Authors' responses to comments from Aparajeo Chattopadhyay on: Illmann et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-575

We thank the referee for the comments on this work. The original comments are shown in black and our responses are marked in blue. Changes made in the text are marked in red.

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.

Response: We thank the referee for the examination of our work.

Specific comments:

Comment 1: 1. Page 4, line 117: A polynomial function was used for CO2 calibration. Any possible reason why a linear correlation was not observed?

Response: This is a common behaviour observed for small molecules like NO, CO and CO_2 when working with FTIR spectroscopy. These instruments are usually operated at a resolution of 1 cm^{-1}. The absorptions of the above mentioned molecules consist of a resolved line spectrum (= discontinuous spectrum) where the energy difference of different transitions between rotational levels are << 1 cm^{-1}. Therefore, a single data point reflects an average of several absorption lines. It is generally possible to obtain a calibration function for the integrated absorption. However, due to the fine structure of the absorption features one has to calculate different calibration functions for different sizes of the integrated absorption. Accordingly, a linear behaviour is only observed for very low integrated absorptions.

Comment 2: 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.

Response: Considering also the comments of Anonymous Reviewer #1 we understand that the way we used the terms "Euler-Cauchy approach" or "Euler-Cauchy model" was confusing. On the one hand, we noticed that in contrast to German the common English term is "Euler method" and we changed this accordingly in the whole manuscript. On the other hand, the method describes only the most basic numerical procedure to solve differential equations. Our simple model, used to describe the temporal behaviour of the quantified species, can be basically written down in calculation programs like Microsoft Excel. Therein, the branching ratios (corresponding to the first-generation yield) of the simplified reaction scheme are included as parameters and varied until the simulated profile matches the experimental data. To avoid misunderstandings we modified the brief model description (page 4, lines 120–124) as follows:

"In order to obtain first-generation yields ~~These yields were corrected for~~ (= yields without impact of secondary reactions in the experimental set-up) ~~using the Euler-Cauchy~~ the temporal behaviour of all quantified species was simulated following the approach previously outlined in the recent literature (Illmann et al., 2021b). Here, the differential equations are constructed based on the simplified reaction sequence of each species and solved by the Euler method using calculation programs like Microsoft Excel. Input parameters are the rate coefficients of each of the sequence's reaction, the initial concentration of 3P2 and a time-dependent OH-concentration calculated based on the 3P2 consumption. The molar formation yields for products of the target reaction are included as variable parameters to be modified ~~varied~~ until the simulated temporal behaviour of each species matches the experimental data. The details are provided within Sect. 3.4."

To avoid confusion, the abstract was modified as follows:

"Employing ~~an Euler-Cauchy model~~ a simple modelling tool to describe the temporal behaviour of the experiments, the further oxidation of 2HPr was shown …"

Comment 3a: 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.

Response: See below (Response to 3a, 3c, 3d)

Comment 3b: Did you try to distill the sample?

Response: No. But if purification could be easily achieved through distillation, the suppliers would offer samples with purities higher than technical grade.

Comment 3c: 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.

Response: See below (Response to 3a, 3c, 3d)

Comment 3d: FTIR itself is not sensitive enough to identify small impurities and a more sensitive method e.g., GCMS could have been used.

Response to 3a, 3c, 3d: As written in the experimental section, we compared spectra of the 85% sample with spectra of a 70% sample where the impurity consists almost exclusively of mesityl oxide (= 4-methyl-3-penten-2-one). FTIR spectra of the 70% sample after subtraction of mesityl oxide were found to be identical to the

FTIR spectra of the 85% sample. Therefore, it is quite certain that the absorption features present in the spectra of the 85% sample belong to 3P2 exclusively. The integrated absorption signals used for the cross section determination are therefore unlikely affected by impurities. Maybe our statement in lines 148 – 149 was not precise enough since we have written that the 70% sample contains “mainly 4-methyl-3-penten-2-one as impurity”. However, the supplier states that the sample contains 30% 4-methyl-3-penten-2-one. We therefore modified the sentence as follows:

“Another sample of 70% purity (technical grade) contains, as stated by the supplier, ~~mainly~~ 30% 4-methyl-3-penten-2-one as impurity.”

