Authors' responses to comments from referee 1 on: Illmann et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-575

We thank the referee for the valuable 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.

Comment 1: In this work, the authors provide a kinetic and mechanistic study of the OH-initiated oxidation of 3-penten-2-one (3P2), and its by-product 2-hydroxy-propanal (2HPr), chemistry that is of potential importance in biomass burning plumes. Major outcomes of the work include a first-time determination of the products of the OH-initiated oxidation of the two species, and a determination of the rate coefficients for their OH reaction (each of which was the subject of one previous study).

It is my opinion that this is likely to be a publishable body of work, although I think there are a few quantitative issues that need to be resolved before publication is recommended.

Response: We thank the referee for the evaluation and the very useful suggestions.

Comment 2: My major comment has to do with the modeling work that is done. I think much more needs to be said about the details of this modeling (even though this is outlined in a recent paper by the same authors), to lend confidence in the key parameters that are derived from it (e.g., k(OH+2HPr), branching ratios for this reaction, 'corrected' yields of various products). First, the details of what is included in the model, how it is run, what parameters are varied, etc., needs to be included. Further, the sensitivity of the model output to the varied parameters needs to be shown (presumably graphically). As examples, how sensitive is the model to the OH/2HPr rate coefficient, to the branching ratios to the two channels in this reaction, etc. What does an 80:20 branching in the OH/2HPr reaction look like compared to 70:30 or 90:10? Etc…

Response: The referee's comment contains quite a lot of aspects. In the following we thus subdivided the comment and we will try to answer point-by-point to the different issues that were addressed.

My major comment has to do with the modeling work that is done. I think much more needs to be said about the details of this modeling (even though this is outlined in a recent paper by the same authors), to lend confidence in the key parameters that are derived from it (e.g., k(OH+2HPr), branching ratios for this reaction, 'corrected' yields of various products). First, the details of what is included in the model, how it is run, what parameters are varied, etc., needs to be included.

Response: On the one hand, we understand from this comment that the referee is missing some details of the modelling work. The approach we use can be written down in calculation programs like Microsoft Excel. It does not aim to fully draw a detailed mechanism, with all radical reactions (like MCM), and is just used to describe the temporal behaviour of the main species in chamber experiments with a defined radical source like methyl nitrite photolysis. In doing so, one can obtain the product yields (branching ratios) of the target reaction. Based on simplified reaction sequences (for instance: A + OH → B + C, A + wall, B + OH → C, C + OH → …) differential equations are constructed for each experimentally quantified species. Input parameters, as described in our recent paper, are the initial concentration of A (which corresponds to 3P2), the rate coefficient for each reaction and the OH-concentration. The whole calculation is based on the Euler method (= Euler-Cauchy approach) which is the most basic numerical procedure to solve differential equations. The time intervals (= step size), in which the differential equations are solved, are typically in the order of < 0.1 s. 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 (but no rate coefficient is determined from the model). 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."

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	$CH_3CH{=}CHC(O)CH_3 + wall \rightarrow$		$\leq 1.0 \times 10^{-4}$ 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	$CH_3C(O)H + wall \rightarrow$		$\leq 1.0 \times 10^{-4}\ s^{-1}$	[a, e]
R8	$CH_3C(O)C(O)H + OH \rightarrow$ products		$1.3 \times 10^{-11}\ cm^{3}\ molecule^{-1}\ s^{1}$	[a, h]
R8a	$\rightarrow CO + CH_3C(O)OONO_2$	[i]		
R8b	$\rightarrow CO + CO_2 + HCHO$	[i]		
R9	$CH_3C(O)C(O)H + wall \rightarrow$		$\leq 1.0 \times 10^{-4}\ s^{-1}$	[a, e]
R10	$CH_3C(OH)C(O)H + OH \rightarrow$ products		$1.7 \times 10^{-11}\ cm^{3}\ molecule^{-1}\ s^{1}$	[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	$CH_3C(OH)C(O)H + wall \rightarrow$		$\leq 1.0 \times 10^{-4}\ s^{-1}$	[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).

