Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., author comment AC2
https://doi.org/10.5194/acp-2022-139-AC2, 2022

Reply on RC3

Yuemeng Ji et al.

Author comment on "Elucidating the critical oligomeric steps in secondary organic aerosol and brown carbon formation" by Yuemeng Ji et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-139-AC2, 2022

Comments: This work systematically investigated the aqueous-phase reaction mechanism and kinetics of glyoxal (GL) using quantum chemical and kinetic rate calculations. The critical oligomeric steps in secondary organic aerosol (SOA) and brown carbon (BrC) formation were elucidated. The authors also revealed that the loss rate of aqueous-phase reaction of GL is higher than that of photolysis and photo-oxidation. This paper is well organized and clearly written. And the outcomes are very helpful to understand the role of the aqueous-phase chemistry of GL in SOA and BrC formation. I recommend publication after the minor comments are addressed.

Response: We are sincerely grateful to your attention on this paper. We have made careful revisions on the original manuscript according to your comments. The changed sentences have been marked as red color in the revised version. Below is our point-by-point response to your comments:

Question 1) Line 28: "produce (SOA) particle mass" is a vague expression. It should be replaced with "produce secondary organic aerosol (SOA) particles".

Response: According to the reviewer's suggestion, the corresponding correction was made. (Please see line 28)

Question 2) Line 60: "have" should be "has".

Response: It was modified as suggested. (Please see line 60)

Question 3) Line 87: MG in "MG+MA/AM reaction systems was not mentioned before. Please clarify.

Response: We are very grateful to the reviewer's helpful comment. The word "MG" is a mistake and it was revised to "**GL**". (Please see line 90)

Question 4) Methods: How does the authors deal with the influence of liquid-phase environment? It should be included in the Methods.

Response: According to the reviewer's helpful comment, the following text was added to "Methods" section: **"The solvent effect of water in the aqueous phase was considered by a continuum solvation model (SMD) (Marenich et al., 2009). The solvation free energy includes two components: the bulk electrostatic contribution and the cavity-dispersion-solvent-structure contribution arising from short-range interactions between the solute and solvent molecules."** (Please see lines 77-80)

Question 5) Line 122: The term of "the natural charge population analysis" should be replaced with "the natural population analysis"?

Response: According to the reviewer's suggestion, the corresponding correction was done. (Please see line 126)

Question 6) Line 147: The results show that "the k values …are 4.14×10^9 M^{-1} s^{-1} and their half-lives ($t1/2$) are lower than $\sim 10^{-4}$ s". How are the half-lives calculated or has the author considered the real atmospheric concentration of hydrogen ion in aerosol?

Response: In this study, the half-lives ($t1/2$) of the R_{H+}21-1 and R_{H+}22-1 pathways were calculated using $t1/2=1/(k\times[H^+])$, where k is the rate constant of the R_{H+}21-1 or R_{H+}22-1 pathway and $[H^+]$ is the concentration of the hydrogen ion in the aqueous phase. Considering the mild acidic condition of the atmospheric aerosol, $[H^+]$ was considered as 10^{-6} M in this study. The following text was added to revised manuscript: **"The $t1/2$ was calculated using the formula, $t1/2=1/(k \times [H+])$, where k is the rate constant of the R_{H+}21-1 or R_{H+}22-1 pathway and $[H^+]$ is the concentration of the hydrogen ion (10^{-6} M) in the weakly acidic solution."** (Please see lines 152-153)

Question 7) Line 156: The authors states "the C–O(H) bond of 1st-CB1 after protonation is elongated by 0.05 Å". Please clarify the reference, that is, what is the C–O(H) bond longer than?

Response: We are very grateful to the reviewer's comment. The C–O(H) bond of 1st-CB1 after protonation is longer than the C=O bond of GL. The corresponding statement was added in the revised manuscript: **"the C–O(H) bond of 1st-CB1 after protonation is elongated by 0.05 Å relative to the C=O bond of GL."** (Please see line 162)

Question 8) Line 188-189: "Current results reveal that cyclic oligomers are difficult to be formed from the CBs with the positive charge center close to O(H) atom". The authors should point out which CBs in Figure 1b are difficult to form cyclic oligomers.

Response: We thank the reviewer for bringing this to our attention. The CBs that are difficult to form cyclic oligomers include 2nd-CB2 and 2nd-CB4 in Figure 1b. The following text was added to revised manuscript: **"Current results reveal that cyclic oligomers**

are difficult to be formed from the CBs with the positive charge center close to O(H) atom, such as 2nd-CB2 and 2nd-CB4 in Fig. 1b." (Please see lines 195-197)

Question 9) According to the data in Figure 4a, the corresponding ΔG_r value in line 217 is -0 kcal mol^{-1}.

Response: We are grateful to the reviewer's attention on this. It is our carelessness to lead to the incorrect ΔG_r value. According to the reviewer's suggestion, we rechecked the data in Figure 4a, and found that the correct ΔG_r value should be -1.0 kcal mol^{-1} rather than -0 kcal mol^{-1}. The corresponding ΔG_r value in line 217 in the original manuscript was corrected as -1.0 kcal mol^{-1}. (Please see line 224)

Question 10) Line 237: the "G_r" should be "ΔG_r".

Response: According to the reviewer's valuable suggestion, the corrections were done as suggested.

Question 11) Line 263: "ammonia salts" should be "ammonium salts".

Response: According to the reviewer's valuable suggestion, the corrections were done as suggested.

Question 12) Line 315: the "conditions" should be "condition".

Response: According to the reviewer's valuable suggestion, the corrections were done as suggested. (Please see lines 244, 270 and 322)