

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 #3)

The subject manuscript, Aqueous chemistry and its role in secondary organic aerosol formation, provides an overview of the role of aqueous-phase chemistry in forming secondary organic aerosols (SOA), focusing on radical versus non-radical reactions and cloud-water versus aerosol-water conditions. While the manuscript potentially offers advancements in the field, it is somewhat difficult to discern the novel aspects of this

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work. The title and much of the paper suggest a review article, however the abstract, and “Experimental section” and “Results and discussion” headers suggest otherwise. It is recommended that the authors address this issue (research vs. review article), discussed in further detail below, before the manuscript is accepted for publication in ACP.

Content and structural comments: While the abstract of the subject manuscript indicates the literature will be used to describe radical (OH) and non-radical aqueous chemistry at cloud-water and aerosol-water relevant concentrations, the extensive presentation of background material in sections 1 and 2 is disorienting. The presentation of so much background material in the introduction obscures the most relevant details and distracts from the objectives and outcomes of the current work. It is suggested that most of the background material be combined with that in section 2 (readers will be ready for the literature review in section 2, primed by sentence on lines 7 and 8, p. 14167). It is also suggested that in combining parts of section 1 with section 2, care be taken to remove the unnecessary repetition and extraneous detail currently in the manuscript.

Response: The manuscript is now reconstructed. We shortened the introduction by moving discussions about field evidence to a new section “atmospheric evidence” (Section 3). Now we have a “non-radical reactions” section (section 5) and a “radical reactions” section (Section 6) and have rearranged the discussions previously in Sections 1 and 2. This reconstruction should address reviewer’s concerns. We also reduced some redundancies; for example, we deleted the sentence from line 6 to 9 on page 14183 and two sentences from line 10 to 15 on page 14187.

A lot of the introduction is devoted to measured O/C ratios for SOA, which is again brought up in the atmospheric implications section; however, it isn’t clear how the subject manuscript contributes anything to that discussion (unless it is in the context of a review article, in which case it doesn’t seem necessary to include in the atmospheric

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implications section).

Response: Now we added an “O/C ratio” section (Section 6.5) in the discussion and included plots of O/C versus initial glyoxal concentrations in Fig. 9 based on our new experimental results. We also changed the section title from “atmospheric implications” to “conclusions.”

While the title and sections 1 and 2 of the paper suggest a review article, the abstract does indicate new experiments and a modeling application will be discussed. In the experimental section, the authors say that the paper “draws heavily” on experiments presented in Tan et al. (2009) and it does not appear that any new experiments were performed for this work. The results of Tan et al. (2009) may be more appropriate in the introduction, as they seem to be what prompted the subsequent data analysis and kinetic modeling presented in the results and discussion. In general, a better description of how the present work builds on previous work of the group (e.g., as presented in Tan et al. (2009)) would be very useful to have in the introduction. Regarding the experimental section, it is recommended that the authors: 1) rename the section (data analysis and kinetic modeling?), unless new experiments were actually performed for this work; and 2) provide the details of the work done specifically for presentation in this manuscript. Some of those details, e.g., regarding the kinetic modeling, seem to be buried in the results and discussion section.

Response: Now we added a new section “methods: new analyses and kinetic modeling” (Section 2) to make it clear that we actually conducted new experiments and new model simulations.

Other comments: p. 14162, sentence 14: suggestion to delete “at least”; sentences 15 and 17: concentrations of? water? glyoxal?

Response: We agree and have deleted “at least” in the revised text because some groups (Noziere and McNeill) have done kinetic studies for non-radical reactions in the aqueous phase. Before concentrations, we added “glyoxal”

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p. 14166, sentence 15: suggestion to replace “these” with “those”

Response: We accept the suggestion.

p. 14169, sentence 9: replace period before OH with a comma

Response: The correction has been made in the revised text.

p. 14170, sentence 6: suggestion to replace “plenty of” with “sample availability is not limited for chemical analyses” or something to that effect

Response: We accept the suggestion.

p. 14172: suggestion to either combine sections 2.2.4 and 2.2.6, or put them in succession, since an organosulfate, as noted, is an ester derived from an inorganic salt

Response: We have moved Anhydride formation before Esterification. We have also switched Figure 1 (D) and (E) accordingly. Now Figure 1 (D) is anhydride formation, and (E) is ester formation.

p. 14173, first paragraph: Is it possible that there is an “acidity threshold” at which acid-catalyzed uptake of glyoxal can be observed, but that may not result in a direct correlation between pH and uptake coefficients below that threshold pH value?

Response: Fratzke and Reilly (Int. J. Chem. Kin. 18, 1986) reported that the kinetic rate of acid-catalyzed oligomerization of glyoxal was not maximum at low pH (actually it was minimum at pH 3) while the equilibrium constant was independent of pH (Please see reviewer #1’s comment, “Section 2.3.1: Fratzke and...” and our response). This indicates acidity does play a role of oligomerization, but that the chemistry is very complicated. There is stronger evidence that glyoxal uptake in aerosols is driven by the liquid water content rather than the acidity. A reference to the Fratzke results is now included in the paper. (See the response to Reviewer #1)

p. 14177, paragraph starting on line 3: The irreversibility of products formed from OH

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radical reactions is included in the section with the header “Reversibility of oligomers formed by acid catalyzed pathways”. It is suggested that the paragraph be moved to a section regarding aqueous-phase chemistry involving OH radicals.

Response: Now we moved the paragraph to the radical chemistry section.

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

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