We agree that impurities, if organic, could perhaps be identified with GC-MS. However, this technique was not available.

The match between spectra of the 85% sample and the 70% sample, after subtraction of 4-methyl-3-penten-2-one, indicates that there is no single compound dominating within the impurities of the 85% sample. Any effect on the observed and quantified reaction products would presume that 1) the impurities would either photolyze or react with OH with rates that are similar to the experimentally observed loss rates of 3P2, and 2) a large fraction of the impurity and hence several compounds would yield the same reaction products as 3P2. This is very unlikely.

Comment 4a: 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.

Response: This behaviour is quite normal in our chambers. In this case, the wall losses are rather affected by the wall properties than by the S/V ratio. In contrast to borosilicate glass (480 L chamber) the surface of quartz glass (1080 L chamber) is acidic which sometimes causes much larger wall losses.

Comment 4b: Please show representative first-order decay plots for wall loss in Supplement.

Response: We do not see any benefit from including representative first-order decay plots for the wall loss since these were determined in each single experiment, as written in the manuscript, and vary from day to day depending on the wall properties. Time-profiles for product studies conducted in both chambers were given in Figs. 8 and 9 (of the originally submitted manuscript). These do clearly show the different behaviour of 3P2 in the dark and in our opinion this is sufficient.

Comment 4c: What are the S/V values for the two chambers?

Response: As mentioned above, the S/V ratios are not responsible for the different behaviour towards the chamber wall.

Comment 4d: What are the wall loss rates for the reference compounds?

Response: The reference compounds did not show any wall loss. For clarity, we included this in lines 154 – 155:

"The first-order wall loss of 3P2 was < 1 ×10^{-5} s^{-1} in all 480 L chamber experiments and in the range of (5–10) ×10^{-5} s^{-1} in the 1080 L chamber experiments, respectively. Typically, the consumption through OH radicals was about one order of magnitude faster than the wall loss. The reference compounds did not show any wall loss. "

Comment 5a: 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.

Response: We thank the referee for this suggestion and updated Fig. 1 and the corresponding figure caption as follows:

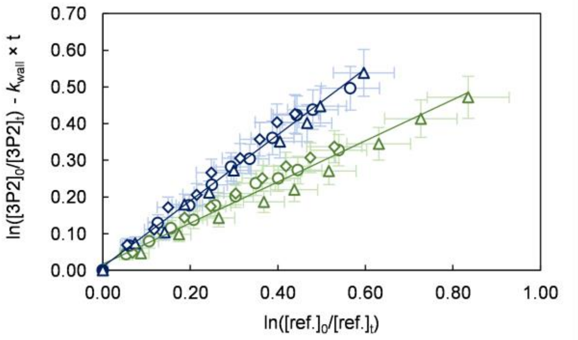

Figure 1. Relative-rate plots of all experiments using isoprene (green) and E2-butene (blue) as references. Different experimental runs for each reference are denoted with different symbols. The error bars consist of a systematic uncertainty and an additional 10% relative error to cover uncertainties derived from the experimental and evaluation procedure, respectively.

Comment 5b: Typically, how much corrections (in percentage) were made on individual data points to account for the 3-penten-2-one wall loss?

Response: Typically, < 10%.

Comment 5c: 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%.

Response: The reviewer observed correctly that there was one experiment, when isoprene was used as the reference compound, yielding slightly lower values. However, we could not find any reason to exclude this experiment from the rate coefficient calculation. The observation that "if only E2-butene data are considered, then the correspondence is much better ~ 10%" is true but might just be coincidence. For the rate coefficient determination it is necessary to perform a statistically relevant number of experiments and hence one should always avoid working with only one reference compound. However, analyzing the data shows they are no outliers. We do not completely understand the statement of referee #3 since, considering only half of our results would end up in optimizing the results, which, for sure, was not intended by the reviewer.

