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

We thank the referees for the additional 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.

A. Comments by Referee 1

Comment 1: In one of my comments, I stated that the abstract should say they used a simple chemical mechanism to describe the experiments, rather than a "modeling tool". Rather than address it, the author chose to criticize my comments and apparently misunderstood this rather obvious point. A "modeling tool" is just a software and/or algorithm, and doesn't describe any chemistry. It is the chemical mechanism implemented in the tool that describes what is happening, and it could be employed using any number of modeling tools. The author seems to think that I don't know the difference between a modeling tool and a mechanism, but after over 40 years working in this field I suspect the problem is more likely with him.

Response: First of all, we would like to emphasize that we never intended to question the expertise of the referee. We understand the referee's point that a software does generally not describe any chemistry and that our wording is not entirely correct. However, the simple chemical mechanism itself does not contain any number. It just says that acetaldehyde and methyl glyoxal are formed through the 2HPr oxidation. The branching ratios are obtained through modelling. Therefore, in our opinion, the referee's suggestion did not completely solve the raised issue either. Nevertheless, we understand that the referee's suggestion is a better wording in order to avoid misunderstandings. The sentence was modified accordingly.

Comment 2: A comment I made regarding the apparent formation of acetaldehyde in the O3 + 2BOL reaction, was also not satisfactorily addressed. Figure 2 shows acetaldehyde coming from the OH-substituted Criegee, but doesn't show a co-product or suggest a mechanism, since its formation is not expected based on what is known of simpler Criegees. I gave a suggested mechanism but I incorrectly wrote "formaldehyde" when I should have written "formyl radicals" (ultimately giving acetaldehyde + CO + HO2 + OH). The authors correctly noted my error, but apparently didn't bother to look at the system and see that the co-product should obviously be formyl. Their main response was that the main point is that acetaldehyde is probably formed from this Criegee (or so the data suggest), but speculation on the mechanism was beyond the scope of the paper. This is a fair point, but in this case, they should not pretend it is a mechanism on Figure 2, but instead should show a "?" and "+ other products" as I suggested in my comment.

Response: We still do not understand this issue since we do not pretend it is a complete mechanism but only a more likely reaction sequence. It is just said that acetaldehyde formation originates from the larger CI. However, in order to make unambiguously sure that the CI further chemistry yields additional unidentified products, we added reaction pathways yielding "products", although we believe that this was obvious from our discussion. Additionally, we replaced the biradical structures of the CIs with zwitterion structures to be consistent with the recommendation by the latest IUPAC Review article (Cox et al., ACP 2020, https://doi.org/10.5194/acp-20-13497-2020).

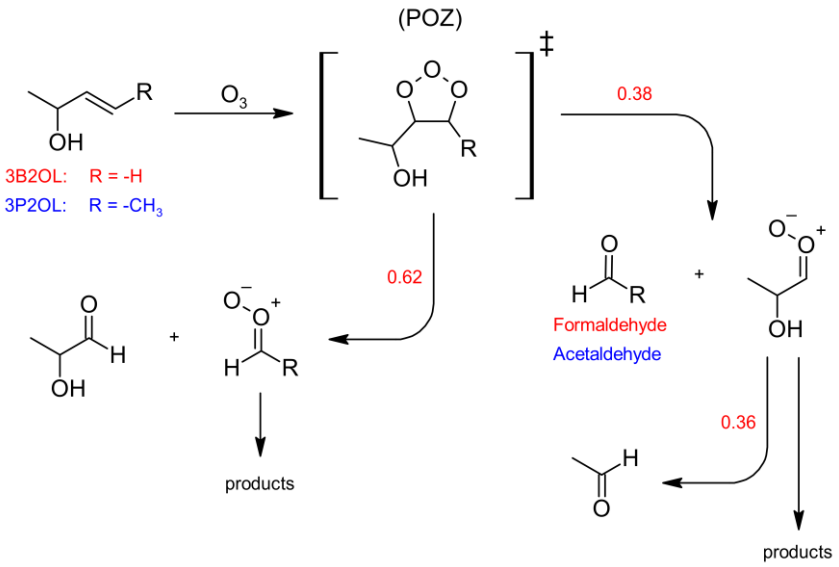

Figure 1. Formation of 2-hydroxypropanal through the ozonolysis of 3-buten-2-ol (3B2OL, red) and 3-penten-2-ol (3P2OL, blue) and respective average branching ratios. For readability reasons only one stereo-isomer is drawn for each Criegee Intermediate.

Comment 3: I also commented on their statement that there was curvature in Figure 4 in the yield plots for 2HPr, but this was not evident in the figure. In response, the author stated that there was curvature for individual experiments, but this is not evident in Figure 4 because it shows all the experiments with a single symbol. Since this curvature is noted in the text, the readers should be able to see it for themselves. Either use different symbols for different experiments in Figure 4 or, if this doesn't show this clearly, then show a plot of a representative experiment as an insert or in a supplement.

