

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

Y. B. Lim et al.

ylim@envsci.rutgers.edu

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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 #2)

The authors present a new analysis of the aqueous-phase reactions of the glyoxal-OH reactive system relevant to SOA formation in wet atmospheric aerosols and cloud droplets. New radical-radical reaction pathways are proposed. The authors conclude that radical-radical reactions are important for modeling in-aerosol SOA formation, but are not needed to describe SOA formation in cloud droplets, where organic concen-

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trations are lower. This is a potentially interesting and valuable contribution to the ever-growing aqueous-phase SOA formation literature. However, the following issues should be addressed before this manuscript will be suitable for publication in ACP:

- A basic question I have is: Is this manuscript presenting new experimental data or only theoretical analysis? Section 3 gives the impression that no new experiments were performed and experimental data already published (Tan et al. (2009)) was used for modeling purposes here. However, the mass spectra in Figures 5 and 6 are presented like new data, and the introduction and abstract suggest new experiments were performed. Some clarification, probably in Section 3, is needed.

Response: In this manuscript we discuss detailed chemistry of Tan et al. (2009) with new experimental data from FTICR-MS. The first sentence of Section 3 (Section 2 in the revised manuscript) was modified to make this more clear:

This paper draws heavily on bulk experiments of OH radical-initiated reactions of glyoxal in the aqueous phase described in detail by Tan et al. (2009) and includes previously unreported analyses of these samples by ultra high resolution Fourier Transform Ion Cyclotron Resonance electrospray ionization mass spectrometry.

- The introductory/literature review sections (1 and 2) of this paper are long and could be more focused. In particular, the discussion of glyoxal SOA formation pathways other than the OH reaction in Section 2 seems a bit out of place, especially since most of these pathways were not included in the model presented in this manuscript. It is a matter of style, but my preference would be to see the authors cut Section 2 down to 1-2 paragraphs and move it into Section 1. That being said, if the authors choose to keep all or some of Section 2, the following content issues should be addressed:

Response: The manuscript is now reconstructed. Please also see our response to reviewer #3's comment.

o Section 2.2.1: glyoxal can also be protonated by NH₄⁺ (see Noziere et al. (2009) or

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Schwier et al.(2010))

Response: Section 2.2.2 (Section 5.2 in the revised manuscript) has been revised to address this. Please see our response to reviewer #1's comment.

o Section 2.2.2: The issues brought up by Anonymous Referee #1 regarding aldol condensation by glyoxal are discussed in detail by Shapiro et al. (2009) in the manuscript and in the interactive discussion. Please refer to pages 2294-2295 of that manuscript for more information.

Response: These points are now included. Please see our response to the reviewer #1's comment, "Section 2.2.2 Page 14170 Aldol condensation. . ."

o Section 2.2.2: This discussion of hemiacetal vs. aldol condensation for glyoxal vs. methylglyoxal is a bit simplistic. Both species can undergo both types of oligomerization, although aldol condensation is more facile for methylglyoxal than glyoxal. Hemiacetal formation is probably dominant for both species. Please see Sareen et al. (2010), Schwier et al. (2010), Krizner et al. (2009).

Response: Line 2 on page 14171 (Section 5.2 in the revised manuscript) has been revised as follows:

The current dominant view is that self oligomerization of glyoxal occurs via hemiacetal formation (Loeffler et al., 2006) and that of methylglyoxal occurs via aldol condensation (De Hann et al., 2009a; Krizner et al. 2009).Note, a cloud-relevant bulk experiment suggested that major oligomerization of methylglyoxal occurs via hemiacetal formation at pH 3 and via aldol condensation at pH 4 (Yasmeen et al., 2009). Sareen et al. (2010) observed both hemiacetal and aldol condensation products from methylglyoxal oligomerization. It appears that both glyoxal and methylglyoxal can undergo hemiacetal formation and aldol condensation (Schwier et al., 2010) and the chemistry could be pH dependent.

o Section 2.2.2: Catalysis by the ammonium ion is not "base catalysis" if its active role

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is to protonate the carbonyl (then it's acting as an acid). Perhaps the authors are referring here to the iminium pathway presented by Noziere et al. (2009) and imidazole formation proposed by Galloway et al. (2009) that required the participation of ammonia. The role of NH_4^+ in promoting aldol condensation and hemiacetal formation has also been discussed by Sareen et al. 2010 and Schwier et al. 2010.

Response: We thank the reviewer for pointing this out and have revised Section 2.2.2 (Section 5.2 in the revised manuscript) paragraph to indicate this. Please see our response to reviewer #1's comment. "Also Section 2.2.2: NH_4^+ catalysis is. . ."

o Section 2.2.3: Why discuss only a few studies on imine formation here? What about imidazole formation (Galloway et al. 2009) or the C-N compounds reported by Noziere et al. (2009)?

Response: We have added imidazole formation and C-N compounds in Section 2.2.3 (Section 5.3 in the revised manuscript). Please see our response to reviewer #1's comment, "Section 2.2.3: Galloway et al. . . ."

o Section 2.2.6: the observations of an organosulfate species by Galloway et al (2009) should be discussed here.

Response: Galloway et al. (2009) and recently Noziere et al., GRL (2010) report that organosulfate formed only under irradiated conditions. We strongly believe that organosulfate forms via radical reactions, not acid catalysis. However, detailed reaction mechanism is unknown. Although further investigations are necessary, we have added those two papers as evidence of radical reactions in the revised text. The following sentence has been added in line 2, page 14173 (Section 5.6 in the revised manuscript):

Similarly, Galloway et al. (2009) and Noziere et al. (2010) reported that organosulfate formed only under irradiated conditions. These studies also provide strong

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evidence for radical-radical reactions.

o Section 2.3.1: The wording of this section doesn't leave room for the role of NH₄⁺ in hemiacetal formation (it would act as an acid, as I discussed above, but "acid catalysis" does not bring this mechanism to mind).