It is the reviewer's personal opinion, as stated by himself, that a difference of 20% is "rather large" in between the two rate coefficient determinations. In our opinion, a difference of 20% is quite good, given that even IUPAC recommendations do not seldomly exceed uncertainties of 20% for species where many datasets are available. The additional mesityl oxide and consequently its reaction products add complexity to the reaction system and the FTIR spectra, which could theoretically interfere with the subtraction procedure. However, it is not our purpose to judge the previous measurements. Moreover, the statement was based on comparing the average values solely. We should have mentioned that considering the uncertainties both values are the same. To avoid confusion, we modified the sentence (line 172) as follows:

"Nevertheless, both determinations agree within 20% and the value obtained here is within the uncertainties of the former study."

Comment 6a: 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 CH2OO i.e., the simplest Criegee Intermediate. Bimolecular self-reaction of CH2OO (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.

Response: Based on our current understanding of O_3 reactions there are no POZ decomposition pathways other than the two decomposition routes yielding one or the other primary carbonyl and the remaining Criegee Intermediates. A fraction of the O_3 + 3B2OL reaction could hypothetically yield an epoxide. As already mentioned in the manuscript, there is no hint for epoxide formation. We did not discuss the whole fate of the Criegee Intermediates since deciphering every reaction channel and possible RO_2 reactions in the experimental system is clearly beyond the scope of this study.

The reviewer suggests secondary sources of both primary carbonyls through self-reaction of the CIs. Bimolecular reactions of Criegee Intermediates are, on the one hand, limited to the fraction of stabilised CIs since the other CI fraction undergoes prompt decomposition or isomerisation. On the other hand, even if the bimolecular rate coefficient of the CH_2OO self-reaction is in the order of 10^{-11} cm^3 $molecule^{-1}$ s^{-1}, the overall rate (the bimolecular rate coefficient times the concentrations) determines whether this reaction can compete with other bimolecular reactions or not. For example, traces of formic acid (ppb levels) were present in the experimental system. Given that sCI levels are well below ppb levels in our experimental system and the rate coefficient of CH_2OO + HC(O)OH is even a factor of 1.5 larger (IUPAC, current recommendation), bimolecular self-reactions of sCIs can be ruled out.

Comment 6b: 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.

Response: We do agree that the marge of error is quite large. However, we do argue that, given the indirect method used to determine the cross-section of 2HPr, this value is quite good. As written in the manuscript the cross section determinations agree within 9% within different experiments, which hence includes the uncertainty derived from the wall loss of 2HPr. The uncertainty for the HCHO yield was already given as well in the manuscript. Combining the uncertainties yields a relative error below 30%. However, we extended the uncertainty considering the fact that the cross section determination is performed in a complex chemical system.

Comment 6c: Does the wall loss follow the first-order decay?

Response: Yes.

Comment 6d: Did you also observe wall loss for 3B2OL and corrected it?

Response: The wall loss for 3B2OL was $< 2 \times 10^{-5}$ s^{-1} and hence negligible.

Comment 7: 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?

Response: This is an interesting point! The plots for both aldehydes are linear. But this is coincidence since secondary formation and loss processes almost compensate each other within the experiments investigating the 3P2 + OH reaction. One should note that it is not possible to simulate the time profiles for both aldehydes without considering the secondary formation due to 2HPr + OH. The non-linearity would become visible with much longer irradiation times.

Comment 8: 8. Figure 5: The fate of CH3CO radical following reaction with O2 and NO is shown to be the formation of CO2 and HCHO. If HCHO is formed by CH3OO reaction, then other products such as methanol are also expected.

Response: This is not true for the conducted experiments. Methanol would be formed from the self-reaction of the methylperoxy radical. As written in the manuscript, all experiments were conducted under conditions where all RO_2 radicals will react with NO. Thus, the CH_3OO radical is converted solely to the CH_3O radical, which results in formaldehyde.

Comment 9: 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.