Response: We modified Fig 4 as follows: 1) different experimental runs are denoted with different symbols, 2) we deleted the regression line in panel (c), and 3) the colours were changed in order to use the same colour code throughout the manuscript. Additionally, we noted that at least for acetaldehyde, methyl glyoxal and PAN + CO_2 the error bars included accuracy errors which is not useful when proving linearity or non-linearity of the plot. Accordingly, the figure was updated and the precision errors included. We hope that in this way it becomes visible for readers that the plots exhibit a high linearity for acetaldehyde and methyl glyoxal in contrast to 2HPr and the sum of PAN and CO_2. Note that, since based on a comment from Referee 2 some new figures were added, we added a Supplement. The former Fig. 4 becomes Fig. 3 in the revised manuscript.

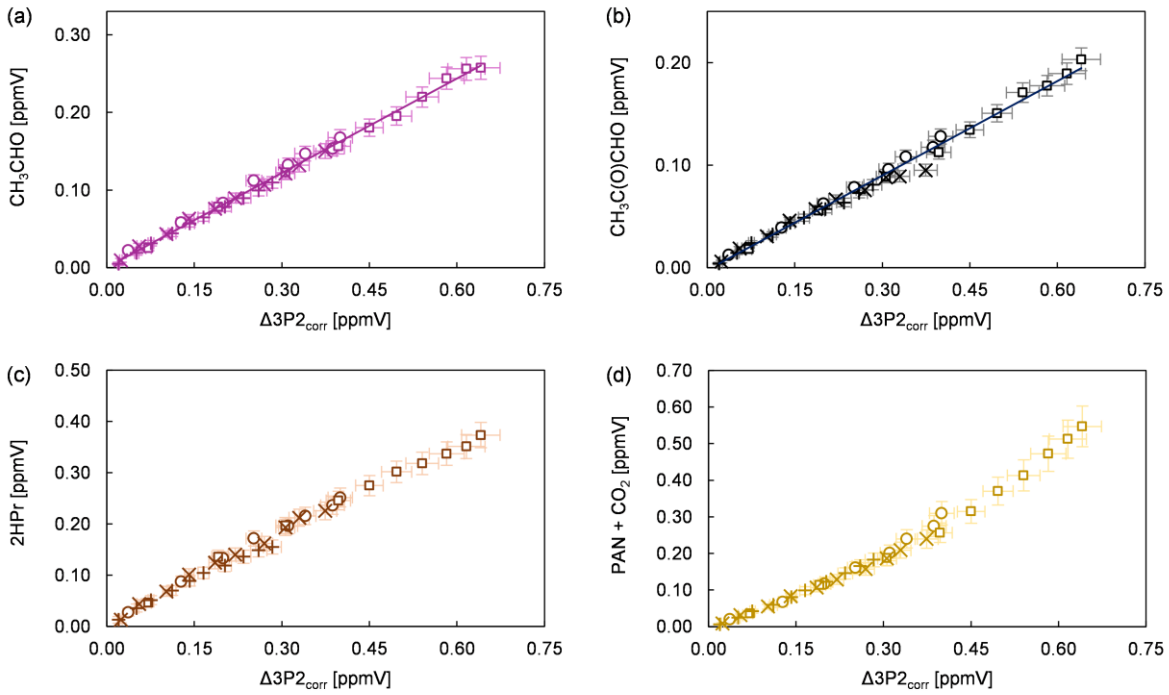

Figure 3. Yield plots for (a) acetaldehyde, (b) methyl glyoxal, (c) 2-hydroxypropanal, and (d) the sum of PAN and CO_2 for all conducted experiments corrected for the wall loss of 3P2. The error bars consist of the corresponding precision error. The data of the 480 L chamber experiments are multiplied with a factor of 0.1 to fit within the scale of 1080 L chamber experiments. Different experimental runs are denoted with different symbols.

Comment 4: With regard my proposed mechanism for forming formaldehyde from the PAN analogue shown on Figure 7, the author criticized my suggesting about what I called a "1,4-H" shift of the PAN analogue, stating it was really a 1,5-H shift, which is less favorable (but not always). But this suggested reaction actually has a 6-member ring transition state, so can't be criticized on this basis. However, there is no need for the authors to accept this suggestion because it does not affect the results of interest, though the possibility of another route for acetaldehyde formation would be of interest in the context of this figure.

Response: Our response did not intend to criticize the referee. But the referee described mechanistically an 1,5-H shift but wrote 1,4-H shift instead. This has just been pointed out in order to be sure that we did not misunderstand the comment. In his original comment the referee asked if this additional route affects the obtained yield for acetaldehyde. Given that both the thermal decomposition and the potential decomposition after the 1,5-H shift would finally yield acetaldehyde and CO_2 we pointed out that this does not affect the results. We agree on the thought on the 6-member ring transition state. In this context, an 1,5-H shift is much faster than an 1,4-H shift in, probably, nearly all cases. However, we were thinking that in this particular case an 1,5-H shift should be much slower given that in RO_2 radicals, for instance, rate coefficients for migration of hydroxyl-H atoms are very low (Vereecken, L. and Nozière, ACP 2020, https://doi.org/10.5194/acp-20-7429-2020). However, the PAN species is of course not a radical. But therefore, we would think an H shift reaction to be a sigmatropic rearrangement which requires a π-bonded system that rearranges during the shift reaction which is not the case. Given that we are not sure if a shift reaction is possible, we prefer to keep the figure as it is. In order to keep H shifts in mind, we added some words with respect to the 2HPr derived RO_2 radical, given that theoretical calculations indicate fast H shifts in acylperoxy radicals:

