

## ***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 #1

Major comments

1) The title of the paper is misleading. Methylglyoxal should be included there as well as about half of the discussion deals with the oxidation of methylglyoxal and compares it to acetic acid.

A) The title is now changed to "Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methyl-

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glyoxal".

2) The abstract and the introduction make it sound as if methylglyoxal is the main source of acetic acid in the atmosphere. This is misleading since the major sources are the reactions of acetyl peroxy radical + HO<sub>2</sub>, OH + acetone and OH + propene (cf e.g., Warneck 2005).

A) The abstract has been revised to avoid confusion. A paragraph in the introduction is now dedicated to discussing atmospheric acetic acid and includes the major atmospheric sources, aqueous concentrations, and Henry's law constant for acetic acid. We now note that the global source of acetic acid is estimated to be ~1400 Gmol/yr. That gas phase reactions of acetyl peroxy radical + HO<sub>2</sub>, OH + acetone and OH + propene are major sources. Direct emissions and aqueous photochemistry also contribute (Warneck 2005; Paulot et al., 2011). Acetic acid/acetate partitions readily into atmospheric waters (Henry's law constant =  $8.8 \times 10^3$  M atm<sup>-1</sup>) (Seinfeld and Pandis, 2006). Concentrations of acetate in cloud water, fog water and dew range from 0.4 – 245 micromolar (Khare et al., 1999).

3) I got confused about the conclusions. In the abstract, it is stated that the observed chemistry is important for SOA in wet aerosols. However, in the experimental section, the authors focus on the experiment at 20 uM acetic acid which is rather relevant for cloud conditions.

A) We performed our experiments at 4 different acetic acid concentrations (20 and 100 uM, 1 and 10 mM) to study the chemistry at cloud relevant concentrations and to understand how that chemistry changes with increasing concentration. Therefore providing insights as to what might happen to acetic acid and methylglyoxal in wet aerosols. This has been made clear up front in Section 3.1: "... experiments with different initial acetic acid concentrations (20 uM - 10 mM)."

4a) The introduction would benefit from some reorganization and clarifications, e.g., - p. 18321, l. 11-15: It is not clear that the first sentence refers to laboratory studies

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under atmospheric conditions. Thus, the conclusion that the acids as identified in the atmosphere are formed from methylglyoxal is rather weak.

A) We did not intend to suggest that the presence of oxalate in the atmosphere means that methylglyoxal is necessarily the only source. Instead that methylglyoxal chemistry forms several products known to exist preferentially in the particle (rather than the gas) phase. Undoubtedly there are also other sources of oxalate and HMWC (e.g., glyoxal). We have rewritten our argument to make clear our intent as follows: "Laboratory studies suggest that the aqueous OH radical oxidation of methylglyoxal in atmospheric waters is a source of SOA because this chemistry forms several organic acids (e.g., oxalate, pyruvate and succinate) and HMWC (Altieri et al., 2008; Tan et al., 2010) that are found predominantly in the particle phase in the atmosphere (Limbeck et al., 2001; Mochida et al., 2003), most likely as salts."

4b) - p. 18322, l. 10: The study by Wang does not seem to be relevant for atmospheric conditions (O<sub>2</sub> depleted, N<sub>2</sub>O saturated). The observed formation of succinic acid is probably only feasible since the organic radical-radical recombination is fast enough as opposed to the peroxy radical formation. However, this fact is only introduced on the next page (p. 18323, l. 9)

A) Good point. We deleted the Wang reference.

4c) - p. 18323, l. 7 ff: The mechanistic details by Guzman et al. are almost literally repeated in Section 3.2. Considering that the introduction is almost as long as the discussion itself, the detailed discussion of Guzman's results in the introduction should be shortened or removed.

A) Good point. The discussion of Guzman has been removed from the introduction.

4d) - p. 18323, l. 28/29: This fact has been mentioned already on p. 18321, l. 12.

A) This sentence is removed.

5) Section 3.1 is very brief and warrants more details on the importance of oxalic acid  
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formation from acetic acid as this is a main conclusion from this study. 5a) The life time of a cloud droplet is on the order of a few minutes, and not 100 min. Thus, the maximum yield will never be reached in clouds as acetic acid will evaporate in between clouds. The authors should add a rough calculation of how much oxalic acid might be expected from 20 uM acetic acid within a few minutes.

A) The yields from 20 uM acetic acid after a typical cloud contact time (10 min) have now been added. Because an air parcel can possibly go through more than 10 cloud cycles and "maximum yields" are frequently provided for comparison purposes, we also report the 100 minute yield.

5b) Has acetic acid ever been found in aerosol particles? Does it show similar behavior as other acids (oxalic, succinic, pyruvic) that mostly partition to the particle phase? If it is indeed found in aerosol at concentrations corresponding to the 'high experimental concentrations' this information should be added (e.g., end of Introduction) as in aerosols processing times of 100 min and longer are much more reasonable than for cloud droplets.