Response: The brief description of the model was updated as written in the response to comment 2. For clarity we added as well an additional table listing the simplified reaction sequence needed to describe the reaction system. This includes the reaction scheme as well as the input (kinetic) data and the parameters (first-generation yields) derived from the modelling. Given that our approach does not fully describe the mechanism, the obtained branching ratios for the reactions listed in the table 2 represent the first-generation yields and not exact branching ratios in the case of 3P2 + OH. For example, the average first-generation yield of acetaldehyde obtained through modelling is 0.38, which corresponds to the branching ratio R4b/R4 according to the simplified reaction scheme. However, given that according to our proposed mechanism acetaldehyde can be formed from addition to both C_α and C_β, one can just conclude that 38% acetaldehyde are formed from 3P2 + OH. Since it is not possible to decipher the branching ratios of the different RO radical decomposition channels, no further statement is possible on the exact branching ratios. By contrast, in the case of 2HPr, the obtained first-generation yields correspond to the branching ratios for the different abstraction channels.

Table 2. Simplified reaction sequence used for the modelling of the temporal behaviour of experimentally quantified species in order to obtain first-generation yields for the respective reactions (3P2 + OH, 2HPr + OH).

Reaction		Branching ratio	Rate coefficient	
R4	$CH_3CH{=}CHC(O)CH_3 + OH \rightarrow$ products		6.2×10^{-11} cm^{3} molecule^{-1} s^{1}	[a, b]
R4a	$\rightarrow CH_3C(OH)C(O)H$	0.68 [c]		
R4b	$\rightarrow CH_3C(O)H$	0.39 [c]		
R4c	$\rightarrow CH_3C(O)C(O)H$	0.32 [c]		
R4d1	$\rightarrow CH_3C(O)OONO_2$	[d]		
R4d2	$\rightarrow CO_2 + HCHO$	[d]		
R5	$CH_3CH{=}CHC(O)CH_3 + \text{wall} \rightarrow$		$\leq 1.0 \times 10^{-4}$ s^{-1}	[a, e]
R6	$CH_3C(O)H + OH \rightarrow$ products		1.5×10^{-11} cm^{3} molecule^{-1} s^{1}	[a, f]
R6a	$\rightarrow CH_3C(O)OONO_2$	[a, g]		
R6b	$\rightarrow CO_2 + HCHO$	[a, g]		
R7	$CH_3C(O)H + \text{wall} \rightarrow$		$\leq 1.0 \times 10^{-4}$ s^{-1}	[a, e]
R8	$CH_3C(O)C(O)H + OH \rightarrow$ products		1.3×10^{-11} cm^{3} molecule^{-1} s^{1}	[a, h]
R8a	$\rightarrow CO + CH_3C(O)OONO_2$	[i]		
R8b	$\rightarrow CO + CO_2 + HCHO$	[i]		
R9	$CH_3C(O)C(O)H + \text{wall} \rightarrow$		$\leq 1.0 \times 10^{-4}$ s^{-1}	[a, e]
R10	$CH_3C(OH)C(O)H + OH \rightarrow$ products		1.7×10^{-11} cm^{3} molecule^{-1} s^{1}	[a, j]
R10a	$\rightarrow CO_2 + CH_3C(O)H$	0.79 [c]		
R10b	$\rightarrow CH_3C(O)C(O)H$	0.21 [c]		
R11	$CH_3C(OH)C(O)H + \text{wall} \rightarrow$		$\leq 1.0 \times 10^{-4}$ s^{-1}	[a, e]

[a] Input parameter; [b] rate coefficient determined within this work; [c] average branching ratio obtained through modelling; [d] average branching ratio (R4d1+R4d2)/R4 = 0.58 obtained through modelling; [e] determined in each individual experiment; [f] rate coefficient from Atkinson et al. (2006); [g] branching ratio (R6a+R6)/R6 = 0.95 from Atkinson et al. (2006); [h] rate coefficient from Atkinson et al. (2006); [i] branching ratio (R8a+R8b)/R8 = 1.0 from Atkinson et al. (2006); [j] rate coefficient from Baker et al. (2004).

Comment 10: 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.

