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Comment

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

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We thank the reviewers for careful reading and helpful comments that improve the quality of our manuscript. Reviewer comments have been copied followed by our responses in bold.

Anonymous Referee 1) 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

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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.

- 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  $10^8$  M/atm calculated in this manner.

**Response: The point of this paragraph is that the uptake of glyoxal is substantial (even the greatest) when aqueous photochemistry is involved. Henry's law constants provide a convenient way to compare uptake for different scenarios. However Henry's law is intended to describe reversible processes, and photochemistry is considered irreversible. In the laboratory (Volkamer et al., 2009), the Henry's constant was presumably obtained when the smog chamber reached equilibrium after photochemical reactions took place. In the atmosphere where summertime photochemistry takes place more than 12-hr per day, glyoxal uptake could be even greater. The text has been changed and irreversibility arguments have been added:**

**Comparable uptake, expressed as a Henry's constant, was reported for wet ammonium sulfate seed particles (46-86% RH) exposed to glyoxal and OH radicals in a smog chamber (Volkamer et al., 2009; Ervens and Volkamer, 2010). It should be noted that OH radical reactions are considered irreversible, and are not intended to be described by Henry's equilibrium partitioning constants. Reactive uptake of glyoxal through aqueous reactions with photochemical oxidants could be substantially greater in the atmosphere where summertime photochemistry takes place more than 12-hr per day.**

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- 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.

**Response:** To state first the currently accepted view, we moved the following sentence from the middle of the paragraph in Section 2.2.2 up to the beginning of Section 2.2.1 (Section 5.1 in the revised manuscript):

The currently accepted view is that self oligomerization of glyoxal occurs via hemiacetal formation (Loeffler et al., 2006) and that of methylglyoxal occurs via aldol condensation (De Haan et al., 2009a).

To address the reviewers concern we have also modified the first paragraph of Section 2.2.2 (Section 5.2 in the revised manuscript) to read:

Jang et al. (2002) first proposed oligomerization of organic carbonyls through aldol condensation on the wet surface of the particle. While aldol condensation of glyoxal was not considered likely by Barsanti and Pankow (2005), Shapiro et al. (2009) reported this possibility based on the observation of pi-conjugated systems suggested by the analyses of UV-Vis spectra, density functional theory, and a kinetic model study. They noted that the observed absorption above 400 nm could be due to pi-conjugated system formation. Alternatively imines (or C-N containing organic compounds) from reactions involving ammonium could be responsible for the UV-Vis absorption observed by Shapiro et al. Aldol condensation of glyoxal would involve the reaction of an enol tautomer of monohydrated glyoxal with dehydrated glyoxal (Fig. 1b) and nucleophilic addition of the enol to the carbonyl in the dehydrated glyoxal.

- Also section 2.2.2: NH<sub>4</sub><sup>+</sup> 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).

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**Response:** We thank the reviewer for pointing this out. The paragraph (line 10, page 14171 in the ACPD manuscript; the second paragraph of Section 5.2 in the revised manuscript) has been revised as follows:

**Oligomer formation via acid catalysis (hemiacetal formation or aldol condensation) can be achieved using a catalyst other than  $H^+$ . For example, acetaldehyde has been reported to form oligomers through amino acid catalyzed (Noziere and Codova, 2008) and ammonium ion (Noziere et al., 2009a; 2009b; 2010) catalyzed aldol condensation. Noziere et al. (2009a; 2009b) also reported that glyoxal oligomerization was enhanced by the presence of ammonium ions. Ammonium catalysis is a variant of acid catalysis.  $NH_4^+$  dissociates to  $NH_3$  and  $H^+$ . The reaction is initiated by  $H^+$  catalysis.  $NH_3$  then either acts as a reactant to form imines or as a catalyst to form aldol condensation products. Noziere et al. (2009a; 2009b; 2010) argue that  $NH_4^+$  catalysis is a major source of oligomers in wet aerosols.**

- Section 2.2.3: Galloway et al. reported formation of imidazoles, a special form of imines, in chamber studies.

**Response:** This reference and a reference by Noziere were added to the relevant sentence (Section 5.3 in the revised manuscript):

**Imines (including imidazoles) are key products in the reaction of glyoxal with ammonium, amino acid or amine, since they react further with themselves or glyoxal to form C-N containing oligomers (De Haan 2009a; De Haan 2009b; Galloway et al., 2009; Noziere et al., 2009b; 2010).**

- 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

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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; De Haan 2009) that the authors reference clearly demonstrate that glyoxal largely stays in the condensed phase upon evaporation and the reasons are probably secondary.

**Response: To address this, we have added the following:**

**This is consistent with reports that the equilibrium constant for glyoxal dimerization is independent of pH and ionic strength (Fratzke and Reilly, 1986); these authors also found that the rates of dimerization and de-dimerization decrease at low pH. - line 22, page 14173 in the ACPD manuscript; Section 5.8 in the revised manuscript**

**And: ...and de-oligomerization is slow, allowing oligomers to stabilize. - line 15, page 14174 in the ACPD manuscript; Section 5.8 in the revised manuscript**

- Section 2.3.3; Could ammonium catalyze the oligomerization/de-oligomerization and thus increase reversibility whereas in drying experiments no ammonium is present?

**Response: The paragraph (line 17, page 14176; Section 5.8 in the revised manuscript) now reads:**

**If the process is reversible, can we expect that glyoxal oligomers remaining in the particle phase after water evaporation will evaporate completely in clean (glyoxal-free) air? While Hastings et al. (2005) found no significant evaporation of dehydrated glyoxal while drying water solutions, ammonium might increase oligomer evaporation by catalyzing oligomerization and de-oligomerization in atmospheric particles. Galloway et al. (2009) observed the evaporation of glyoxal**

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from glyoxal SOA formed on ammonium sulfate seed particles after 9 hours of exposure to clean air. The process is so slow that it is not likely to be an important sink for glyoxal in the atmosphere.

- 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 RO<sub>2</sub>+RO<sub>2</sub> importance and formation of RO according to the mechanism.

**Response: Formic acid is not a good reference for the comparison because it is also formed by the reaction of glyoxylic acid with hydrogen peroxide in samples awaiting analysis by IC and formic acid cannot be measured in real-time experiments by ESI-MS. High yields of oxalic acid (> 100%) at cloud relevant concentrations (1e-5 – 1e-4 M of initial glyoxal concentrations) indicate that the decomposition from RO<sub>2</sub> is dominant, whereas the RO<sub>2</sub>+RO<sub>2</sub> pathway is almost negligible.**

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

**Response: It is also mentioned in the text (line 24, page 14185 in the ACPD manuscript; last paragraph of Section 6.4 in the revised manuscript).**

- 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).

**Response: We accept this and figure 1 (B) has been changed accordingly.**

- Figure 1 (D): The product (C<sub>4</sub>H<sub>8</sub>O<sub>7</sub>) has the same number of hydrogen atoms but

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one oxygen atom less than the sum of the two reactants (2 C<sub>2</sub>H<sub>4</sub>O<sub>4</sub>); hence it has been reduced. Should one of the glyoxylic acid reactants be glyoxal?

**Response: The proposed reaction is esterification and one oxygen atom has been reduced because of the loss of a water molecule.**

- 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.

**Response: \* has been added for all radical compounds.**

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 14161, 2010.

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