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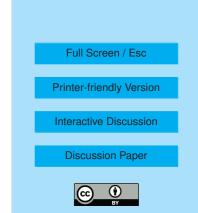
Interactive Comment

## 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 #2

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This study investigated the oligomer formation from the photo-oxidation of acetic acid in the aqueous phase. Using results from these and methylglyoxal+OH radical experiments, radical mechanisms responsible for oligomer formation from methylglyoxal oxidation in clouds and wet aerosols are proposed. Increasing attention has been paid to the oligomers and SOA produced by oxygenated small molecule organic compounds through aqueous reaction. However, currently it is difficult to directly get the information about the structure of oligomers because of unavailable standards. It is significant for one to propose reasonable structures and formation of oligomers based on available experimental observations. The results reported by the authors are interesting and may have important consequences on oligomers formation in the wet aerosols. I



recommend the publication after the following concerns are properly addressed.

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.

2. Page 18321, line 26: Please tell the reader the meaning of " $\cdot$ KCO<sub>2</sub>" where it is the first time for its appearance.

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.

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  $H_2O_2$  concentration in the batch experiments.

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

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weight compounds. I was wondering the reason that the authors did not observe this process is because the pH is high in this study.

6. Page 18327, line 23-26: Is there any contradiction about the explaining for the formation of  $C_6H_9O_6^-$ ? Is the  $C_6H_9O_6^-$  "not explained" or "explained" by pyruvic acid photolysis? Considering your following describe "Guzman et al. (2006) proposed that the recombination of ketyl radicals (CH<sub>3</sub>C(OH)C(O)OH, denoted as ·K) from pyruvic acid photolysis leads to the formation of  $C_6H_9O_6^-$ . We expect that similar chemistry leads to the formation of  $C_6H_9O_6^-$  in the OH radical oxidation of methylglyoxal..." I think the  $C_6H_9O_6^-$  is "explained" by pyruvic acid photolysis.

7. It is very interesting to see that the authors propose a reasonable structure of  $C_6H_9O_6^-$  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  $C_6H_9O_6^-$  or the similar substance for MS test? This could facilitate verifing your series of radical-radical chemistry schemes.

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