Response: As already written in the manuscript, the rate coefficient was estimated based on the method used previously by Baker et al. (2004). In this study the rate coefficients of in situ generated hydroxycarbonyls were obtained by a non-linear regression analysis of a plot of the formed hydroxycarbonyl vs. ln([precursor]0/[precursor]t). For this procedure, it is not necessary to include the first-generation yield of the in situ generated species since the plots profile depends only on the rate coefficient ratio *k*(hydroxycarbonyl + OH)/*k*(precursor + OH). This method is applicable only if the target species has no or at least no significant wall loss. Hence, only a very limited number of experiments allowed us to apply this approach and we therefore prefer to consider the value obtained here as an "estimated rate coefficient", as written in the abstract, and to assign an expanded uncertainty. We understand, however, that how we derived *k*(2HPr+OH) was not clearly written and we would therefore include an additional figure showing the non-linear plot following the procedure outlined by Baker et al. (2004):

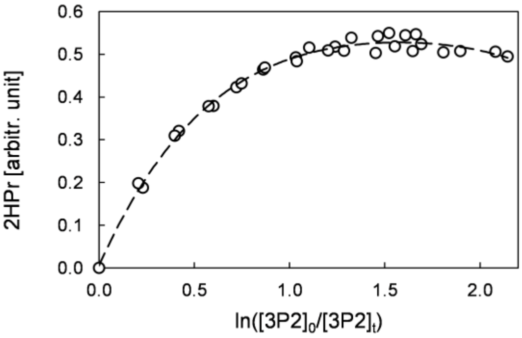

Figure 8. Non-linear plot for the formation of 2HPr from the 3P2 + OH reaction according to Baker et al. (2004) used to estimate the rate coefficient of 2HPr + OH.

We further modified the corresponding paragraph (page 13, lines 329–332) as follows:

"Applying the approach presented by Baker et al. (2004) to these experiments allows to estimate ~~yields~~ a value of (2.2 ± 0.6) × 10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the rate coefficient of 2HPr + OH ~~which is about 30% larger than previously reported~~. The non-linear plot, drawn according to the previously mentioned approach, is presented in Fig. 8. Our estimation is about 30% larger than previously reported (Baker et al., 2004). ~~Given~~Taking into account that both determinations are based on the in situ generation of the α-hydroxyaldehyde this is still an excellent agreement."

Given that both determinations are based on the in situ generation of the aldehyde and thus the rate coefficient is determined from a complex chemical system, this is, in our opinion, an excellent agreement. Moreover, within the uncertainties assigned to our value, which is stated as an estimated value, both determinations are the same.

Comment 11a: 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.

Response: See above.

Comment 11b: Did you do any sensitivity analysis?

Response: Yes, we did. Our conclusions, the given branching ratios as well as their assigned uncertainties are based on a careful sensitivity analysis. Based on the suggestion from Anonymous Reviewer #1 we updated Fig. 9 (Fig. 8 in the originally submitted manuscript) in order to show sensitivity analysis and included the temporal behaviour of acetaldehyde and methyl glyoxal, assuming different branching ratios for the 2HPr + OH reaction. We also included explicitly the sensitivity analysis in the corresponding paragraph (page 14, lines 346–360):

"Molar formation yields for acetaldehyde and methyl glyoxal, derived from 3P2 + OH, and the branching ratio $k_b/[k_a + k_b]$, resulting in methyl glyoxal through 2HPr + OH, were included as parameters in the simplified model (Illmann et al., 2021b) and varied until the experimental time profiles are reproduced by the simulation. Since the OH initiated oxidation of 2HPr is expected to proceed solely through (a) and (b) the branching ratio k_a~~$/[k_a + k_b]$~~ is given as 1 – k_b~~$/[k_a + k_b]$~~ (Fig. 7). Table 2 shows the simplified reaction sequences and the rate coefficients needed to describe the reaction system. These sequences do not follow the nomenclature used in the proposed mechanisms (Figs. 5 and 7) since the simplified model does not differentiate if a product is formed directly from a parent compound through more than one pathway.

