

## ***Interactive comment on “Modelling the impact of gas-phase pyruvic acid on acetaldehyde and peroxy radical formation in the boreal forest” by Philipp G. Eger et al.***

**Anonymous Referee #1**

Received and published: 3 December 2020

### General comments

Building upon the results reported in a previous study (Eger et al., doi.org/10.5194/acp-20-3697-2020), this paper presents a modeling analysis of the potential impact of pyruvic acid photolysis on the chemistry and composition of the boreal forest boundary layer, for the conditions of summer and autumn campaigns at the SMEAR II field station in Hyytiälä, Finland. An observationally-constrained box model is used to investigate the contributions of pyruvic acid photolysis to the formation of acetaldehyde and peroxy radicals ( $\text{HO}_2$  and  $\text{CH}_3\text{C}(\text{O})\text{O}_2$ ), and these contributions are reported to be significant and potentially dominant. The analysis takes account of reported large disagreements

C1

in the overall quantum yield and product channel contributions for pyruvic acid photolysis, and therefore highlights an urgent need for further experimental studies on the photochemistry of this species.

As with Eger et al. (2020), this paper highlights a potentially important role for pyruvic acid in the boreal forest environment. A difficulty I have is whether the reported observationally-constrained modeling study is genuinely robust enough to allow the reported quantitative conclusions to be drawn, and therefore if this paper builds substantially upon the information already reported by Eger et al. (2020). I have some serious concerns about the simplicity of the chemical mechanism used and the organic chemistry it represents. As presented (Table S2), the mechanism is a substantially simplified representation of the likely set of processes that were actually occurring in the vicinity of the campaign site. While the use of simplified chemistry can be fully adequate and justifiable, there is only limited discussion of and justification for the processes that are included and (more importantly) those that are omitted in the present work. As a result, I find it quite difficult to judge how reliable some of the reported conclusions are, particularly those that relate to radical sources and contributions (see further below).

In addition, the complete set of observations that are ideally required to allow the model to be constrained are not available for either of the autumn (IBAIRN) or summer (HUMPPA) campaigns. In particular, the abundance of pyruvic acid itself was not measured during HUMPPA, but was derived from the inferred emission rate of monoterpenes using a parameterization based on the autumn IBAIRN campaign. Eger et al. (2020) report that (unlike monoterpenes) pyruvic acid emission depends on both T and PAR, and the present paper indicates that the IBAIRN parameterization may not be transferable to other times of the year (page 8, line 3). Despite this, this is exactly what is done for the HUMPPA simulation without any further discussion, justification or caveats. It is noted that the most impressive result (i.e. 94 % of acetaldehyde formation) is derived from that analysis and appears in the Abstract. Conversely, acetaldehyde was not measured during IBAIRN, and the reported contributions of pyruvic

C2

acid photolysis for that campaign only take account of the acetaldehyde sources that are represented in the model, which are probably incomplete.

Although the presented work, and the previous study of Eger et al. (2020), provide interesting evidence for an important role for pyruvic acid in the boreal forest environment, the model used in the present modeling study is too simplistic to allow the reported quantitative conclusions to be drawn. The authors should consider addressing the shortcomings and omissions in the chemical mechanism and represented precursor species, possibly by using a customized version of an existing tool such as the MCM. I agree with the recommendations for further experimental studies on the photochemistry of pyruvic acid and on its emission rate, but these recommendations already appear in Eger et al. (2020).

#### Specific comments

The chemical mechanism used for the reported simulations (Table S2) contains only selected reactions. Some of these have incomplete product sets and some are parameterized, and I can find no clear discussion or justification of what these are based on or why they are considered adequate. With the exception of pyruvic acid photolysis itself, very little is represented explicitly or fully. As a result, there is a potentially enormous amount of missing organic chemistry which could otherwise contribute to the formation of the species of interest (i.e. acetaldehyde and peroxy radicals, including HO<sub>2</sub> and CH<sub>3</sub>C(O)O<sub>2</sub>), suggesting that the simulated contributions arising from pyruvic acid photolysis are consistently overestimated.

One very clear indication of missing organic chemistry is the CH<sub>3</sub>C(O)O<sub>2</sub> budget reported in sections 3.2 and 3.3. Decomposition of the (observed) PAN is calculated to be the major or dominant CH<sub>3</sub>C(O)O<sub>2</sub> source. However, because PAN is a reservoir (rather than a primary source) this is approximately balanced by CH<sub>3</sub>C(O)O<sub>2</sub> loss by reaction with NO<sub>2</sub>, indicating that an equivalent primary source is required from elsewhere. This is clearly not fully represented in the simulations. As discussed in

C3

the literature (e.g. Fischer et al., doi.org/10.5194/acp-14-2679-2014), the sources can include oxidation or photolysis of co-called “immediate” precursor carbonyls (e.g. acetaldehyde, methylglyoxal, acetone, MEK) and a suite of terpene and isoprene oxidation products. In practice, CH<sub>3</sub>C(O)O<sub>2</sub> can be formed from the reactions of O<sub>3</sub> with α-pinene, limonene, 2-carene and 3-carene (i.e. the measured terpenes and also many other BVOCs), from the further chemistry of peroxy radicals containing the C(OO)C(=O)CH<sub>3</sub> substructure. These are formed as co-products with OH, following decomposition of relevant Criegee intermediates and reaction of the resultant vinyloxy fragment with O<sub>2</sub>. The relevant chemistry in the applied chemical mechanism,

