Atmos. Chem. Phys. Discuss., 11, C9686–C9690, 2011
www.atmos-chem-phys-discuss.net/11/C9686/2011/

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.

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Received and published: 3 October 2011

Response to Referee #2

1. Page 18320, line 3-8: As I know, Zhang et al. (2010) also investigated the aqueous OH-oxidation of MACR and MVK and found that they would contribute to SOA mass, you should mention this here.

Zhang, X., Chen, Z. M., and Zhao, Y.: Laboratory simulation for the aqueous OH oxidation of methyl vinyl ketone and methacrolein: significance to the in-cloud SOA production, Atmos. Chem. Phy., 10, 9551–9561, 2010.

A) The reference is now cited.

2. Page 18321, line 26: Please tell the reader the meaning of “KCO2” where it is the first time for its appearance.

A) This was a typo. It should be CO2. Corrected

3. Page 18326, line 13: The current hypothesis for the in-cloud formation of SOA is that gas-phase oxidation of VOCs in the interstitial spaces of clouds produce water soluble species, which will dissolve into the cloud droplets. Further oxidation of these water soluble species generates semi-volatile compounds, which will form SOA upon the cloud droplets evaporate (Blando and Turpin, 2000). It is true that acetic acid is abundant in clouds, fogs, and aqueous aerosols. The question is whether OH radical in the aqueous phase is sufficient to oxidize all the acetic acid. The authors should compare this reaction rate with other OH-initiated oxidation processes in the aqueous phase and evaluate the importance and probability of OH oxidation of acetic acid.

A) To address the potential atmospheric importance of acetic acid/acetate as an atmospheric aqueous SOA precursor, we added a table (see below) and the following discussion. Glyoxal and methylglyoxal react with OH faster than acetic acid and have comparable concentrations. The other previously studied aqueous SOA precursors given below also have higher OH radical rate constants but are found at much lower concentrations than acetate. Acetate oxidation will be competitive with these (glycolaldehyde, methyl vinyl ketone, methacrolein).

4. Page 18326, line 20: Again, have the authors considered about the absence of oligomers in OH-acetic acid reactions is probably due to the availability of OH radical? I highly suggest that the authors increase the initial H2O2 concentration in the batch experiments.

A) OH radical concentrations were ∼10-12 M throughout experiments. This concentration is atmospherically relevant. It was sufficient for formation of oligomers from methylglyoxal at 1 mM. Oligomers did not form from acetic acid at the identical concentrations, despite the fact that acetic acid is an intermediate product of methylglyoxal + OH radical. We have now made this more clear in Section 3.2. Also, we measured the formation of glyoxylic acid and oxalic acid from acetic acid, as predicted by our model (published by Tan et al., 2010), suggesting that acetic acid was oxidized.

5. Page 18327, line 10: It is interesting to know that radical-radical reactions are proposed to explain the inconsistent results between the previous and current studies. As I know, most studies focusing on the particles phase reactions all agree that the acid analyzed esterification is a very important pathway in producing high molecular weight compounds. I was wondering the reason that the authors did not observe this process is because the pH is high in this study.

A) The pH was 3.3 for the highest concentration experiments. It is possible that acid catalyzed esterification would form oligomers in our mixed standard if our experimental concentrations were even higher. Bulk experiments that have observed oligomer formation in the absence of OH radical have been conducted at much higher concentrations. The goal of our paper was to explore the chemistry of acetic acid and methylglyoxal in the presence of OH radical, using control experiments to help us to ascertain whether or not the observed products were indeed a result of OH radical reactions. Yong et al, ACP 2010 and Ervens and Volkamer ACP 2010 review evidence pertaining to the radical and non-radical reactions of glyoxal at concentrations relevant to clouds and wet aerosols. They conclude that both types of reactions are capable of forming oligomers, but that OH radical reactions are faster. Noziere et al., PCCP 2010 argues that ammonium is an effective catalyst in wet aerosols. It is important to acknowledge that the chemistry in wet aerosols is complex and there is much yet to learn. We have added a paragraph to Section 4 to relay these points and to review the impact that the conclusions of our new paper have on our previous publications (as recommended by Referee #3).

6. Page 18327, line 23-26: Is there any contradiction about the explaining for the

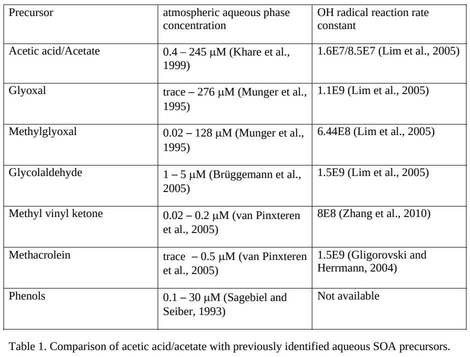
formation of C6H9O6-? Is the C6H9O6- “not explained” or “explained” by pyruvic acid photolysis? Considering your following describe “Guzman et al. (2006) proposed that the recombination of ketyl radicals (CH3C(OH)C(O)OH, denoted as K) from pyruvic acid photolysis leads to the formation of C6H9O6-. We expect that similar chemistry leads to the formation of C6H9O6- in the OH radical oxidation of methylglyoxal: : :” I think the C6H9O6- is “explained” by pyruvic acid photolysis.

A) We revised the text as "C6H9O6- in the methylglyoxal + OH radical experiment is not formed via pyruvic acid photolysis" to avoid confusion. We do see C6H9O6- in pyruvic acid + UV experiments. In this case, it was formed from pyruvic acid photolysis. But we do not see C6H9O6- in pyruvic acid + OH experiments. We think this is because the OH radical reactions are faster. If pyruvic acid photolysis were the source of C6H9O6- in the methylglyoxal + OH radical experiment, then we would also notice the formation of C6H9O6- in the pyruvic acid + OH radical experiment since pyruvic acid is the first generation product of methylglyoxal + OH. The ketyl radical in the methylglyoxal + OH radical experiment must form via another pathway. We have now made this argument more clearly in the text.

7. It is very interesting to see that the authors propose a reasonable structure of C6H9O6- based on the fragment ions and also show a mechanism for the formation of these ions, but, there are still uncertainties for those hypothesizes. If possible, can you synthesize the corresponding acid of C6H9O6- or the similar substance for MS test? This could facilitate verifing your series of radical-radical chemistry schemes.

A) We are not currently able to do this. We have made it clear in the text that this is a proposed structure. Other structures are possible. In fact, C6H9O6- was seen in four distinct IC peaks, suggesting that several compounds present with m/z- 177.

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



Precursor	atmospheric aqueous phase concentration	OH radical reaction rate constant
Acetic acid/Acetate	0.4 – 245 µM (Khare et al., 1999)	1.6E7/8.5E7 (Lim et al., 2005)
Glyoxal	trace – 276 µM (Munger et al., 1995)	1.1E9 (Lim et al., 2005)
Methylglyoxal	0.02 – 128 µM (Munger et al., 1995)	6.44E8 (Lim et al., 2005)
Glycolaldehyde	1 – 5 µM (Brüggemann et al., 2005)	1.5E9 (Lim et al., 2005)
Methyl vinyl ketone	0.02 – 0.2 µM (van Pinxteren et al., 2005)	8E8 (Zhang et al., 2010)
Methacrolein	trace – 0.5 µM (van Pinxteren et al., 2005)	1.5E9 (Gligorovski and Herrmann, 2004)
Phenols	0.1 – 30 µM (Sagebiel and Seiber, 1993)	Not available

Table 1. Comparison of acetic acid/acetate with previously identified aqueous SOA precursors.

Fig. 1. New Table 1