

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 #1

Received and published: 15 July 2011

The authors present results from laboratory experiments studying the oxidation of acetic acid in aqueous solution. This study is one in a series from the same group based on which they suggested detailed chemical mechanisms that lead to secondary organic aerosol (SOA) mass in the aqueous phase. The formation of SOA from relatively simple molecules (C2 and C3) in the aqueous phase is an emerging topic in SOA modeling attempts but neither the detailed mechanisms nor precursors are known in detail. Thus, the current study is a welcome contribution to this field. However, the paper is very brief and lacks some detail on firm conclusions. I have several comments that should be considered before final publication.

C6432

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.

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 + HO₂, OH + acetone and OH + propene (cf e.g., Warneck 2005).

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 μM acetic acid which is rather relevant for cloud conditions.

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

- p. 18322, l. 10: The study by Wang does not seem to be relevant for atmospheric conditions (O₂ depleted, N₂O 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)

- 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.

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

C6433

5) Section 3.1 is very brief and warrants more details on the importance of oxalic acid formation from acetic acid as this is a main conclusion from this study.

a) 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 μM acetic acid within a few minutes.

b) 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.

c) 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?

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).

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).

Minor comments

p. 18320, l. 20-24: The statement that current models cannot predict SOA mass is

C6434

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).

p. 18321, l. 20 and 24. Should the radical be $\dot{\text{A}}\text{C}\text{H}_2\text{CO}(\text{OH})$ (the first one in line 24)?

p. 18321, l. 26: KCO_2 is not defined.

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

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

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

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

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

p. 18324, l. 19: The reactants to form OH should be Fe(II) (ferrous ion), H_2O_2 and NO_3^- (nitrate ion)

Technical comments

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

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

p. 18323, l. 8: '3' in $\text{CH}_3\text{C}(\text{O})$ should be subscript

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

C6435