O<sub>3</sub> + terpenes → OH

therefore omits the C<sub>10</sub> organic radical co-product and all its associated organic chemistry. The missing chemistry for this pathway (and for other pathways) not only includes sources of CH<sub>3</sub>C(O)O<sub>2</sub> and other peroxy radicals, but the set of ozonolysis pathways also potentially produces “immediate” CH<sub>3</sub>C(O)O<sub>2</sub> precursors such as methylglyoxal (and larger C(O)C(O)CH<sub>3</sub> species) and acetone. In general terms, the OH- O<sub>3</sub>- and NO<sub>3</sub>-initiated chemistry represented for monoterpene oxidation is severely limited, inadequately parameterized or completely absent, and the chemistry of other BVOCs (e.g. sesquiterpenes) is also not considered, even though reported to be significant at SMEAR II (Hellén et al., doi.org/10.5194/acp-18-13839-2018).

It is noted that the authors confirm that there must be missing sources of CH<sub>3</sub>C(O)O<sub>2</sub> in their model (final sentence of section 3.3), to account for the observed formation of CH<sub>3</sub>C(O)OOH during HUMPPA reported by Crowley et al. (doi:10.5194/acp-18-13457-2018). In view of this, it is not clear why the reported contributions of pyruvic acid photolysis to CH<sub>3</sub>C(O)O<sub>2</sub> formation (e.g. in the Abstract) are not adjusted downwards, or at least qualified, to reflect this.

Other than pyruvic acid photolysis, the only sources of acetaldehyde represented in the model appear to be the reactions of OH with ethane, propane and n-butane. These are

C4

highly parameterized, only making fractional yields of acetaldehyde and no other products, and incorrectly acting as a radical sink. Other than a brief footnote to Table S2, no justification for this representation is given. There are potentially other precursors to acetaldehyde that may be individually or collectively important, including ethanol, larger oxygenates (e.g. propanal and MEK: Hellén et al., doi.org/10.5194/acp-4-1771-2004), any species with a C=CHCH<sub>3</sub> substructure (e.g. propene, 2-butenes, 2-butenal, 2-hexenal: Hellén et al., doi.org/10.5194/bg-3-167-2006, doi.org/10.5194/acp-4-1771-2004) and additional alkanes to those already represented.

#### Other comments

Page 2, line 13: Should probably also include CO<sub>2</sub> for completeness. The description in section 2.2.1 also identifies formation of CH<sub>3</sub>C(O)OH + CO as an "important" channel. If this is the case, should these products also be listed here?

Page 2, line 21: CH<sub>3</sub>C(O)O<sub>2</sub> and HO<sub>2</sub> (i.e. the other pyruvic acid photolysis products of interest) are also more immediate precursors to PAA.

Page 3, line 2: Is "large" emphasizing that the biogenics are large (i.e. monoterpenes rather than isoprene) or indicating that the emissions are large? It is not clear.

Page 3, line 15: Presumably, photolysis rates of other species were also required and were/could be calculated in the same way. The reaction listing in Table S2 also includes photolysis of glyoxal and H<sub>2</sub>O<sub>2</sub> (although the former photolysis rate is based on that of NO<sub>2</sub>), but somewhat surprisingly not CH<sub>3</sub>CHO. There are probably other omissions too, such that the species for which photolysis is represented seem rather arbitrary.

Page 4, lines 17-32: Some of the presented information would seem to require associated citations. Currently, there are none.

Page 4, reaction (R5): The products of this reaction should be HO<sub>2</sub> + CO<sub>2</sub>.

Page 4, line 31: For clarity and consistency, "CH<sub>3</sub>CO<sub>3</sub> + HO<sub>2</sub>" should be written "CH<sub>3</sub>C(O)O<sub>2</sub> and HO<sub>2</sub>".

C5

Page 5, line 6: "UPAC".

Page 5, line 9, and Table 1: "CH<sub>3</sub>CO<sub>3</sub>" should be "CH<sub>3</sub>C(O)O<sub>2</sub>" for consistency. Please also check whole paper for consistency.

Page 5 and Table 1: The considered products of pyruvic acid photolysis are given as either "CH<sub>3</sub>CHO" or "CH<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub>". Although these are the products of interest, they do not describe either the primary photolysis products, or the full set of products following secondary chemistry (which I think are "CH<sub>3</sub>CHO + CO<sub>2</sub>" and "CH<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub> + CO<sub>2</sub>").

Page 5, lines 1-10. From what is written, it is not clear why the IUPAC recommendation differs so much from the recent study of Reed Harris et al. (2017). Perhaps the studies on which the IUPAC recommendation is based should also be cited and described, as IUPAC presumably judged those to be more reliable and convincing.

Pages 5 and 6, sections 2.2.2 and 2.2.3. It should probably be stated again clearly what measurements were used to constrain the model for each of the campaign simulations, so that the additions and omissions can be placed in context.

Page 5, line 24: "OH" should be "The concentration of OH".

Page 5, lines 28 and 29: The basis for the assigned additional OH reactivity for unmeasured OVOCs sounds rather arbitrary. In practice, there could be an abundance of both missing sources and missing sinks of OH that are unaccounted for in the simple model used.

Page 6, line 27: delta-limonene should probably be d-limonene. Is delta-carene 2-carene or 3-carene?

Page 10, line 2: Should "preceding" be "proceeding"?

Page 11, lines 14, 16 and 22. Insert "photolysis" after "pyruvic acid".

C6

