

Review of acp-2020-975 revision: "Impact of pyruvic acid photolysis on acetaldehyde and peroxy radical formation in the boreal forest: Theoretical calculations and model results." by Eger et al..

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 (HO_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$) 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 (CH_3COH) and CO_2 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 CH_3COH 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:

line 94: "unumolecular".

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.

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, β -pinene, 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.

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? 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, $\text{HOCH}_2\text{C}(\text{O})\text{OONO}_2$, $\text{HC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{OONO}_2$, 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.

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

line 230: "sifnificant".

Line 326: "coeffocient".

lines 328-329: "...is reminiscent of the chemistry of other α -OH alkyl radicals...". I understand the mechanistic point, but can $\text{CH}_3\text{C}(\text{OH})\text{OO}\cdot$ 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 $\text{CH}_3\text{CO} + \text{HO}_2$) 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 $\text{CH}_3\text{C}(\text{OH})\text{OO}\cdot$ a Criegee? If so, some clarification of this, and reference to Vereecken et al. (2017), might be helpful. Regarding the phrase on line 328-329 (in quotes above), perhaps omitting the word "other" would help.

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>)?

line 427: "neglectd".

line 428: ". (see Fig. S"

line 433: Is the word "coincidentally" necessary here? It is logical that the NO/NO_x ratio tends to maximise in the middle of the day when NO_2 photolysis is most rapid.

line 449: "productio".

line 456: "indirect".

line 463: For consistency, and equation balancing, the HCHO photolysis reaction needs to specify two O_2 molecules in a bracket.

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.

Line 471: "enhanved".

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.

Line 481: This information should probably be qualified to reflect that the $\text{CH}_3\text{COH} + \text{O}_2$ rate coefficient was elevated by an order of magnitude over the calculated value to make it contribute.