A) People have measured concentrations of some organics in aerosols that are higher than expected based on their volatility and on their Henry's law constant (We are not aware that this is the case for acetate). There are many possible reasons for this (e.g., sampling artifacts, components of larger compounds that are altered by solvent extraction, changes in Henry's law partitioning due to ionic strength effects. Our argument is different. We are certain that the concentrations of water soluble organics are very high in wet aerosols. This organic soup is quite complex and very difficult to study. So we have taken a gradual approach. By increasing the concentrations of acetic acid in solution, by separately increasing the concentrations of methylglyoxal in solution, we can get some insights into how these organics might behave at the still higher organic concentrations in wet aerosols, and how their behavior differs. We have now made this argument more clearly in Sections 3 and 4.

5c) The pH will have a crucial impact on the results as shown in Figure 3 (and S1) since at low pH the oxidation of oxalic acid and acetic acid is about equally fast whereas at higher pH the latter is much faster and thus oxalic acid might have a chance to build up. Did the pH drop during the experiments from 6.6 to 3.3 or was it a variation of pH between different experiments. Have any experiments been performed at a constant (buffered) pH?

A) All experiments were performed under free pH conditions. The within experiment variation in pH is small. The lowest pH (3.3) is from the highest concentration experiments. Under experimental and typical atmospheric cloud pH, acetate reacts with OH approximately two times faster than oxalate. These experiments are used to validate the aqueous chemical model. The model (Tan et al., 2010) takes pH into consideration. This is now stated more clearly in the text (methods and results).

6) Are the results presented in Section 3.2 new? It seems to me that this section (or at least a large fraction of it) only repeats what has been discussed in previous studies by the same group (Altieri et al., 2008; Tan et al., 2010).

A) Methods now state that the FT-ICR MS and MS/MS of a methylglyoxal +OH radical experiment sample is new. We used these to explore the structure and formation mechanisms of methylglyoxyl oligomers, specifically m/z- 177 and 249. The ESI-MS/MS result of m/z- 231 was previously published, but structure analysis was reinvestigated.

7) How can the results presented in the paper help to improve current attempts of mechanistic modeling of SOA in the aqueous phase? It would be useful to add rate constants and branching ratios to the schemes 1-7 (or summarize this data in a Table).

A) The complete reaction list is a subset of methylglyoxal aqueous chemistry model. This dilute chemistry model was published by Tan et al. (2010), and is relevant to the chemistry in clouds and fogs. This is now stated in Section 3.1. We are currently working on expanding this model to account for the chemistry at higher concentrations where organic radical – radical reactions become important. That will be the subject of

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another paper.

Minor comments

8) p. 18320, l. 20-24: The statement that current models cannot predict SOA mass is somewhat outdated. The recent addition of so-called semivolatile precursors (cf e.g., Robinson et al., Science 2007) has lead to a great improvement in mass prediction (perhaps for wrong reasons as the authors state correctly later).

A) Good point. We have refined our argument as follows to accommodate this comment and a question from Reviewer 3, who did not know why we mentioned O/C ratios: While the refined treatment of intermediate volatility organic compounds (IVOCs) has in some cases brought predicted organic aerosol mass into better alignment with measured mass, formation of SOA through gas phase reactions followed by vapor pressure driven partitioning (from traditional or IVOC precursors) does not account for observed atmospheric SOA properties. This is the lead in to talk about O/C ratios - atmospheric evidence for aqueous SOA.

9) p. 18321, l. 20 and 24. Should the radical be CH<sub>2</sub>CO(OH) (the first one in line 24)?  
Yes. Corrected.

10) p. 18321, l. 26: KCO<sub>2</sub> is not defined.

A) This is a typo. This should be just CO<sub>2</sub>.

11) p. 18322, l. 5/6: move 'organic' before 'concentrations' in l. 5 so it reads 'as organic concentrations increase: : '

A) Done.

12) p. 18322, l. 21: Clarify 'predicted reaction components'

A) Done

13) p. 18322, l. 29: Define IC-ESI-MS here (and not on the next page)

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A) We moved the description here.

14) p. 18323, l. 10: Strictly, the reaction of ketyl or acetyl radicals with oxygen (= biradical) are also radical-radical reactions. Clarify here that you mean radical-radical reactions of the organic radicals.

A) Now we use organic radical-radical reactions throughout the manuscript.

15) p. 18323, l. 21: Did you use four concentrations of acetic acid? In Figure S1, there are only 3 shown.

A) The 10 mM acetic acid experiment was conducted at a lower OH radical concentration than the other three experiments. Thus the chemistry was slower. For this reason, we did not show it in Figure S1. We have now indicated this in the methods and Figure caption.

16) p. 18324, l. 19: The reactants to form OH should be Fe(II) (ferrous ion), H<sub>2</sub>O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (nitrate ion)

A) Corrected.

Technical comments

17) p. 18323, l. 2: 'glycolaldehyde' misspelled

A) fixed

18) p. 18323, l. 3: remove 'Yao'

A) Corrected

19) p. 18323, l. 8: '3' in CH<sub>3</sub>C(O) should be subscript

A) The sentence was removed in consolidating the Guzman discussion in one place, as suggested above.

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

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