

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.

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Response to Referee #3

1. Page 18320; Line 17 (Abstract): It should say “as a SOA: : :”

A) We respectfully disagree. The noun (aerosol) begins with a vowel, so the pronoun should be “an”

2. 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

C9871

past. After reading the manuscript, it is very clear that the importance of acetic acid in the paper is minor comparing to methylglyoxal and pyruvic acid experiments, and some of them have been left for supplemental information.

A) We now explain more clearly in the abstract and body of the paper what experiments and analyses are new. Acetic acid + OH experiments (and control experiments) conducted at 4 concentrations are new and are central to this paper because they validate the potential for acetic acid to be an SOA precursor and because they provide critical new insights into oligomer formation from aqueous methylglyoxal chemistry. Samples from these experiments were analysed by IC, ESI-MS and ESI-MS after preseparation by IC (IC-ESI-MS). Also new are the FT-ICR MS-MS analyses of methylglyoxal + OH radical experiments and IC-ESI-MS analyses of pyruvic acid experiments (with UV and with OH radical). We do not agree that the importance of SOA from acetic acid is minor. The atmospheric concentrations and OH radical reaction rates for acetic acid and other studied “aqueous” SOA precursors suggest that acetic acid could be an important precursor, at least through cloud processing (see response to Referee #2).

3. 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 and errors that report those measurements?

A) The main point of the first paragraph of the introduction is to point out that traditional secondary organic aerosol formation (gas phase reactions forming semi-volatile species that partition into particulate organic matter), although clearly important, does not explain the concentrations, vertical profiles and properties (e.g., LV-OOA and O/C ratios) of secondary organic aerosol found in the atmosphere. This suggests that other SOA formation processes might be important. Liquid water is much more abundant in the atmosphere (in clouds and in aerosols) than is particulate organic matter. Small water-soluble organic compounds and OH radicals readily partition into atmospheric waters, and laboratory studies, a few models, and field measurements provide evi-

C9872

dence for secondary organic aerosol formation through aqueous chemistry. We have edited this paragraph to clarify these points.

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

A) We are working on an expanded aqueous methylglyoxal model that includes organic radical-radical reactions. This model will be presented, validated and applied in a subsequent publication. Briefly, $\text{C}^*\text{H}_2\text{C}(\text{O})\text{OH}$ forms preferentially to $\text{CH}_3\text{C}(\text{O})\text{O}^*$ (* denotes radical) and 100% of $\text{C}^*\text{H}_2\text{C}(\text{O})\text{OH}$ converts to peroxy radical.

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

A) Reactions in Scheme 1 are now numbered.

6. Lines 27-30: Is the production of glycolic acid considered 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?

A) Oxalate is the most abundant dicarboxylic acid in the atmosphere and is almost entirely found in the particle phase, perhaps as a salt. It is considered a tracer for SOA formation through cloud processing (although not through chemistry in wet aerosols). Atmospheric glycolate is also found mostly in the particle phase. So because acetic acid + OH forms oxalate and glycolate, aqueous acetic acid oxidation is a source of SOA. In the acetic acid + OH radical experiments, almost all the oxalic acid is formed from glyoxylic acid. Very little oxalic acid is formed from glycolic acid. We have now made this point more clear.

7. 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."

A) The Altieri et al (2008) explanation for the formation of oligomers from methylglyoxal

C9873

+ OH radical has been shortened considerably.

8. Page 18323; Line 15: how critical is the fate of acetic acid? What is the percentage of pyruvic acid converted to acetic acid?

A) Acetic acid is the major OH radical oxidation product of pyruvic acid. In our dilute aqueous chemistry model (Tan et al., 2010), 100% of methylglyoxal is oxidized to pyruvic acid and 100% of pyruvic acid is oxidized to acetic acid. About 85% of acetic acid is oxidized to glyoxylic acid and subsequently to oxalic acid. Reaction rate constants are from the literature. At cloud-relevant concentrations this model predicts well oxalate formation from methylglyoxal (Tan et al., 2010), suggesting this chemistry is reasonable. We have added a sentence to make this more clear.

9. 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.

A) We have added a paragraph to Section 4 to summarize the current state of knowledge from our past experiments. Our previous OH radical oxidation experiments conducted with pyruvic acid, glyoxal, methylglyoxal, glycolaldehyde and this work with acetic acid validate, in large part, the dilute aqueous chemical mechanism which we documented in our previous publications (Tan et al. 2009, 2010; Perri et al. 2009; Lim et al. 2005). This dilute chemical mechanism draws from past literature, including measured rate constants. This dilute aqueous chemistry model reproduces well the concentrations of total carbon, pyruvic acid and oxalic acid in laboratory experiments conducted with glyoxal or methylglyoxal and OH radical at cloud relevant concentra-

C9874

tions in the presence and absence of acidic sulfate (i.e., 30 μ M; Tan et al., 2009, 2010).