"A theoretical investigation on the C_5-acylperoxy radical indicates that H migration reactions (1,5-H, 1,6-H or 1,7-H shift) of larger acylperoxy radicals might be fast enough to compete with the bimolecular reactions at low ppb levels of NO (Knap and Jørgensen, 2017). However, based on the predicted effects of the substitution pattern on the reactivity towards H migration reactions (Vereecken and Nozière, 2020) one would not expect the unimolecular reaction of the smaller hydroxypropionylperoxy radical to be competitive, at least not under our experimental conditions."

B. Comments by Referee 2

Comment 1: The manuscript is significantly improved – in particular, the inclusion of Table 2 and Figure 8, as well as the additional information provided in the new Figure 9, is helpful. I have one point that should be addressed further, however: In Figure 9, uncertainties in the measured product mixing ratios (2HPr, CH3CHO, CH3COCHO) should be shown. I am guessing that the +/- 0.05 uncertainties on the ka and kb values are too 'optimistic'?

Response: Thank you for raising this point! Indeed, our analysis was focused on reproducing the entire profiles and, in this context, did only consider precision errors, although for the overall uncertainties accuracy errors of all species should have been considered. We therefore re-performed the sensitivity analysis with respect to the accuracy errors. We refined our model and considered the acetaldehyde and methyl glyoxal yield from 2HPr + OH separately (formerly the sum of both was set to 1). k_a and k_b are then obtained from normalization of the corresponding yields. In order to find the maximum uncertainty on the branching ratios k_a and k_b two scenarios were defined in which acetaldehyde is simulated for the upper limit of the accuracy error and methyl glyoxal for the lower limit, respectively, or the inverse case. These scenarios were simulated for a variety of 2HPr yields within the accuracy error. This procedure changed slightly the average branching ratios and the assigned errors. They are, however, identical to the former values considering the assigned uncertainty. In order to address this analysis properly, main parts of Sect. 3.4 were re-written and accuracy errors added to the corresponding figures. Given that the modelling part became much more predominant within this section, we changed the heading from "2-Hydroxypropanal + OH and yields correction" into "2-Hydroxypropanal and modelling". Additionally, the figures show simulations for the different scenarios. A similar analysis was performed for PAN + CO_2. Additional graphical representations of the sensitivity analysis were added to a new Supplement. The original Figs 3 and 8 were also shifted to the Supplement. The main text of Sect. 3.4 was modified as follows:

"Among the class of α-hydroxyaldehydes mechanistic information on the OH reaction and photolysis at atmospheric pressure were reported merely for glycolaldehyde (Niki et al., 1987; Bacher et al., 2001; Magneron et al., 2005). Baker et al. (2004) reported rate coefficients for the OH reaction of a series of hydroxyaldehydes synthesized in situ via the reaction of OH radicals with precursor alcohols. The authors obtained $k = (1.7 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 2HPr + OH through a nonlinear least squares analysis of the data of the 2-methyl-2,4-pentanediol oxidation (Baker et al., 2004). Under tropospheric daytime conditions both photolysis and OH initiated oxidation are important removal processes for glycolaldehyde (Bacher et al., 2001). However, assuming a similar behaviour for 2HPr, photolysis is expected to be negligible under the experimental conditions of the present study, since the OH radical level is much higher while photolysis frequencies are lower than within the troposphere. Including the above rate constant of 2HPr + OH into the model described previously (Illmann et al., 2021b) results in a corrected average yield of 0.68 ± 0.27, which is about 15% higher than determined from the yield plot, without proper corrections (Fig. 3~~Fig. 4~~). Hence, a significant fraction of the α-hydroxyaldehyde is subject to OH radical initiated oxidation.

Based on the SAR approach by Kwok and Atkinson (1995) and the mechanistic information reported for the glycolaldehyde oxidation (Niki et al., 1987; Bacher et al., 2001; Magneron et al., 2005) one would expect

