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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Pyruvic acid in the boreal forest: first measurements and impact on radical chemistry" *by* Philipp G. Eger et al.

Anonymous Referee #1

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General Comments:

The manuscript presents gas-phase measurements of pyruvic acid in the boreal forest during the IBAIRN campaign. The average mixing ratio of pyruvic acid was 96 pptv with a maximum of 327 pptv. The contribution of isoprene oxidation and direct emission of gaseous pyruvic acid to the source strength is assessed in this work. The photolytic fate of gaseous pyruvic acid results in the production of acetaldehyde and peroxy radicals in the boreal forest. This is an interesting manuscript for the readers of Atmospheric Chemistry and Physics and should be published after a revision. Specific comments are provided below to improve the manuscript before publication.

Specific Comments:

1) The revised version of the manuscript should change its title by deleting the word "First". Such attribution is unnecessary and conflicts with other previous field measurements of pyruvic acid. In addition, while measuring pyruvic acid as described, the manuscript should indicate what other species were monitored. It is unlikely that the work was specific for pyruvic acid but that a mass range was analyzed. This range should be provided in the text and considerations for correlated species should be made in the revision to avoid fractionation of the data by reporting it together.

2) References to original papers introducing a concept or finding as well as the most recent literature should be both carefully highlighted in the manuscript. For example, in p. 1 l. 28, by reading Magel et al. (2006) it is clear the concept for the wide availability of pyruvic acid in the central metabolism of plants is not introduced by them but actually by Eisenreich et al., Trends in Plant Sciences 2001, 7, 78-84, DOI: 10.1016/S1360-1385(00)01812-4. Similarly, the source for Jardine et al. (2010) could be checked. In addition, in p. 2 l. 13 and l. 15, there have been four recent reports for the heterogeneous photooxidation of aromatics emitted during biomass burning that produced oxocarboxylic acids, including pyruvic acid by Pillar et al., which should be briefly described here: i) Pillar et al., Environmental Science & Technology 2017, 51, 951-4959, DOI: 10.1021/acs.est.7b00232; ii) Pillar et al., Environmental Science & Technology 2014, 48, 14352-14360. DOI: 10.1021/es504094x; iii) Pillar-Little et al., Environments 2018, 5, 104. DOI: 10.3390/environments5090104; and iv) Pillar et al., Journal of Physical Chemistry A 2015, 41,10349-10359. DOI: 10.1021/acs.jpca.5b07914.

3) P. 2 l. 21-23 and p. 8 l. 25: There are some differences with more current literature than the cited, which need to be considered here and estimated during a comparison of phase processes and drivers for pyruvic acid loss in the conclusions sections of the manuscript. Particularly, the photochemical loss of pyruvic acid in water was evaluated by Eugene and Guzman, J. Phys. Chem. A 2017, 121, 15, 2924-2935, DOI: 10.1021/acs.jpca.6b11916, to occur with a lifetime of only ∼22 min, and was indicated to vary by ∼2-times in the gas phase. Similarly, the lifetime for the loss of pyruvic acid

reacting with OH radical in water was evaluated to be 1-10 days and in the gas phase to be 2-months.

4) P. 2 l. 28-30: It would be important to indicate here that one of the factors that enhances the solubility of pyruvic acid, as indicated to be "highly soluble" was explained in a paper by Guzman et al., J. Am. Chem. Soc. 2006, 128, 10621-10624, DOI: 10.1021/ja062039v; in terms of a cooperative reversible equilibrium of hydration that converts the carbonyl group into a geminal diol. Similarly, for the mention of pyruvic acid "partitioning into the aerosol-phase" there should be a description here of recent work discussing the crystal structure of pyruvic acid by Heger et al., Acta Crystalographica E 2019, 75 (6), 858-862, DOI: 10.1107/S2056989019007072, and the novel study of the partitioning of gas phase pyruvic acid into water by Eugene et al., Langmuir 2018, 34, 9307-9313, DOI: 10.1021/acs.langmuir.8b01606. The last Langmuir paper should also be connected to the text about water clusters of pyruvic acid and pyruvate in p. 4 l. 26, and to the text in p. 8 l. 19-21 by including the reactive uptake coefficient of gaseous pyruvic acid by water reported to be 0.06. Finally, connected to the contribution of pyruvic acid to "SOA formation",it would be appropriate to include original related literature and the most updated papers: i) Guzman et al., J. Phys. Chem. A 2006, 110, 3619-3626, DOI: 10.1021/jp056097z; ii) Guzman et al., J. Phys. Chem. A 2006, 110, 931-935, DOI: 10.1021/jp053449t; iii) Xia et al., J. Phys. Chem. A 2018, 122, 6457-6466, DOI: 10.1021/acs.jpca.8b05724, iv) Eugene and Guzman, Molecules 2019, 24, 1124; DOI: 10.3390/molecules24061124 et al., Environ. Sci. Technol. 2019, DOI: 10.1021/acs.est.9b03742; v) Mekic at al., Environ. Sci. Technol. 2018, 52, 12306-12315, DOI: 10.1021/acs.est.8b03196; and vi) Mekic et al., Atmos. Environ. 2019, 219, 117046, DOI: 10.1016/j.atmosenv.2019.117046.

5) P. 4 l. 15: In standard analytical chemistry work the limit of detection (LOD) is established with a 99% chance of being greater than a blank for three times the standard deviation. It is confusing here that a value of 15 pptv is provided with 2 sigma for 10 s. This issue requires clarification.

6) P. 4 l. 23-24: More details about how the oxidation was accomplished in this work (and not in the reference cited) should be provided here. An associated calibration curve should be added to the supplementary information.

7) P. 5 l. 4-5: This statement is unclear. What is the meaning of a 30 % ± 10 pptv mixing ratio? Clarify the units.

8) From p. 5 l. 22 to p. 6 l. 14, and Figure S1: The general idea and the analysis are acceptable but do not explain that the anion at m/z 87 could also be assigned to 3-oxopropanoic acid.

9) P. 7 l. 21-30: This observation for the activity associated to the saw mill appears anecdotic in the context of evaluating pristine emissions from the natural boreal forest environment. The revisions should consider if the text is contradicting the objective of the manuscript.

10) After the text is revised, and the calculations are rechecked based on the comments above and the inclusion of the reactive uptake coefficient of gaseous pyruvic acid by water in the model, some editions of section 3.2 will be needed in the revised manuscript.

Technical Corrections:

P. 3. l. 20: Delete "but unexplored atmospheric component".

P. 4 l. 18-20: The statement "Laboratory . . . lower" is unnecessary and can be deleted.

P. 9 l. 26: Add a mention to "Gas Phase".

P. 10 l. 3: Insert "gaseous" before pyruvic.

P. 12 l. 9: add "in the gas phase" at the end.

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