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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid" *by* Y. Tan et al.

Anonymous Referee #3

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General Comments

The authors hypothesize that the OH oxidation pathway from isoprene to pyruvic acid via methylglyoxal continues further to acetic acid and wonder if the later could be a source of oligomers (oligoesters) in SOA. They work with acetate (20 uM - 10 mM) arguing that these concentrations are representative of samples of dew, cloud water and fog water. To confirm this hypothesis, they studied the OH radical reaction of acetic acid and predicted that succinic acid and oligomers should be formed by acid catalysis channels previously suggested by this group. Contrarily, the authors neither find oligomer formation nor succinic acid production from acetic acid. The observed

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products were glyoxylic, glycolic, and oxalic acid. The authors were unable to quantify acetic and glycolic acid because of chromatographic coelution, and only quantified the fate of 25% of the original carbon in a typical experiment. The surprising finding appears to create a conflict with a series of reports supporting acid catalysis and requires considering other possible pathways of product formation. Tan et al. state that the mechanisms leading to the formation of higher molecular weight compounds remain ambiguous. In order to rationalize the unknown possible pathways a new experiment of methylglyoxal oxidation oxidation with OH radical is presented. Several related concepts to photoinduced radical mechanisms are used to analyze again previous work. Complications also arise during the interpretation of previous data by this radical mechanism that warrant further study in this research area. A better understanding of the processes here described will be needed. The publication will be welcome to constrain the role of acid catalysis mechanisms in SOA production.

Specific Comments

Page 18320

Line 17 (Abstract): It should say "as a SOA. . ."

Lines 15-19 (Abstract) and page 18322, lines 1-2: It would be important to distinguish in the manuscript how much of this work is new because the group has already published the results of methylglyoxal and pyruvic acid reactions with OH radical in the past. After reading the manuscript, it is very clear that the importance of acetic acid in the paper is minor comparing to mehtylglyoxal and pyruvic acid experiments, and some of them have been left for supplemental information.

Page 18321

Lines 3-8: A deeper insight of the relevance of the high O/C ratios contribution to SOA mass should be provided in the introduction. How fundamental is the concept of O/C ratios to the mass balance of SOA mass? Can the authors constrain the limitations

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and errors that report those measurements?

Lines 19-23 (and Scheme 1): The efficiency of these reactions towards methyl and peroxyl radical production should be added.

Line 26 (and Scheme 1): There is no number for reactions 1 and 4 in Scheme 1.

Lines 27-30: Is the production of glycolic acid considerable to be an important contribution to the formation of oxalic acid? Would the authors be able explain how important is the production of oxalic acid?

Page 18322

Lines 10-18: A simpler explanation should be provided in this paragraph, such as "The proposal by Altieri et al. (2008) for the recombination of radicals derived from acetic acid oxidation to produce succinic acid and higher molecular weight oligomers is not viable."

Page 18323

Line 15: how critical is the fate of acetic acid? What is the percentage of pyruvic acid converted to acetic acid?

Lines 18-24-: The experimental results clearly discard the original hypothesis of the manuscript based on previous work of this group. How are previous publications by these authors affected by this finding? Can a paragraph that reconsiders their previous reports be included in the discussion as a way of summarizing the new state of knowledge. What previous concepts should or should not be consider relevant? This paragraph will benefit the readers because there is a large amount of publications where the authors presented acid catalysis as a dominant mechanism of SOA production for these compounds.

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Line 3: Would Tan et al. be able to contrast the concentration of acetate with some

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other species?

Line 7: Describe how temperature was measured. Was that the temperature of the thermostat? Did you monitor the temperature during the reaction?

Line 23: An explanation to the large change in pH during the experiment is needed in the discussion section. How does the change in pH affect the course of the reaction?

Page 18325

Line 6: Specify the percentages of solution and mobile phase infused in addition to the composition of the mobile phase.

Line 16: Why is there a residual of H2O2? Was not catalase used to stop the reaction?

Page 18326

Lines 25-26: This statement explaining that acid catalysis is not enough to produce oligomers at the relevant concentrations should be included in the abstract.

Page 18328

Lines 9-29 (including schemes 3, 5, and 7): Previous studies with ketyl radical (generated during the photolysis of pyruvic acid) have provided detailed mechanisms to explain the production of higher molecular weight oligomers via radical mechanisms (J. Phys. Chem. A 2009, 113, 10512 and J. Phys Chem. Lett. 2010, 1, 368) that should be related to this work.

Page 18329

Lines 18-21: The stability of the same ketyl radical (Scheme 3) has already been discussed in the past (J. Phys. Chem. A 2006, 110, 931 and J. Phys. Chem. A, 2006, 110, 3619) and a better connection to those concepts is needed in this statement.

Page 18337

Figure 3: If only ~25% acetate is converted to oxalate, do the authors feel confident

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there is no need to monitor the fate of the remaining 75% carbon?

Supplemental information, page 2: The caption should be written in a different way, “peak with retention time” is repeated five times in three lines.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 18319, 2011.