Figure 9 summarises an analysis of the model sensitivity on the branching ratios k_a and k_b. As can be seen in panel (a), a variation from $k_a = 1.00$ and $k_b = 0.00$ (sim1) to $k_a = 0.50$ and $k_b = 0.50$ (sim3) exhibits no measurable influence on the temporal profile in the beginning of the first irradiation period, corresponding to a 3P2 consumption of < 30%. Hence, t~~T~~he secondary oxidation of both acetaldehyde and methyl glyoxal ~~is almost~~was negligible immediately after switching on the lamps for the first time. This allows to derive values for the first-generation yields of acetaldehyde and methyl glyoxal from 3P2 + OH in these experiments. The branching ratios (k_a and k_b) chosen for sim1 to sim3, depicted in panel (a), completely fail in reproducing the profile for both reaction products for the entire duration of the experiment. ~~On the other hand, as stated above, secondary oxidation processes dominate in the end of the second irradiation period.~~ Panel (b) in Fig. 9 shows the optimum range for the branching ratios that allows a simultaneously fit of the experimental time profiles for both acetaldehyde and methyl glyoxal. Accordingly, ~~only a small variation in the parameters' values allows reproducing the time profile of the entire experiment and~~ the branching ratios k_a~~$/[k_a + k_b]$~~ and k_b~~$/[k_a + k_b]$~~ were found to be 0.79 ± 0.05 and 0.21 ± 0.05, respectively. This is in excellent agreement with SAR predictions (Kwok and Atkinson, 1995) which estimate 0.8 and 0.2 for the branching ratios, respectively, as well as former results on the OH reaction of glycolaldehyde at atmospheric pressure (Niki et al., 1987; Bacher et al., 2001; Magneron et al., 2005).

Based on these results, the temporal profiles of acetaldehyde and methyl glyoxal are well-reproduced for all conducted experiments. ~~the~~Their corrected yields ~~for acetaldehyde and methyl glyoxal~~ in the 3P2 + OH reaction are 0.39 ± 0.07 and 0.32 ± 0.08, respectively. Hence, while larger molar yields were observed for acetaldehyde than for methyl glyoxal without proper corrections, the model predicts both first-generation yields to be the same within the accuracy errors, which ~~proves~~ indicates their formation according to the same reaction channel. The branching ratios of the simplified reaction scheme, obtained through modelling, are given in Tab. 2."

