Referee 1

The referee's comment are in black, our replies in blue and changes to the text in red.

General comments This is a revised and updated paper, presenting an analysis of the impact of pyruvic acid photolysis on the chemistry and composition of the boreal forest boundary layer, for the conditions of a 2016 autumn campaign (IBAIRN) at the SMEAR II field station in Hyytiälä, Finland. The observationally-constrained box modelling analysis has been substantially improved by use of a detailed and previously peer-reviewed chemical mechanism (Sander et al., 2019), allowing a much more reliable and informative assessment of the contributions of pyruvic acid photolysis to the formation of acetaldehyde, peroxy radicals (HO2 and CH3C(O)O2) and related products at the campaign location. The work has also benefitted greatly from being able to take account of the recent experimental study of Samanta et al. (2021), characterising the primary formation of methylhydroxy carbene (CH3COH) and CO2 from the photodissociation of pyruvic acid, a piece of work presented at the AGU and published since my previous review in early December 2020. The results of that study are further enhanced by the inclusion of a theoretical assessment of the fate of CH3COH under tropospheric boundary layer conditions. This is now a very complete piece of work, providing a thorough analysis of the impact of pyruvic acid photolysis on the chemistry and composition of the boreal forest boundary layer during the IBAIRN campaign. This paper is entirely suitable for publication in ACP. Some comments on the revised paper are given below. These are mainly minor and typographical, but with one or two suggestions of where some further information might be helpful to the inquisitive reader:
We thank the referee for this very positive assessment of the revised manuscript.

line 94: "unumolecular".
Corrected

line 145: "...monoterpenes (henceforth referred to as MT)...". A very minor point, but I note that the term "monoterpenes" is used a further 9 times, although the abbreviation "MT" is subsequently used 17 times.
We have now used the abbreviation MT or MTs throughout

Line 185: I am reassured that the chemical mechanism is based on that for CAABA/MECCA, as previously reported in Sander et al. (2019), and therefore a vast improvement on that used in the original analysis reported in the first version of this paper. In view of the importance of monoterpenes in this work (α-pinene, βpinene, 2- + 3-carene, limonene and camphene are reported as detected on line 228), some information should be given on how the speciation was constrained in the model. I note that the mechanism in Sander et al. (2019) includes explicit α- and β-pinene chemistry (partly informed by MCM), and chemistry for carene and camphene that feeds into the pinene mechanisms. There does not appear to be any limonene chemistry, although that is in MCM. I'm sure these points are clarified in the "complete reaction scheme and source of rate coefficients" in the data archive for this paper, but that appears to be unavailable without contacting the authors (which is incompatible with anonymous review). Some brief information in the main text/SI about monoterpene speciation and chemistry in the model calculations would be helpful.
The MTs were split according to the GC-AED measurements. We have added the following text:

Based on the GS-AED measurements, the MTs were split into α-pinene (49 %), β-pinene (13 %), Δ-carene (27 %) and camphene (8 %). Limonene is not included in the standard chemical mechanism of CAABA/MECCA but as its contribution to the MTs was only 3 % it was treated as Δ-carene (increasing its contribution to 30 %).

Line 195: I agree that peroxyacyl nitrate burdens are invariably dominated by PAN itself, but a 90 % contribution seems a little high to me and requires more justification. PAN/(total PANs) increases with processing time because many larger PANs (e.g., PPN, MPAN) and their precursors are degraded to species that form PAN. Therefore, I'm not sure ratios based on airborne measurements over the Arctic (Roiger et al., 2011) and the Pacific (Roberts et al., 2004) are necessarily an appropriate guide. Based on Williams et al. https://doi.org/10.1029/97GL00548, 1997) and Roberts et al. (doi:10.1029/2001JD000947, 2002), PAN/PPN seems to be around 5 or 6 in relatively young anthropogenic dominated air masses, consistent with an upper limit contribution of a bit less than 90 % (upper limit because there are higher PANs too); and in biogenic (isoprene) dominated environments, the PAN/MPAN ratio is typically 4-10 (again probably depending on processing time). The average contributions over all conditions in the Roberts et al. (2002) SOS study are about 80% PAN, 11% PPN, 2% PiBN and 7% MPAN. Detection of other higher PANs has also been reported (e.g., PBN by Grosjean et al., https://doi.org/10.1021/es00039a013, 1993), and the oxidation of the monoterpenes is expected to make large PANs (e.g., those derived from pinonaldehyde, limononaldehyde and caronaldehyde). In view of this, how sensitive are the calculations to (e.g.) a 10 % change in the assigned PAN contribution?

