# Interactive Comments on « Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid » by Tan et al., in Atmos. Chem. Phys. Discuss., 11, 18319–18347, 2011

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**General comments:** Studying aqueous phase photooxidation (OH-oxidation) of acetic acid, the paper re-investigates chemical mechanisms of methylglyoxal + OH reaction of oligomerization. The methylglyoxal + OH experiments of oligomerization have been previously performed by the same group (Altieri et al., 2008). These processes were interpreted as oligoesterification starting from acetic acid. To my point of view, these interpretations were not fully convincing since these oligoesterification mechanisms did not require any radical (except for the formation of acetic acid itself) although the authors demonstrated that OH radicals were necessary for oligomer formations. Therefore, I am very enthusiastic about the present re-investigation because the proposed radical oligomerization mechanism seems to be in much better agreement with the experimental results. I have a few specific comments:

- Line 24 p.18321: replace $\cdot O_2CH_2CO(OH)$ by $\cdot CH_2CO(OH)$
- Line 19-20 p.18323: esterification pathway proposed by Altieri et al. (2008) should be recalled
- Line 28 p.18323: add : "**as an end reaction product**," oxalate is largely found in the particle phase…
- 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.
- Lines 9-10 p.18324: Why were the initial concentrations of acetic acid and $H_2O_2$ chosen as the OH radicals preferentially attack $H_2O_2$ (more than 63 %) rather than acetic acid in most cases?
- Lines 23-26 p.18327 and scheme 3:
    - I don't understand the link between the phrase in brackets and the one before.
    - If pyruvic acid is formed during the OH-oxidation of methylglyoxal, its direct photolysis can form $C_6H_9O_6^-$ (m/z$^-$ 177). In this case, $C_6H_9O_6^-$ appears as a second generation reaction product, and thus, one should observe a flat initial slope on the curve of $C_6H_9O_6^-$ signal as a function of reacted methylglyoxal.

    - On the other hand, the formation of $C_6H_9O_6^-$ 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 $C_6H_9O_6^-$ signal as a function of reacted methylglyoxal should allow the authors to determine the mechanism of its formation:

    - If it is flat, it corresponds to a second generation product (alike from pyruvic acid photolysis)
    - If it is a linear initial slope (non null), it corresponds to a first generation product (alike scheme 3).
    - Remark: if the $C_6H_9O_6^-$ 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.
- Lines 18-21 p.18329: the authors are suggesting that $R^\bullet$ radicals are more reactive towards dissolved $O_2$ than $R\text{-}^\bullet C(OH)\text{-}R'$ radicals. This could be discussed more deeply in regard of the references (and those therein) proposed below.
- Figure 3 (p.18337): The disagreement observed before 50 min between IC and ESI-MS online measurements illustrates the ionization competition artefact one can encounter with online (infusion) ESI-MS experiments. This could be discussed in the text.
- Scheme 1 and Figure 3: oxalic acid seems to be a primary reaction product (from fig 3): how the authors explain its formation ?
- Scheme 2 and Figure 5 can be grouped together
- Scheme 4 and Figure 6 can be grouped together

## References that could help with the discussion on the mechanisms :

Abramovitch S. and J. Rabani, Pulse radiolytic investigation of peroxy radicals in aqueous solutions of acetate and glycine, *J. Phys. Chem.*, 80, 14, pp. 1562-1565, 1976.

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