abstraction of the aldehydic H atom to dominate compared to abstraction of the carbon-bonded H atom of the –CH(OH)– entity for the OH reaction of 2HPr, as presented in Fig. 6~~Fig. 7~~. The abstraction from the terminal $–CH_3$ group and the –OH group is expected to be negligible due to the much lower group rate constants. The hydroxypropionyl radical formed according to channel (a) will either eliminate carbon monoxide and react with O_2 to form acetaldehyde or react with oxygen to form a hydroxypropionylperoxy radical (Fig. 6). The latter radical, resulting from channel (2a), may either yield peroxyhydroxypropionyl nitrate or will be converted to the corresponding RO radical (Fig. 6~~Fig. 7~~). This species will readily eliminate CO_2 and finally form acetaldehyde as well. A theoretical investigation on the C_5-acylperoxy radical indicates that H migration reactions (1,5-H, 1,6-H or 1,7-H shift) of larger acylperoxy radicals might be fast enough to compete with the bimolecular reactions at low ppb levels of NO (Knap and Jørgensen, 2017). However, based on the predicted effects of the substitution pattern on the reactivity towards H migration reactions (Vereecken and Nozière, 2020) one would not expect the unimolecular reaction of the smaller hydroxypropionylperoxy radical to be competitive, at least not under our experimental conditions. By analogy to the OH initiated oxidation of 3-hydroxy-2-butanone (Aschmann et al., 2000) one would expect reaction with oxygen to predominate over decomposition for the hydroxyalkyl radical formed following channel (b), thus leading to methyl glyoxal (Fig. 6~~Fig. 7~~). Hence, the 2HPr + OH reaction appears to be ~~is expected as~~ a secondary source of acetaldehyde and methyl glyoxal in the experimental system.

In order to investigate the 2HPr + OH reaction, methyl nitrite and NO were added for a second time, after a 3P2 consumption of about 70%, to shift the reaction system towards secondary oxidation processes. Applying the approach presented by Baker et al. (2004) to these experiments, as shown in Fig. S2 in the Supplement, allows to estimate a value of $(2.2 \pm 0.6) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} for the rate coefficient of 2HPr + OH. ~~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). Taking into account that both determinations are based on the in situ generation of the α-hydroxyaldehyde this is still an excellent agreement. ~~As shown in Figure 9, 2HPr (green) passes through a small maximum during the second irradiation period.~~ In panel (c) of Fig. 7 it can be observed that the ~~The~~ mixing ratio of acetaldehyde (purple circles) increases continuously over the second irradiation period, while that of methyl glyoxal (black circles) is reaching relatively fast a plateau. ~~at the end of the reaction in the case of methyl glyoxal (black)~~This is in qualitative agreement with the proposed mechanism. Peroxy nitrates other than PAN, formed through 3P2 + OH, could not be detected. Traces of the analogue peroxyhydroxyacyl nitrate resulting from glycolaldehyde oxidation have only been previously observed when the corresponding RO_2 radical was generated through the reaction of glycolaldehyde with Cl atoms in the presence of NO_2 (Niki et al., 1987). Magneron et al. (2005) did not detect any PAN-type species in the glycolaldehyde + OH system and therefore concluded that this species is probably ~~likely~~ unstable and readily dissociates. Hence, abstraction of the aldehydic H atom following channel (a) will likely result exclusively in the formation of acetaldehyde irrespective of the branching ratio between the (1a) and the (2a) channel (Fig. 6~~Fig. 7~~).

~~Molar formation yields for acetaldehyde and methyl glyoxal, derived from 3P2 + OH, and the branching ratio kb/[ka + kb], 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 is given as $1 – k_b$ (Figure 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 ka and kb. 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, the secondary oxidation of both acetaldehyde and methyl glyoxal 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. 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, the branching ratios k_a and 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).~~

The molar formation yields of acetaldehyde and methyl glyoxal, derived from 3P2 + OH as well as from 2HPr + OH were included as parameters in a 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 the channels (a) and (b), the product yields of acetaldehyde and methyl glyoxal, from 2HPr + OH, should correspond to the branching ratios k_a and k_b, respectively (Fig. 6). Their sum should, in turn, equal unity. 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. 4 and 6) since the simplified model does not differentiate if a product is formed directly from a parent compound through more than one pathway.