On the other hand we are not sure how to interpret that "much more needs to be said about the details of this modelling (even though this is outlined in a recent paper by the same authors)". Are more details needed here than previously outlined in our recent paper? If not, in our understanding, it is not necessary to repeat the fundamentals of our approach (and a brief summary was already given in the experimental part) and we therefore think that the additional table is sufficient for traceability.

"what parameters are varied": This is basically said in the experimental section. However, for clarity this is included in the additional table and the description in the experimental section has been modified as shown above.

Further, the sensitivity of the model output to the varied parameters needs to be shown (presumably graphically) [see Response (b)]. As examples, how sensitive is the model to the OH/2HPr rate coefficient [see Response (a)], to the branching ratios to the two channels in this reaction, etc [see Response (b)]. What does an 80:20 branching in the OH/2HPr reaction look like compared to 70:30 or 90:10? Etc… [see Response (b)]

Response (a): The model was not used to determine *k*(2HPr+OH) since it would not be possible to obtain both its first-generation yield and its rate coefficient at the same time. 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. For the modelling we used the reference value given by Baker et al. (2004). 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):

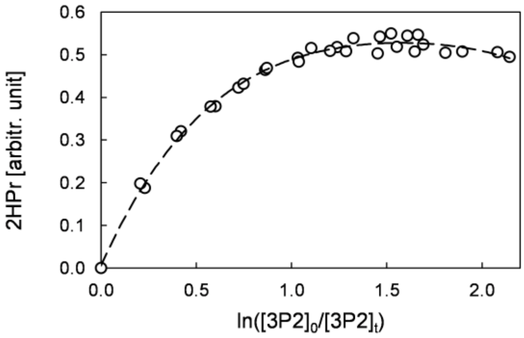

Figure 8. Non-linear plot for the formation of 2HPr from the 3P2 + OH reaction according to Baker et al. (2004) used to estimate the rate coefficient of 2HPr + OH.

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 $(2.2 \pm 0.6) \times 10^{-11}$ 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."

Response (b): We thank the referee for this very valuable suggestion! Our conclusions, the given branching ratios as well as their assigned uncertainties are based on a careful sensitivity analysis. We agree, however that it might very valuable to show this graphically. We therefore updated Fig. 9 (Fig. 8 in the originally submitted manuscript) 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."

