

## ***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 Dr. Monod

- Line 24 p.18321: replace  $\text{*O}_2\text{CH}_2\text{CO}(\text{OH})$  by  $\text{*CH}_2\text{CO}(\text{OH})$  Done.
- Line 19-20 p.18323: esterification pathway proposed by Altieri et al. (2008) should be recalled The part has been revised.
- Line 28 p.18323: add : “as an end reaction product,” oxalate is largely found in the particle phase. . . This sentence has been removed to tighten and shorten the introduction as requested by Reviewer #1.

- Line 11 p.18324: is the lamp at 254 nm representative of atmospheric conditions? This lamp may artificially photolyze intermediate reaction products that absorb light below 300 nm, and thus add some more organic radicals that are not atmospherically relevant.

The purpose of these experiments is to study OH radical oxidation and not photolysis. In the atmosphere, most of the OH radicals in cloud water come from the gas phase. In order to produce atmospherically-relevant concentrations of OH radicals in our experiments we photolyze hydrogen peroxide with a 254 nm lamp. Atmospherically-relevant concentrations of hydrogen peroxide and a solar spectrum lamp would not produce high enough OH radical concentrations. To investigate the possibility that the presence of hydrogen peroxide or UV affects the experimental results, we have conducted control experiments with H<sub>2</sub>O<sub>2</sub> and separately with UV and methylglyoxal, pyruvic acid, acetic acid and a mixed standard of major products. In the absence of OH radicals, some of these organics photolyze. We can model their photolysis rates in the reaction vessel and we can see that, in the presence of OH radicals, their photolysis rates are too slow to compete with their OH radical reactions (Tan et al., 2010). This is true for all the compounds we have investigated to date, and we expect that it is also true for other unmeasured intermediates. Note, for example, that pyruvic acid photolyzes in the absence of H<sub>2</sub>O<sub>2</sub>. However, the higher molecular weight products that form from pyruvic acid + UV do not form when OH is present. If photolysis was fast enough to compete with OH radical oxidation, we would observe pyruvic acid photolysis products in pyruvic acid + OH radical experiments. We have tried to make this more clear, in a concise way.

- Lines 9-10 p.18324: Why were the initial concentrations of acetic acid and H<sub>2</sub>O<sub>2</sub> chosen as the OH radicals preferentially attack H<sub>2</sub>O<sub>2</sub> (more than 63 %) rather than acetic acid in most cases?

H<sub>2</sub>O<sub>2</sub> photolysis was used to generate the OH radicals. We used our chemical model (Tan et al., 2010) to estimate the concentration of H<sub>2</sub>O<sub>2</sub> needed to obtain the same

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OH radical concentrations in the 20  $\mu\text{M}$ , 100  $\mu\text{M}$ , and 1mM acetic acid experiments. This is now stated in the methods section.

- Lines 23-26 p.18327 and scheme 3: o I don't understand the link between the phrase in brackets and the one before. o If pyruvic acid is formed during the OH-oxidation of methylglyoxal, its direct photolysis can form  $\text{C}_6\text{H}_9\text{O}_6^-$  ( $m/z$ - 177). In this case,  $\text{C}_6\text{H}_9\text{O}_6^-$  appears as a second generation reaction product, and thus, one should observe a flat initial slope on the curve of  $\text{C}_6\text{H}_9\text{O}_6^-$  signal as a function of reacted methylglyoxal. On the other hand, the formation of  $\text{C}_6\text{H}_9\text{O}_6^-$  through scheme 3 shows it is a first generation product (i.e. formed through different radicals but no stable molecular intermediate) Therefore, the value of the initial slope of the curve of  $\text{C}_6\text{H}_9\text{O}_6^-$  signal as a function of reacted methylglyoxal should allow the authors to determine the mechanism of its formation: o If it is flat, it corresponds to a second generation product (alike from pyruvic acid photolysis) o If it is a linear initial slope (non null), it corresponds to a first generation product (alike scheme 3). o Remark: if the  $\text{C}_6\text{H}_9\text{O}_6^-$  signal is an infusion ESI-MS signal, in case a flat initial slope is observed, it can be due to a possible ionisation competition artefact in the ESI (see my comments on figure 3), which artificially reduces the targeted signal. This should be avoided with HPLC-ESI-MS. - Lines 13-29 p.18328: all these mechanisms could be discussed in regard of the primary / secondary character of each reaction product's signal. Oligoesterification seems to form secondary products while radical-radical reactions seem to form primary reaction products.

a) Our experiments show that  $\text{C}_6\text{H}_9\text{O}_6^-$  ( $m/z$ - 177) forms in pyruvic acid + UV experiments (as seen by Guzman), but not in pyruvic acid + OH experiments. This is because pyruvic acid photolysis is not fast enough to compete with its OH radical reaction. Therefore, we think that the  $\text{C}_6\text{H}_9\text{O}_6^-$  ( $m/z$ - 177) in the methylglyoxal + OH experiments must form directly. We have made this point more clearly now.

b) While this is a very good idea, we do not have the data needed to make these plots, including real time methylglyoxal concentrations in the higher concentration ex-

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periments.

c) We saw C<sub>6</sub>H<sub>9</sub>O<sub>6</sub><sup>-</sup> in ESI-MS analyses after pre-separation by IC. Therefore, we know that this ion is not an artifact of electrospray ionization. We have added a comment to this effect.

- Lines 18-21 p.18329: the authors are suggesting that R<sup>\*</sup> radicals are more reactive towards dissolved O<sub>2</sub> than R<sup>\*</sup>-C(OH)-R' radicals. This could be discussed more deeply in regard of the references (and those therein) proposed below.

The references are appreciated. Reviewer #3 also provided references to help with this. After reading these, we have added the following references, which most directly address this issue: J. Phys. Chem. A 2009, 113, 10512; J. Phys. Chem. A 2006, 110, 931 and J. Phys. Chem. A, 2006, 110, 3619.

- Figure 3 (p.18337): The disagreement observed before 50 min between IC and ES-IMS online measurements illustrates the ionization competition artefact one can encounter with online (infusion) ESI-MS experiments. This could be discussed in the text. This point is now added in the figure caption.

- Scheme 1 and Figure 3: oxalic acid seems to be a primary reaction product (from fig 3): how the authors explain its formation?

Oxalic acid is formed from glyoxylic acid (Lim et al., Environ. Sci. Technol. 2005 and references therein). The production of glyoxylic acid before oxalic acid is shown in Figure 1. We have now also added glyoxylic acid to Figure 3.

- Scheme 2 and Figure 5 can be grouped together - Scheme 4 and Figure 6 can be grouped together We tried to group these figures but the grouped figure became too big and difficult to read.

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