Figure 7 summarises an analysis of the model sensitivity, observing also the accuracy of all quantified species. For all species but 2HPr accuracy was defined as a 10% relative error plus the corresponding detection limit. The accuracy of 2HPr is given as a 30% relative error plus the detection limit due to the uncertainty of the cross section determination. Panel (c) - (f) show different model runs for acetaldehyde and methyl glyoxal in which the 2HPr yield was set to 0.66, represented by the solid line in panel (b). As can be seen in panel (c), without considering the 2HPr + OH reaction the simulated profile represents roughly the experimental methyl glyoxal data during the first irradiation period. By contrast, the acetaldehyde profile matches the experimental data only in the beginning of the first irradiation corresponding to a 3P2 consumption of < 30%. The temporal profiles of both species completely fail in reproducing the measured data during the second irradiation, where more than 70% of the 3P2 is already consumed. This demonstrates unambiguously that a secondary source for both acetaldehyde and methyl glyoxal is needed to describe the experimental system, namely the α-hydroxyaldehyde oxidation. However, the match between the simulated and experimental time profiles in the beginning of the first irradiation allows to set values for the first-generation yields of acetaldehyde and methyl glyoxal from 3P2 + OH in these experiments. Panel (d) shows the optimum model run that allows a simultaneous fit of the experimental time profiles for both acetaldehyde and methyl glyoxal. In order to assess the errors for the branching ratios k_a and k_b, two scenarios were defined which represent the limiting cases and thus enable to determine the maximum variation of k_a and k_b. Accordingly, panel (e) shows a model run in which acetaldehyde is simulated for its lower limit of the accuracy error and methyl glyoxal for the upper limit, respectively, (scenario 1) while panel (f) represents the inverse case (scenario 2). These scenarios were modelled for different strengths of the secondary source of acetaldehyde and methyl glyoxal, means that the 2HPr yield from 3P2 + OH was varied within the limits imposed by the accuracy of the 2HPr measurement, as shown in panel (b). For both scenarios, the obtained first-generation yields of acetaldehyde and methyl glyoxal from 3P2 + OH were found to be independent from the 2HPr yield. Since the formation of acetaldehyde and methyl glyoxal from the 3P2 + OH reaction does not necessarily depend on 2HPr, this observation is rather self-consistent and serves merely as a validation of our model. Based on the proposed 3P2 + OH mechanism one would expect their yields to be the same, thus their ratio should equal unity. This does correspond to scenario 1 while an acetaldehyde/methyl glyoxal ratio > 1 is observed for scenario 2 (Fig. S3 in the Supplement). Although within the accuracy errors this indicates a small bias between the acetaldehyde and methyl glyoxal quantification. The sum of the acetaldehyde and methyl glyoxal yield from 2HPr + OH correlates with the 2HPr yield from the 3P2 + OH reaction, where larger values are observed when the input 2HPr yield

is lowered (Fig. S4 in the Supplement). In order to reproduce the entire time profiles of acetaldehyde and methyl glyoxal, an overestimation of the 2HPr mixing ratio and hence the strength of the secondary acetaldehyde and methyl glyoxal source is compensated for by an underestimation of the acetaldehyde and methyl glyoxal yield in the model. Hence, this behaviour can be rationalized in terms of an antagonistic effect. The sum of the acetaldehyde and methyl glyoxal yields becomes unity when a 2HPr yield of about 0.54 and 0.61 is used in the model for scenario 1 and 2, respectively. Considering the yield of 0.66, used to match the experimental data in panel (b), this might indicate an overestimation of the 2HPr mixing ratios. However, the differences are within the accuracy due to the rather uncertain 2HPr cross section. The branching ratios k_a and k_b were obtained by scaling of the acetaldehyde and methyl glyoxal yield. These were found to be independent from the 2HPr yield within the 2HPr accuracy limits and almost indistinguishable in between scenario 1 and 2 (Fig. S5 in the Supplement). Accordingly, the average branching ratios k_a and k_b are 0.73 ± 0.08 and 0.27 ± 0.08, respectively. Within the uncertainties, this is in 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. Their corrected yields 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 indicate their formation according to the same reaction channel. The branching ratios of the simplified reaction scheme, obtained through modelling, are given in Tab. 2.

~~By considering the formation of CH3C(O) radicals from the oxidation of 3P2, acetaldehyde and methyl glyoxal the model underestimates PAN + CO2 at longer reaction times as depicted by the sim1 simulation in Figure 10. This can be partly explained by an additional source of CO2 in the experimental system, since it is also a co-product of acetaldehyde via channel (5a) in the 2HPr + OH reaction (Figure 7). Given that abstraction of the aldehydic H atom of 2HPr is expectedly leading solely to acetaldehyde, the yield of CO2 from 2HPr oxidation depends only on the ratio between decomposition of the hydroxypropionyl radical and its reaction with oxygen (Figure 7).~~

Figure 8 shows time profiles obtained from an experiment performed in the 480 L chamber, in which PAN and CO_2 were quantified, as well as simulated profiles from different model runs. As presented in panel (b), the experimental data are reproduced solely for less than the first half of the irradiation period, if only PAN and CO_2 formation from 3P2 + OH are considered in the model. This corresponds to a 3P2 consumption of < 30% which is consistent with the non-linearity of the yield plot observed for higher 3P2 consumption levels (Fig. 3). As discussed before, PAN and CO_2 formation are affected from the further oxidation of acetaldehyde and methyl glyoxal. However, CO_2 elimination from the 2HPr derived RO radical (Fig. 6) is an additional source of CO_2 in the experimental system according to pathway (5a). Given that abstraction of the aldehydic H atom of 2HPr is expectedly leading solely to acetaldehyde, the yield of CO_2 from the 2HPr oxidation depends only on the ratio between decomposition of the hydroxypropionyl radical and its reaction with oxygen (Fig. 6). In order to assess the uncertainty on the sum parameter PAN + CO_2 due to secondary chemistry, the temporal profile of PAN + CO_2 was simulated assuming both acetaldehyde and methyl glyoxal at the upper (scenario 3) and lower limit (scenario 4) of the measurement accuracy (Fig. 8). Hence, the strength of the secondary sources of $CH_3C(O)$ radicals in the experimental system was either maximized or minimized in the model. Moreover, the temporal behaviour of PAN + CO_2 was simulated without considering CO_2 formation from 2HPr + OH (dashed lines) and assuming the CO_2 yield to equal the acetaldehyde yield (solid lines). In both scenarios (panel (d) and (f) of Fig. 8) the temporal profiles are nearly indistinguishable during the first half of the irradiation time and one obtains the same first-generation yield for the sum parameter PAN + CO_2, used to determine the $CH_3C(O)$ radical yield. The entire profile is reproduced solely when the CO_2 yield from 2HPr + OH is equalized to the acetaldehyde yield in scenario 3 (panel (d)). In scenario 4, where the secondary