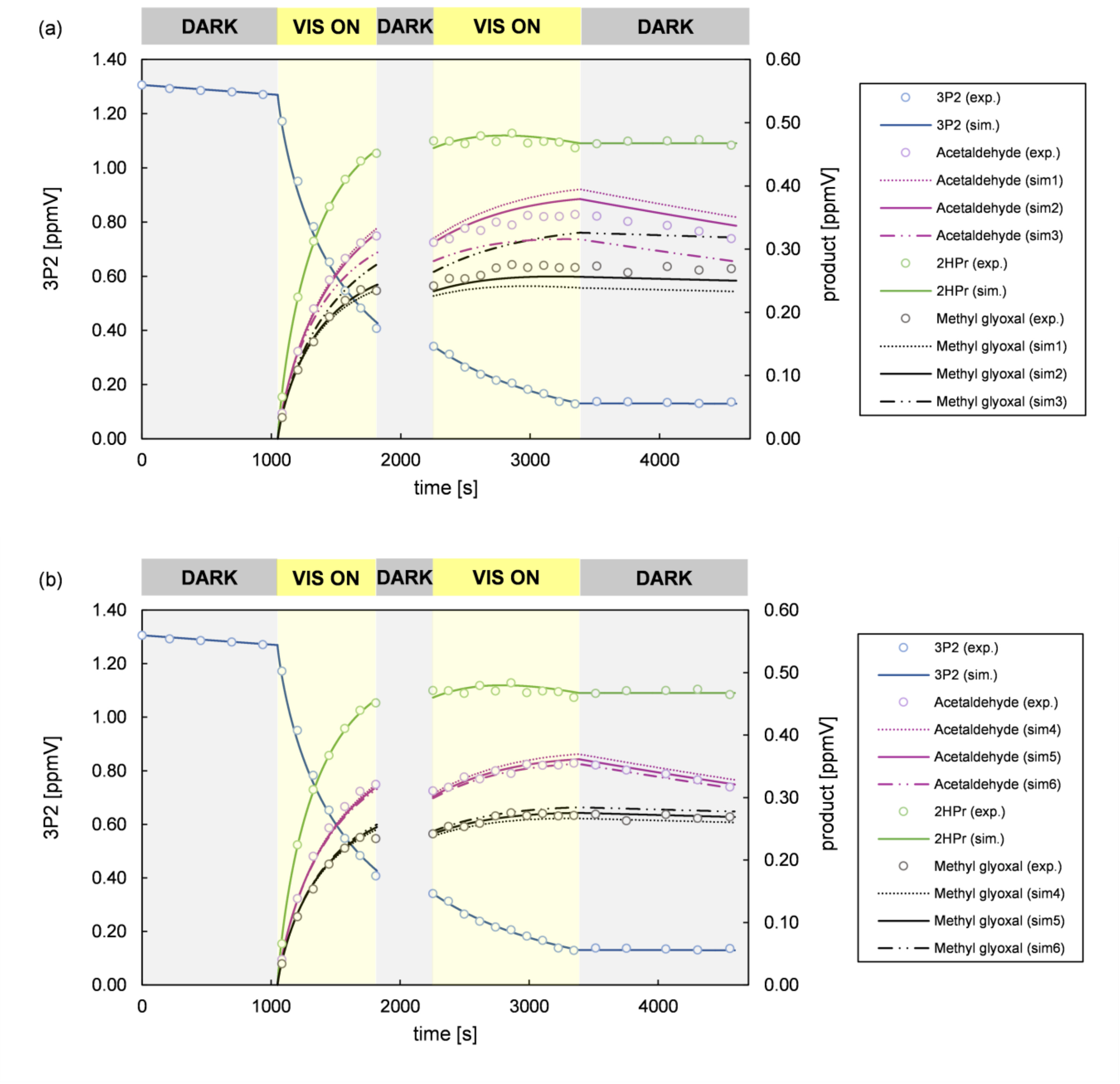

Figure 9. Experimental and simulated time profiles for a 3P2 + OH experiment, performed in the 1080 L chamber, with a ~~second~~ supplementary addition of methyl nitrite and NO during the second dark phase of the experiment. The experimental set-up did not allow the quantification of CO_2. The parameters 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).

More minor remarks:

Comment 3: How is the 3P2 introduced into the chamber and how is its initial concentration determined? In particular, if this calibration is volumetric or similar, how is the 85% purity of the purchased sample dealt with?

Response: The 3P2 is introduced into the chamber by the injection via a Hamilton^{TM}-syringe into a heated stream of bath gas. However, this method was employed for preparing an experiment, and not used for the determination of the initial concentration. The concentrations are obtained by subtracting a calibrated reference spectrum of 3P2 where the 3P2 cross sections were determined previously by injection of various volumes of diluted solutions (3P2 in dichloromethane) into the 480 L chamber. These highly diluted solutions are prepared from weighted 3P2 samples considering the 85w% purity.

Comment 4: Page 6 – Did the authors determine a wall loss for the reference species used in the k(OH) determinations? If so, were they negligible? What fraction of the 3P2 loss is due to the walls compared to the loss due to OH reaction in a typical experiment?

