

***Interactive comment on* “Chemical insights,
explicit chemistry and yields of secondary organic
aerosol from methylglyoxal and glyoxal” by
Y. B. Lim et al.**

Anonymous Referee #4

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In recent years water-soluble di-carbonyls draw more attention due to their great potential in forming highly oxidized products in the atmospheric waters. The present work integrates recently developed methylglyoxal aqueous-phase chemistry (spans from dilute to concentrated conditions) with previously published glyoxal chemistry. This manuscript provides insights for the detailed chemistry and leads to a better understanding. The manuscript is well-written and I recommend publication after the author addresses some minor concerns outlined below.

General comments:

1. Page 1, line 23-25, “At cloud relevant concentrations ($10^{-6} \sim 10^{-3}$ M; Munger et

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al., 1995) of glyoxal and methylglyoxal, the major photooxidation products are oxalic acid and pyruvic acid, and simulated SOA yields (by mass) are $\sim 120\%$ for glyoxal and $\sim 80\%$ for methylglyoxal.” Apparently according to Fig 9 the overall mass yield depends on the initial glyoxal/methylglyoxal level, e.g. at 10^{-3} M glyoxal the mass yield drops to $\sim 80\%$ (i.e. net mass loss?). This is interesting and consistent with Lee et al (ACPD, 2012) who indicated that under CERTAIN conditions (3mM glyoxal + 13.3mM H₂O₂ + light) fragmentation could dominate the whole glyoxal/methylglyoxal processing and eventually lead to mass loss. However, it seems that in Lee et al (ACPD, 2012) the mass reduction is due to the presence of H₂O₂ (the major product would be HCOOH rather than oxalic acid), i.e. Lee et al created cloud-relevant OH level (by means of the H₂O₂ photolysis) but probably a much higher H₂O₂ level than cloud condition. What is the major reason for the mass loss at $10^{-3} \sim 10^{-1}$ M glyoxal, as shown in Figure 9? What is the gas-/aqueous-phase H₂O₂ level in the atmospheric simulations?

2. Page 9, line 1: I myself don't think the SOA yield here is well defined. Glyoxal in the atmospheric waters can undergo various pathways and subsequently contribute to SOA, such as reversible reactions (depends on many factors such as sulfate level), irreversible reactions (glyoxal+OH, glyoxal+NH₄⁺) or surface-limited processes. In the present work the SOA yield only covers the glyoxal+OH pathways, which doesn't always play a dominant role in the aqueous-phase chemistry of glyoxal.

In addition, to my knowledge, currently many 3D chemical transport models only include basic aqueous-phase chemistry for cloud, not for wet aerosols, simply because they cannot afford big calculations. In order to use these yields, phase-transfer needs to be included for glyoxal/methylglyoxal as well as OH. Given that glyoxal might only contribute to limited mass to the total SOA (California: Washenfelder et al., 2011; Mexico City: Waxman et al., 2013), these parameters (yields derived in this work) might not be entirely feasible for 3D modelers at this moment.

3. Page 10, line 6-7, “Oligomers were calculated as the sum of products with higher carbon number than the precursor (Lim et al., 2010).” Please provide the detailed

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characteristics of the oligomers since they dominate the SOA mass under concentrated conditions, e.g. what products are actually summed into this oligomer, also please show the product distributions of oligomers formed from glyoxal and methylglyoxal, respectively. In addition, it will be great if the authors could discuss in the context of ambient measurements available since some of the model scenarios in this work are ambient relevant. I am particularly interested in looking for evidence or tracers for the wet aerosol processes and apparently more insights of the oligomers would help a lot. According to Lim et al (2010), compounds such as tartaric acid and malonic acid are major products of the radical-radical chemistry of glyoxal. It seems to me that malonic acid has been reported in aerosol samples in many locations, but tartaric acid, on the other hand, is rarely seen at remarkable level. The present manuscript is an important extension of Lim et al (2010). Based on Lim et al (2010) and Table S1 of this work, I guess tartaric acid is probably not speciated in this work (i.e. lumped into C4D which is included in the oligomers formed from glyoxal under concentrated condition).

Supplementary Material:

4. Table S1: Reaction 207 and 208 show the OH reaction of MA and TA, but these two don't come in the abbreviation list. I go back to Lim et al (2010) and found that MA and TA refer to malonic and tartaric acid, respectively. Are they lumped in those dimers (e.g. C3D or C4D)? Anyway please double check the reaction list.

Reference

Lee, A. K. Y., et al. (2012), Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol formation through oxidative cloud processing, *Atmos. Chem. Phys. Discuss.*, 12, 6019–6047, www.atmos-chem-phys-discuss.net/12/6019/2012/, doi:10.5194/acpd-12-6019-2012.

Washenfelder, R. A., et al. (2011), The glyoxal budget and its contribution to organic aerosol for Los Angeles, California, during CalNex 2010, *J. Geophys. Res.*, 116, D00V02, doi:10.1029/2011JD016314.

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Waxman, E. M., et al. (2013), Secondary Organic Aerosol formation from Semi- and Intermediate-Volatility Organic Compounds and Glyoxal: Relevance of O/C as a tracer for aqueous multiphase chemistry, *Geophys. Res. Lett.*, DOI: 10.1002/grl.50203.

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