formation of $CH_3C(O)$ radicals was set to the lower limit, the model slightly underestimates the sum of PAN and CO_2 at the end of the experiment (panel (f)). However, in both scenarios the model predicts the sum of PAN + CO_2 to be significantly lower than experimentally observed at the end of the irradiation period, when the CO_2 formation from 2HPr is set to 0 (dashed lines). When introducing larger PAN + CO_2 yields for 3P2 + OH it is possible to match the observed profile for the second half of the experiment. Although, in this case the model overestimates PAN + CO_2 formation in the first half of the experiment, in which secondary formation is expected to be almost negligible.

For the hydroxyacetyl radical Méreau et al. (2001) concluded, based on *ab initio* calculations, that decomposition cannot compete with the O_2 reaction ~~in the case of the structurally similar hydroxyacetyl radical~~. Niki et al. (1987) observed CO_2 instead of CO formation in the glycolaldehyde oxidation when secondary oxidation processes were minimized in the experimental system. These findings together with the significant discrepancy of the simulated and experimental time profile for PAN + CO_2 at long irradiation times, when a CO_2 formation from 2HPr oxidation is not included in the model, suggest that decomposition of the hydroxypropionyl radical is negligible and $k_{2a}/[k_{1a} + k_{2a}] = 1$ (see Fig. 6~~Fig. 7~~). Including the additional CO_2 source in the model improves significantly the consistency between the simulated and experimental PAN + CO_2 profile at long irradiation times, although slight discrepancies remain in some experiments ~~As shown in Figure 10 for a 480 L chamber experiment the entire time profile of PAN + CO_2 is reproduced when the additional source of carbon dioxide is included into the model.~~ One should note that in this regard the time profile does no longer represent merely the formation of $CH_3C(O)$ ~~acetyl~~ radicals. However, given that both the simulation with and without the additional CO_2 source are indistinguishable in the first part of the irradiation period (Fig. 8~~Fig. 10~~) it is still possible to derive the corrected average yield for PAN + CO_2 (0.56 ± 0.14) representing the yield of $CH_3C(O)$ radicals.

~~The lowering of the PAN + CO_2 yield due to the correction is consistent with the presence of secondary processes since both acetaldehyde and methyl glyoxal further oxidation contributes to the $CH_3C(O)$ radical formation in the experimental system. Besides, as~~ As for acetaldehyde and methyl glyoxal, the yields for 2HPr and PAN + CO_2 are the same within the assigned accuracy thus indicating their formation in the same reaction channel. Since ~~As~~ carbon dioxide formation might be easily affected from processes on the chamber walls ~~and~~ the corrected yield for PAN + CO_2 should, therefore, be still regarded as upper limit. A build-up of CO_2 from the walls might become relevant at longer irradiation times and this supposedly explain the remaining small discrepancies at irradiation times > 10 min in some experiments. However, the reproducibility of the yields ~~without correction~~ is essentially the same as for 2HPr for experiments performed in both chambers. Besides, separate control experiments, in which synthetic air was irradiated with the same set of lamps, did not show significant CO_2 production. Therefore, the influence of off-gasing processes on its temporal behaviour is probably negligible in the beginning of the experiments, when the formation of the products in the target reaction dominates over secondary chemistry. An overestimation of the $CH_3C(O)$ radical yield is thus unlikely. Uncorrected and corrected molar yields, namely first-generation yields, of all quantified products are summarised in Table 3.

Combining the yields of the 3P2 oxidation products leads to a carbon balance close to unity (0.98 ± 0.18). The branching ratios for the pathways α_{ON} and β_{ON} (Fig. 4~~Fig. 5~~) forming $RONO_2$ species are expectedly very minor channels. ~~This is in agreement with previous work in which $RONO_2$ species from the OH oxidation of α,β-unsaturated ketones were indicated only in our experimental set-up resulting from tertiary RO_2 radicals (Illmann et al., 2021b).~~ This is in agreement with previous findings in our laboratory, where the production of $RONO_2$ species in the OH oxidation of α,β-unsaturated ketones was observed only in conjunction with the formation of tertiary RO_2 radicals (Illmann et al., 2021b). Further~~Besides~~, Praske et al. (2015) reported a low overall $RONO_2$ yield of 0.040 ± 0.006 for MVK oxidation."

