

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

Anonymous Referee #2

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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 concentrations 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

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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.

- 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:

o Section 2.2.1: glyoxal can also be protonated by NH_4^+ (see Noziere et al. (2009) or Schwier et al.(2010))

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.

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).

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

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)?

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

o Section 2.3.1: The wording of this section doesn't leave room for the role of NH_4^+ in hemiacetal formation (it would act as an acid, as I discussed above, but "acid catalysis" does not bring this mechanism to mind).

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.

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.

More detailed comments:

Abstract, line 19: 'catalyzation' should be 'catalysis'

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.

Page 14170, line 26: Shapiro is misspelled.

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

Page 14174, line 28 – Page 14175, line 1: You state the ionic strength from 0.05 to

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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.

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.

Figure 1 does not add much and can be removed.

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

REFERENCES

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Kroll, J. H., et al. *J. Geophys. Res.-Atmos.*, 110 (D23), D23207, doi:10.1029/2005JD006004, 2005.

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