 2 does show the details necessary to understand how we derived a cross section for 2HPr. Given that acetaldehyde can only be formed from the larger CI, one cannot use 3P2OL for the cross section determination since there are two pathways forming acetaldehyde. We gave some thoughts to an in-depth analysis of the O₃ reaction, including all RO₂ reactions possible in the

experimental system, and this would deliver enough material for a paper of its own. Therefore, it is clearly beyond the scope of this study to include a whole mechanism.

Comment 4: 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.

Response: If the H atom of the OH-group were abstracted, this could not result in formaldehyde since there is only one H atom at the corresponding carbon atom. We agree that based on the current knowledge of CI chemistry one would also expect methyl glyoxal as a product. However, we could not confirm its formation in our experiments. On the other hand, the referee does also suggest that acetaldehyde is formed from the larger CI. This is the relevant information. Therefore, we do not see the necessity to include further speculations since this would not change our conclusions.

Comment 5: 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.

Response: We do not know how to understand this comment. What does “it appears that the authors' responses were adequate” mean? Either they are adequate or the referee should comment on that, if not. Moreover, Reviewer #1 has to judge if our responses to his comments are adequate.

Comment 6: 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.

Response: When Fig. 4 is first introduced (lines 229-230) it is said that 3P2 is corrected for the wall loss whereas no corrections were mentioned for the quantified products. Besides, the axis' inscriptions in Fig. 4 include the index “corr.” only for 3P2. This all implies that no corrections were performed on the products' data. However, we understand that at least when introducing the figure this should be clearly pointed out. We therefore added in the parentheses in line 230:

“Plots of the identified products (in ppmV **without corrections**) [...]”

On the other hand, inclusion of corrected product data in Fig. 4 would presume that we calculated the corrected mixing ratio for each data point. This is not the way we performed corrections. As written in the manuscript, the first-generation yields were obtained through modelling of the temporal behaviour of each quantified species, given that beside 2HPr all other reaction products have secondary sources in the experimental system. Therefore, we prefer to keep Fig. 4 as it is.

Comment 7: 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.

Response: The referee is missing an important point since we have written "a small but precise curvature IN EACH EXPERIMENT". When plotting each experiment separately, the plot for 2HPr is precisely non-linear. But all experimental data are shown in one plot as written in the figure caption. Besides, the data from 480 L chamber were scaled to fit within the scale of the 1080 L data. Due to the statistical variation the non-linearity might be nearly invisible when combining all data. We had to find a middle way between giving all information without overloading the figure.

To avoid misunderstandings we modified the paragraph (lines 294 – 295) as follows:

"On the other hand, the yield plots of 2HPr show a small but precise curvature when the data set ~~is~~ of each single experiment is plotted separately. This effect becomes nearly invisible in Fig. 4 due to statistical scattering when combining all data and scaling the data of the 480 L chamber experiments into the scale of the 1080 L chamber experiments."

Comment 8: The failure to observe the PAN analogue CH₃-CH(OH)-CO-OONO₂ 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 -NO₂, forming HNO₃ and (ultimately) CO₂ 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?

Response: This is a very interesting point describing a potential additional loss process of the PAN analogue, besides the thermal decomposition. However, the referee is describing an 1,5 H-shift (instead of 1,4 H-shift), which is expected to be much slower than a 1,4 H-shift. Since no information on the thermal stability of the PAN analogue is available, any further statement on a competition between an H-shift induced decomposition and the classical thermal decomposition would be highly speculative. On the other hand, while the H-shift reaction would yield, as the referee suggested, acetaldehyde and CO₂, the thermal decomposition would recycle the RO₂ radical which, in turn, yields acetaldehyde and CO₂ as well. Therefore, the modelled time profiles and thus the obtained branching ratios are independent from whether the PAN analogue species is just thermally unstable or additionally decomposes through the H-shift reaction.