Response: The reference compounds did not show any wall loss. The ratio between the first-order loss due to OH and the wall loss was typically > 8. For clarity, we added:

“The first-order wall loss of 3P2 was < 1 $\times 10^{-5}$ s^{-1} in all 480 L chamber experiments and in the range of (5–10) $\times 10^{-5}$ 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 5: Page 7 – The formation of acetaldehyde from the large Criegee radical formed in the 3B2OL / O3 system is a bit surprising to me. A standard pathway for decomposition might be to form OH and methylglyoxal, rather than acetaldehyde? Can the authors provide any further ideas or speculation on its formation mechanism? (Any chance of impurities existing in the alcohol?).

Response: We were also quite surprised about the formation of acetaldehyde since we also expected rather methyl glyoxal formation through the larger CI after elimination of OH and reaction with O_2. Traces of methyl glyoxal might be present in the system. Due to the superposition of absorption features we can, however, neither confirm nor rule out its formation.

If acetaldehyde was formed through an impurity of the 3B2OL sample this would indicate an unidentified unsaturated species since due to the high amounts of CO, used as OH scavenger, the acetaldehyde formation must originate from an O_3 reaction. The purity of the 3B2OL sample is 97%. Given that the experimentally observed formation of acetaldehyde accounts for about 14% of the 3B2OL consumption this is quite unlikely resulting from an impurity. Any further speculation on the mechanism are beyond the scope of this study.

Minor corrections, suggestions, etc.:

Comment 6: I don’t know what an Euler-Cauchy model is. Please explain briefly.

Response: We believe that this is a misunderstanding. We used the term “Euler-Cauchy model” just to name the approach we used. The Euler method is a basic numerical procedure to solve differential equations. However, we noticed that while in German the method is referred to “Euler-Cauchy”, the English term seems to be “Euler method”. We exchanged the term in the whole manuscript and modified the abstract 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 7: Page 2, line 33, I suggest “Unsaturated ketones are of increasing interest as …”

Response: Corrected.

Comment 8: Page 2, line 43, I suggest "is believed to be a …"

Response: Corrected.

Comment 9: Page 2, line 48, I suggest "Some field measurements of BB plumes…"

Response: Corrected.

Comment 10: Page 2, line 59, I suggest changing "Besides" to "In particular" (or something similar).

Response: We changed into "In particular".

Comment 11: Page 2, line 59, Change "expand" to "expanding".

Response: Corrected.

Comment 12: Page 6, line 167: Maybe "all of the experimental results" instead of "the whole…"

Response: We changed into "Table 1 summarises the results obtained from all conducted kinetic experiments".

Comment 13: Page 7, line 184: 'coexist' instead of 'coexists'.

Response: Corrected.

Comment 14: Page 12, line 290: Specify that this is from the OH + 3P2 reaction.

Response: We modified as follows:

"… is derived for 2HPr in the 3P2 + OH reaction, from the regression analysis of all experiments …"

Comment 15: Page 14, line 360, also Page 16, line 392: The equivalent yields of the two products does not prove that they come from the same pathway. I suggest using different wording here. 'suggests' or 'consistent with'?

Response: Pages 14, line 360 has been modified as written above (Response (b) to Comment 2). We replace "proving" with "indicating" in line 392 on page 16.

Comment 16: Page 17, top: Nitrates are quite strong absorbers in the IR. Was there any sign of their formation? Can any limit on their yield be obtained, using nitrate IR cross sections (which are reasonably transferable) from other works?

Response: We did not find any clear indication for formation of organic nitrates. The shape of the residual spectra made any attempt to estimate an upper limit for their formation highly speculative. Therefore, we prefer to give no values.

Comment 17: Page 17, line 413: Specify that it is 3P2 that you are referring to.

Response: We modified as follows:

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

Comment 18: Page 17, line 419: While I agree that 3P2 (and by-products) are a source of PAN, the overall contribution to NOx reservoirs will depend on the concentrations of 3P2 relative to other PAN sources. Perhaps 'soften' the language here?

Response: The paragraph refers only to the potential of 3P2 to form NO_x reservoir species and not to the contribution of this reaction to the overall NO_x reservoir sources.