The referee is correct that 90% may be on the high side. Unfortunately, there are no measurements of the fractional contribution of PAN to PANs at Hyytiälä and use of data from an isoprene dominated environment (with high MPAN) is unlikely to be representative. In any case, PAN, which is in equilibrium with acetylperoxy radical and NO_2, does not contribute to the net CH_3CO production rate (see Figure 7) and changing its mixing ratio by a few percent will not impact our results or conclusions.

In addition, the model should allow a speciation to be calculated. I count about 35 PANs in the mechanism in Sander et al. (2019). I realise that many will be unimportant for the IBAIRN conditions, but they include PAN, PPN, PiPN, MPAN, the small oxygenated species, HOCH2C(O)OONO2, HC(O)CH2C(O)OONO2, and those derived from pinonaldehyde and norpinonaldehyde. The modelled speciation is something that could be informative in a wider context, and which could be reported and applied in this work.

We agree that the speciated, modelled PANs would be useful for comparison with speciated measurements of PANs. However, no such measurements were available during IBAIRN, and we feel that this extra information would detract from the focus of this paper, which is on CH_3CHO, $CH_3C(O)O_2$ and HO_2 formation from PA photolysis.

line 229: Should "Δ-" be "d-" (or "D-") for limonene?
Correction made

line 230: "sifnificant".
Correction made

Line 326: "coeffocient".
Correction made

lines 328-329: "...is reminiscent of the chemistry of other α-OH alkyl radicals...". I understand the mechanistic point, but can CH3C•(OH)OO• be described simply as an α-OH alkyl radical? It is a biradical, which looks like a Criegee intermediate (biradical/zwitterion). If so, I think it would decompose/rearrange to form either a dioxirane (anti-) or PAA (syn-) (based on Table 28 in the SI of Vereecken et al., https://doi.org/10.1039/c7cp05541b, 2017). The products presented here (formation of CH3CO + HO2) are compatible with formation and fragmentation of hot PAA, so is this effectively the same species and process reported by Vereecken et al. (2017) and is CH3C•(OH)OO• a Criegee? If so, some clarification of this, and reference to Vereecken et al. (2017), might be helpful.

The specific chemistry for a Criegee intermediate is due to its singlet wavefunction (best described as CH3C(OH)=O+O-), which allows for re-arrangement with new bond formation in the dioxirane or PPA products mentioned. The CH3C•(OH)OO• intermediate described here, however, must instead have a triplet wavefunction as the reaction of CH3COH + 3O2 occurs on the triplet surface. The same-spin electrons prevent formation of the needed new bonds after rearrangements and because of this, unimolecular reactions are energetically not accessible and the fate of the triplet intermediate is reaction with O2. We now note explicitly in the paper that the triplet and singlet forms have very distinct chemistries.

The decomposition of the $CH_3C^\bullet(OH)OO^\bullet$ triplet diradical intermediate, forming $CH_3C^\bullet=O$ + HO_2, is reminiscent of the chemistry of α-OH alkyl radicals with unpaired electrons, and should occur rapidly owing to the sufficiently high energy content of the peroxyl-alkyl diradical (Hermans et al., 2005, 2004; Dillon et al., 2012; Olivella et al., 2001; Dibble, 2002). Note that this chemistry is very distinct from that of the singlet $CH_3C(OH)OO$ Criegee intermediate.