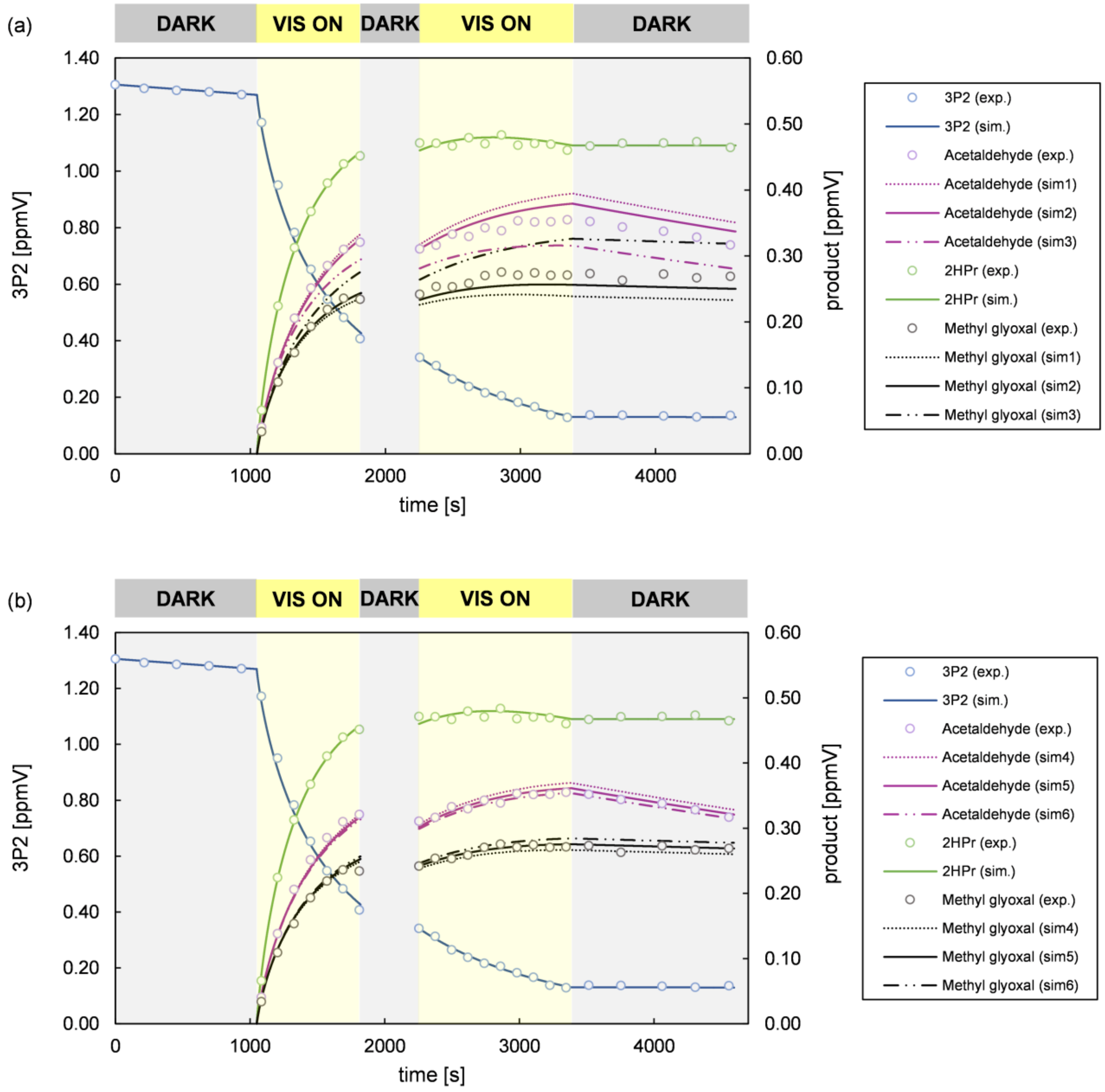

Figure 9. Experimental and simulated time profiles for a 3P2 + OH experiment, performed in the 1080 L chamber, with a ~~second~~ supplementary addition of methyl nitrite and NO during the second dark phase of the experiment. The experimental set-up did not allow the quantification of CO_2. The parameters k_a and k_b used in the simulation runs are: 1.00 and 0.00 (sim1), 0.90 and 0.10 (sim2), 0.50 and 0.50 (sim3), 0.84 and 0.16 (sim4), 0.79 and 0.21 (sim5), and 0.74 and 0.26 (sim6).

Comment 12: 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.

Response: The referee is referring to the lifetime of 2HPr while line 416 refers to the ketone 3P2. We noticed that the paragraph was confusing since 3P2 was mentioned only in the equation of the lifetime but not precisely in the sentence itself. For clarity, we modified line 413 as follows:

"The atmospheric lifetime of 3P2 with respect to OH radicals …"

For the α-hydroxyaldehyde we wrote: "The gas-phase oxidation of the first-generation product 2HPr by OH radicals would generate mainly acetaldehyde (~80%) hence increasing the potential of forming NO_x reservoirs. However, by comparison with glycolaldehyde photolysis of 2HPr may also be competitive." This is already in agreement with the referee's comment. As already mentioned, we did not observe a photolysis rate for 3P2 in our chambers. Scaling the $J(NO_2)$ of our chambers to typical values within the troposphere, the upper limit of the 3P2 photolysis cannot dominate over the loss via OH.

Minor technical correction:

Comment 13: 1. Title: The word "main" could be omitted as there are other major oxidation products.

Response: With due respect, we would like to keep "main". With a formation yield of 68 ± 27% 2HPr is the main product of the reaction of 3P2 with OH radicals.

Comment 14: 2. Page 9, line 229: Also add 2HPr.

Response: In our opinion it is right that 2HPr is not mentioned here, since its identification is only possible after subtraction of all other species. Besides, the intention in this paragraph is a stepwise discussion of the results. Consequently, 2HPr is discussed in the end of Sect. 3.3 since this paragraph is a very important part of our study and leads over to the 2HPr + OH investigations discussed in Sect. 3.4. The reviewer's suggestion would disrupt the logical structure.