The Figs. 7 and 8 (formerly 9 and 10) were replaced as follows:

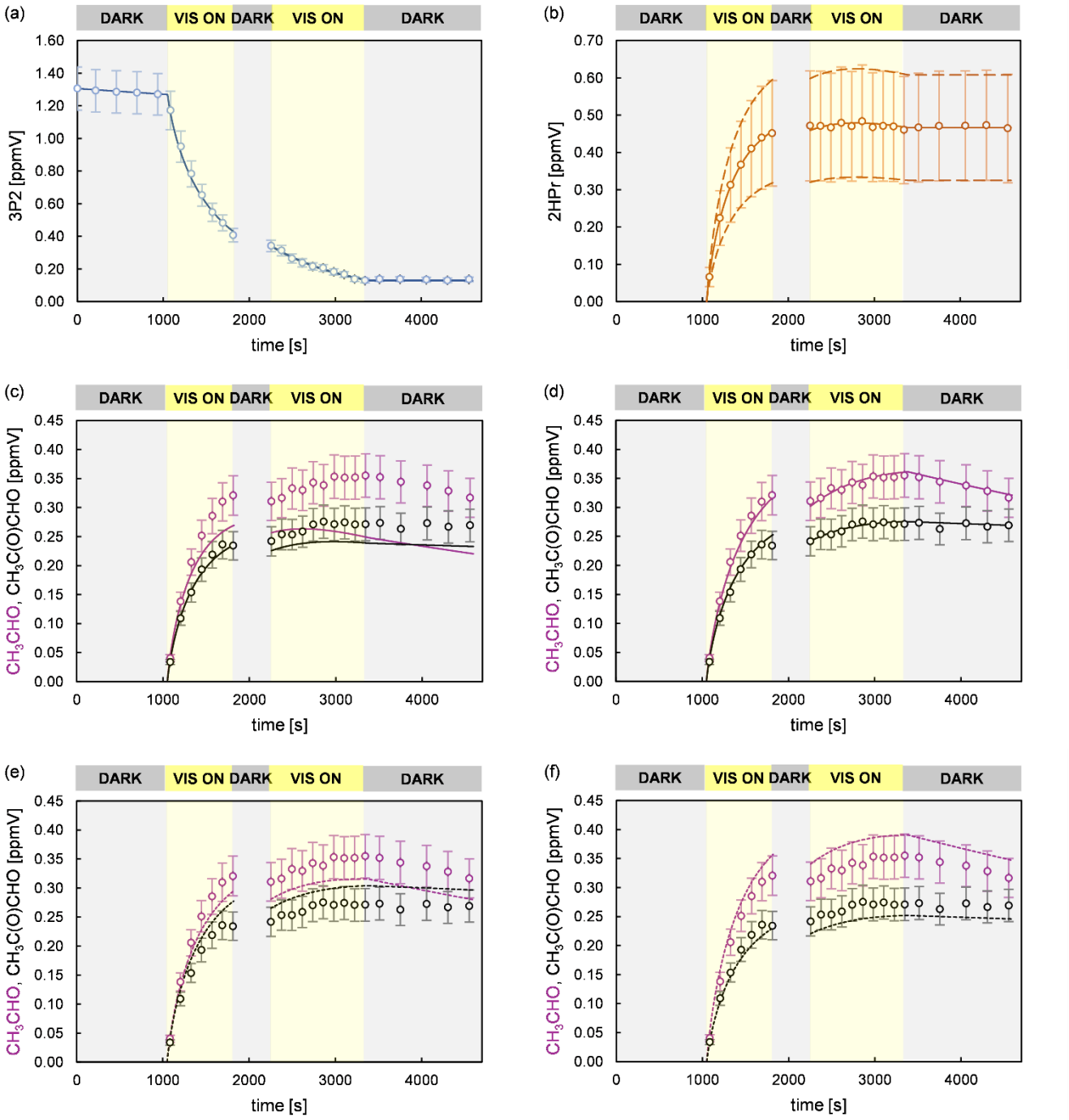

Figure 79. Experimental and simulated time profiles for a 3P2 + OH experiment, performed in the 1080 L chamber, with a supplementary addition of methyl nitrite and NO during the second dark phase of the experiment. The experimental set-up did not allow the quantification of CO_2. ~~The parameters k_a 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).~~ The circles represent the experimental data. The error bars represent the accuracy error for each species. The lines show the simulated profiles of (a) 3P2, and (b) 2HPr assuming the average yield (solid line) and the upper and lower limit (dashed lines). The simulated profiles of acetaldehyde and methyl glyoxal are shown considering the average 2HPr yield (c) without their secondary formation, (d) with the optimum parameters used to reproduce the experimental data, (e) for the lower and upper limit of acetaldehyde and methyl glyoxal (scenario 1), respectively, and (f) for the upper and lower limit of acetaldehyde and methyl glyoxal (scenario 2), respectively.