Response: This is now discussed in Section 2.2.2 (Section 5.2 in the revised manuscript): "Oligomer formation via acid catalysis (hemiacetal formation or aldol condensation) can be achieved using a catalyst other than H⁺. . . . Ammonium catalysis. . . ." Section 2.3.1 (section 5.8 in the revised manuscript) is intended to discuss whether oligomerization is greater at low pH, as the title suggests.

o Section 2.3.1: glyoxal can take on either 1 or 2 waters. Since few totally un-hydrated glyoxal molecules will exist in the aqueous phase, probably the carbonyl of the singly hydrated species is the one that participates in hemiacetal formation. Is this what is meant by "dehydrated glyoxal"? Please change the language to make this more clear.

Response: We have clarified as follows (Section 5.8 in the revised manuscript):

In the cloud-relevant experiments by Loeffler et al. (2006), water evaporation increases the concentration of glyoxal near the droplet surface. This shifts the equilibrium so that **dihydrated glyoxal becomes singly hydrated or even unhydrated**. This (partially) dehydrated glyoxal, then, either reacts. . .

o Section 2.3.3: Schwier et al. 2010 found that oligomer formation by glyoxal was not reversible upon dilution over a timescale of several hours.

Response: It is difficult to conclude that glyoxal oligomerization via acid catalysis is irreversible based on information provided in Schwier et al. (2010). Quantitative data on the behavior of glyoxal oligomers formed via hemiacetal formation/aldol condensation as a function of time and with dilution would be helpful (perhaps, online mass spectra for key m/z's representing hemiacetal/aldol condensation products like Galloway et al. presented). Besides, it is questionable

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that a 10-fold dilution is enough to test the reversibility. However, their results certainly show that glyoxal oligomers are stable, and we do mention this. We have added them and made the following changes (Section 5.10 in the revised manuscript):

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 from glyoxal SOA formed in the dark on ammonium sulfate seed particles after 9 hours of exposure to clean air. **Although quantitative data on the behavior of glyoxal oligomers formed via hemiacetal formation/aldol condensation as a function of time and with dilution would be helpful, Schwier et al. (2010) also observed no reversible process of glyoxal oligomers upon dilution over several hours. The data to date suggest this** process is so slow that it is not likely to be an important sink for glyoxal in the atmosphere.

More detailed comments: Abstract, line 19: 'catalyzation' should be 'catalysis'

Response: It is corrected.

Page 14164, line 6: By 'smog chamber SOA' the authors seem to mean 'SOA formed by condensation of low-volatility organic material from the gas phase.' Of course glyoxal has been shown to form SOA in smog chambers. (Liggio et al. 2005, Kroll et al. 2005, Galloway et al. 2009, Volkamer et al. 2009) Please change the language here to be more accurate.

Response: Line 3, page 14164 "smog-chamber" has been deleted. Instead, "(formed via vapor pressure driven partitioning)" has been added at the end of "Traditional SOA." Line 7-8 "smog chamber SOA" has been changed to "traditional SOA."

Page 14170, line 26: Shapiro is misspelled.

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Response: It is corrected.

Page 14173, line 8: should “the” be there? It reads better “. . .SOA formation through aqueous chemistry...”

Response: “the” is deleted.

Page 14174, line 28 – Page 14175, line 1: You state the ionic strength from 0.05 to 4.0 M NaCl corresponds to effective Henry’s constant $8.5 \times 10^5 \text{ M atm}^{-1}$ and $1.9 \times 10^6 \text{ M atm}^{-1}$. This is confusing to the reader because in a later statement in the same paragraph, you corresponded 0.05 M NaCl to $1.9 \times 10^6 \text{ M atm}^{-1}$, which seems opposite what is stated in the first sentence.

Response: We thank the reviewer for pointing this out. The numbers were wrong. As ionic strength increases from 0.05 to 4.0M NaCl, the effective Henry’s constant decreases from $1.9 \times 10^6 \text{ M atm}^{-1}$ to $8.5 \times 10^5 \text{ M atm}^{-1}$ (Ip et al., 2009). The correction has been made in the revised text (Section 5.9):

They also observed that a further increase in ionic strength from 0.05M to 4.0M in NaCl solutions, the effective Henry’s constant decreases from $1.9 \times 10^6 \text{ M atm}^{-1}$ to $8.5 \times 10^5 \text{ M atm}^{-1}$: this is known as “salting-out effect.”

Page 14183, line 2: You have 74.000, but directly beneath this you use 74.00036. Later in the manuscript, all decimals disappear for the m/z-. Please present this data consistently throughout the paper.

Response: We take this point. In the revised text, we have used 5 decimal points for FTICR-MS data and integers for ESI-MS data. 74.000 has been changed to 74.00036, the average value in Table 1.

Figure 1 does not add much and can be removed.

Response: We do not agree. We strongly believe Figure 1 helps readers to view current findings of SOA formation via non-radical reactions of glyoxal in

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the aqueous phase. So, it should not be removed.

Consider combining Figures 5 and 6 into a single figure with two panels to allow easy comparison.

Response: Although this is a nice suggestion, we rather keep them separately because those two figures were obtained from different analyses: Figure 5 from FTICR-MS and Figure 6 from ESI-MS.

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

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