However, we do not expect that this dilute chemistry model is appropriate for prediction of SOA formed in wet aerosols. The concentrations of organics dissolved in aerosol water are very high. In order to better understand how the chemistry differs at the high organic concentrations found in aerosol water, we have conducted experiments with glyoxal, methylglyoxal and acetic acid with increasing concentration. As concentrations increase, the formation of high molecular weight products increases. While Altieri proposed that high molecular weight products (oligomers) from methylglyoxal + OH radical formed through esterification reactions, Lim et al (2010) provided evidence that oligomers formed from glyoxal + OH radical formed through organic radical-radical reactions. In this paper we show that the oligomer formation mechanism proposed by Altieri is not viable, and provide evidence suggesting that, as for glyoxal, methylglyoxal oligomers form through organic radical-radical reactions. Organic radical-radical reactions have also been implicated in the formation of oligomers from other organics (e.g., Liu et al., 2009; Sun et al., 2010). It seems that there is a consensus that oligomers formed through photolysis or OH radical reactions are formed in this way. Radical-radical reactions are faster than non-radical reactions and produce oligomers irreversibly. However, high molecular weight products clearly also form through dark (non-radical) reactions, and the relative importance of radical and non-radical pathways to SOA formation in wet aerosols is not well understood (e.g., Ervens et al., 2010; Lim et al., 2010 and references therein). This work focuses on the OH radical chemistry. When organic radical-radical reactions are included in our aqueous chemistry model, the model predicts that oligomers will be the dominant products of glyoxal + OH radical at aerosol-relevant organic concentrations, whereas organic acids will be the dominant products at cloud-relevant concentrations (Lim et al., 2010). We are currently expanding the methylglyoxal chemistry to account for organic radical-radical reactions that lead to the formation of oligomers at high concentrations. This paper provides important insights needed to develop this expanded model. This paper also shows that radicals produced from the OH radical reaction of acetic acid lead to the

C9875

formation of oxalate, but do not contribute to oligomer formation.

10. As Page 18324; Line 3: Would Tan et al. be able to contrast the concentration of acetate with some other species?

A) We have added a new table that shows the concentrations and OH radical reaction rate constants for acetic acid and several other "aqueous" SOA precursors. (See Table 1; response to Referee #2). Considering the large atmospheric burden of acetic acid, we expect that acetic acid is a potentially important precursor of SOA production through cloud processing.

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

A) We monitored the temperature during the reaction using a thermometer. It remained within +/- 2 degrees C.

12. 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?

A) The discussion about pH range was provided in the response to Referee #1. pH was lowest for the highest concentration experiment. For all experiments, acetic acid + OH radical is faster than oxalic + OH radical.

13. Page 18325; Line 6: Specify the percentages of solution and mobile phase infused in addition to the composition of the mobile phase.

A) Thank you. This was an omission on our part. The flow rates of solution and mobile phase were identical (0.11 mL/min). Now stated.

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

A) We did not add catalase to our samples. (Note substantially higher doses of catalase are needed to effectively destroy H₂O₂ in acidic solutions.)

C9876

15. 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.

A) This statement has been added.

16. 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.

A) Although the source of the ketyl radical is different, the 2009 JPCA paper proposes the formation of m/z - 177 from the ketyl radical. Appropriately, we now acknowledge this important contribution.

17. 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.

A) These two Guzman 2006 papers are now referenced and their contributions discussed. One proposes that they observed the formation of organic radical-radical reaction products from ketyl radicals instead of peroxy radical products because hydrogen bonding stabilizes the ketyl radical and the formation of the peroxy radical is endothermic. The other paper confirms this hypothesis with evidence from low temperature experiments (77 K) and electron magnetic resonance. The 2009 JPCA paper confirms that the major peak is m/z - 177.

18. Page 18337; Figure 3: If only 25% acetate is converted to oxalate, do the authors feel confident there is no need to monitor the fate of the remaining 75% carbon?

A) About 85% of acetic acid is converted to glyoxylic acid and subsequently to oxalic

C9877

acid, with about 15% being converted to formaldehyde, formic acid and then CO₂. We now state this. The referee misinterpreted our statement. We were intending to report the mass of oxalate present per mass of acetate reacted at 10 min and at peak. We now state this more clearly as well.

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

A) We revised the caption.

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

C9878