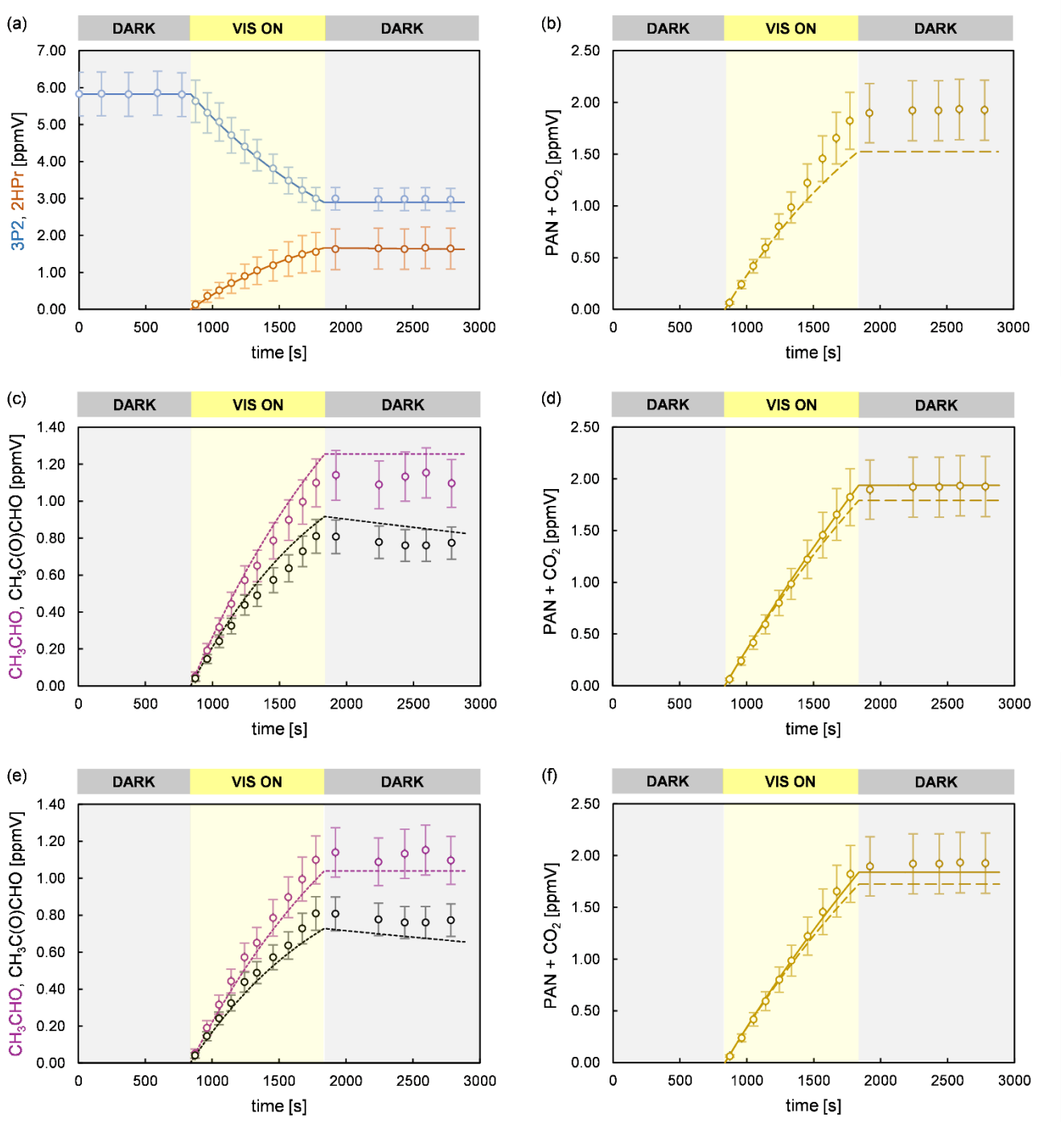

Figure 89. Experimental (circles) and simulated (lines) temporal ~~Temporal~~ behaviour of 3P2, 2HPr, acetaldehyde, methyl glyoxal and PAN + CO_2 in an experiment performed in the 480 L chamber. ~~The sim1 simulation run considers only the formation of PAN and CO_2 due to $CH_3C(O)$ radicals formed in the reaction system. The sim2simulation run includes also the additional CO_2 source from 2HPr + OH.~~ The error bars of the experimental data represent the accuracy error. Model runs of the sum parameter PAN + CO_2 are shown considering only the formation of PAN and CO_2 due to $CH_3C(O)$ radicals formed in the reaction system (dashed line) and including additionally the CO_2 source from 2HPr + OH (solid line). The model run in panel (b) considers only primary PAN and CO_2 formation from 3P2 + OH. Panel (c) and (d) represent model runs according to scenario 3 (acetaldehyde and methyl glyoxal at the upper limit of the accuracy error) and panel (e) and (f) according to scenario 4 (acetaldehyde and methyl glyoxal at the lower limit of the accuracy error), respectively.

Comment 2: Also, as mostly an aside [and in reference to the authors' response (a)], one can obtain the 2HPr yield from a plot such as that shown in Figure 8, if appropriate units/normalization is done. (The whole product profile scales with this yield value).

Response: We agree that the profile scales with the yield. But in our understanding it is not possible to derive the yield and the rate coefficient from that plot at the same time. However, we understood this comment to be informative solely given that no further changes were requested.