Regarding the phrase on line 328-329 (in quotes above), perhaps omitting the word "other" would help.
"Other" has been deleted.

line 380: A reference would seem to be required for organic acid concentrations. What about Millet et al. (https://doi.org/10.5194/acp-15-6283-2015)?
Reference to Millet et al, 2015 added

line 427: "neglecetd".
Correction made

line 428: ". (see Fig. S" line 433: Is the word "coincidentally" necessary here? It is logical that the NO/NOx ratio tends to maximise in the middle of the day when NO2 photolysis is most rapid.
"coincidentally" has been deleted.

line 449: "productio".
Correction made

line 456: "indrect".
Correction made

line 463: For consistency, and equation balancing, the HCHO photolysis reaction needs to specify two O2 molecules in a bracket.
Correction made

line 470: I think "and HCHO" needs to be deleted here, because there are too few values given and HCHO is given a value in the next sentence.

Correction made

Line 471: "enhanved".

Correction made

Lines 475-478: The first sentence of the conclusions could be much clearer. A comma after "major product of its photodissociation" would make it clearer, but I suggest splitting the sentence up into two or three sentences might be helpful.

We have modified the sentence and now write:

We have combined measurements of pyruvic acid in an autumn campaign in the boreal forest (IBAIRN) with theoretical calculations designed to characterise the fate of the methylhydroxy carbene radical (CH_3COH, the major product of its photodissociation) with a box modelling study. We investigated the impact of pyruvic acid photolysis on the rates of production of acetaldehyde (CH_3CHO) and the peroxy radicals $CH_3C(O)O_2$ and HO_2.

Line 481: This information should probably be qualified to reflect that the CH3COH + O2 rate coefficient was elevated by an order of magnitude over the calculated value to make it contribute.

We have modified the text to write:

The reaction of CH_3COH with O_2 is slow, but will contribute to its fate (and thus the formation of $CH_3C(O)O_2$ and HO_2) in the lower atmosphere where O_2 concentrations are high if the rate constant used (elevated by an order of magnitude compared to the highly uncertain theoretical value) is correct.

Referee 2

The referee's comment are in black, our replies in blue and changes to the text in red.

The manuscript is vastly improved; the authors have done a great job of considering (via theoretical methods and box modeling) the chemistry of CH3C:OH which has recently been reported to be a major pyruvic acid photolysis product. I think the manuscript is acceptable essentially as is, and I have only a few minor corrections to suggest:
We thank the referee for this very positive assessment of the revised manuscript.

Line 245: Should be J-Pyr, not J-NO2?
Corrected.

Line 347: Maybe mention that this is a formate ester.
We have added the chemical formula to the text.
....forming a 1-hydroxyethylester (CH3CH(OH)OC(O)H).

Page 13, It might be helpful to indicate that the text from line 392 to the end of the section all belongs to Scenario B (i.e., involves the CH3COH chemistry).
The text referred to is preceeded by "Scenario B" . We have removed a paragraph-break and the text "in the box-model" so that it is clear that the rest of the section deals with Scenario B.
In scenario B, we consider the effects of using photodissociation quantum yields of 0.2, 0.5 and 1 (scenarios $B_{0.2}$, $B_{0.5}$ and B_1, respectively). Photolysis at wavelengths < 340 nm was considered...etc.

Also, for scenario A, repeating the IUPAC quantum yield information would be helpful, I think.
We have added this information as suggested.
Scenario A: In this scenario we used pyruvic acid cross sections, quantum yields and product yields according to the IUPAC recommendations (IUPAC, 2020) with a photodissociation quantum yield (ϕ) of 0.2 at 1 bar pressure and branching ratios of 0.6, 0.05 and 0.35 for reactions R1, R2 and R3 as listed in section 1.1.

Line 470: Delete 'and HCHO' ?
Correction made

Also, I think these data are in Fig S6, not S5.
Correction made

There are typos on lines 94, 131, 327, 428, 449, 456, 471, 484.
Typos found and corrected