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Interactive comment on “Aqueous chemistry and its role in secondary organic aerosol (SOA) formation” by Y. B. Lim et al.

Anonymous Referee #1

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There is growing evidence that processing of small organic molecules in aqueous aerosol or clouds is important for formation of secondary organic aerosol. The paper advances the understanding of these processes, presents a thorough analysis and provides a quantitative framework that is based on experimental results for inclusion of these processes in models - a valuable contribution. The work demonstrates a fundamental difference between cloud and aerosol processing in that radical-radical reactions become important for aqueous aerosol; these radical-radical reactions will produce larger organic molecules, with direct implications for volatility of these compounds. The content of the paper is appropriate to Atmospheric Chemistry and Physics, it is well written, and the data analysis is clear and supports the conclusions. This manuscript could be accepted for publication as is, but the following comments are provided for the authors' consideration.

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- Section 2.1 Page 14168; Line 16. Volkamer et al. calculate Henry's law constants based on LWC (molality). Ervens et al. (ACPD 10, 12371 2010) show that for example the Kroll and Galloway Henry's law constants are also $\sim 10^8$ M/atm calculated in this manner.
- Section 2.2.2 Page 14170 Aldol condensation for glyoxal is unlikely and was not included in Barsanti and Pankow; UV-Vis spectra cannot identify the process in which a chromophore is formed or unambiguously identify the nature of the reaction products.
- Also section 2.2.2: NH_4^+ catalysis is a variant of acid catalysis; Noziere (2009) should be extended to the JPCA reference 113 p.231 2009; and PCCP 12 p. 3864 2010 references (see below).
- Section 2.2.3: Galloway et al. reported formation of imidazoles, a special form of imines, in chamber studies.
- Section 2.3.1 Fratzke and Reilly (Int. J. Chem. Kin. 18 p. 775 1986) show that the dimerization of glyoxal and the reverse reaction are slower at low pH and show a complicated pH dependence. It could be helpful to integrate this paper into the discussion of the effect of pH and oligomerization in general. E.g., p. 14174 line 14 could be reviewed in this light.
- Section 2.3.1: A related question is whether oligomerization is fast and thus glyoxal oligomerizes during evaporation or whether de-oligomerization is slow and thus glyoxal stays in the form of larger, smaller vapor pressure oligomers during evaporation. Currently, the authors argue the first point. It would be helpful to state how the second possibility is ruled out, especially for aerosol with its high glyoxal concentrations, which thermodynamically favors oligomers. However, the papers (Loeffler 2006; DeHaan 2009) that the authors reference clearly demonstrate that glyoxal largely stays in the condensed phase upon evaporation and the reasons are probably secondary.
- Section 2.3.3; Could ammonium catalyze the oligomerization/de-oligomerization and

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thus increase reversibility whereas in drying experiments no ammonium is present?

- Section 4.1. It would be helpful to see the comparison between measured and modeled formic acid for the Tan 2009 data. This will provide an idea about the RO₂+RO₂ importance and formation of RO according to the mechanism.

- Section 4.3 p. 14185 Although it is mentioned in the figure it could be helpful to mention here that these are mass yields.

- Figure 1 (B): For the enol form of the singly hydrated glyoxal, the reactivity of the unhydrated aldehyde carbon is expected to be significantly higher for three related reasons: 1. it is sterically more approachable; 2. it is more nucleophilic 3. the carbocation formed on the other carbon after nucleophilic attack on another glyoxal molecule is more stabilized due to the presence of two OH groups. Thus, the proposed aldol self reaction would be more likely to result in a different product and terminate at a trimer (a dicarboxylic acid).

- Figure 1 (D): The product (C₄H₈O₇) has the same number of hydrogen atoms but one oxygen atom less than the sum of the two reactants (2 C₂H₄O₄); hence it has been reduced. Should one of the glyoxylic acid reactants be glyoxal?

- Table S1: it is stated that * means radical. CHOHOH does not have a star, but looks like a radical. It would be helpful to clarify the nomenclature.

- P. 14170, line 26: Shapiro is misspelled

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