Reply on RC2

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-AC3, 2022

Comments: α-dicarbonyls play important roles in the secondary organic aerosol (SOA) and brown carbon (BrC) formation in the atmosphere, but their sources remain unclear. Ji et al. selected GL as a model compound, and systematically investigated its aqueous-phase oligomerization mechanisms, kinetics, and contributions to SOA and BrC formations using quantum chemical calculations and some modeling methods. The simulation results were supported by previous experiments and can provide useful data for assessment on the role of α-dicarbonyls in SOA and BrC formations. The manuscript is well written and can be easily understood. The following minor aspects may be useful to further improve its quality:

Response: We are sincerely grateful to your attention on this paper. We have made careful revisions on the original manuscript according to your comments and suggestions. The changed sentences have been marked as red color in the revised version.

Question 1) LINE 94 and 97: Why is the 6-311+G(3df,3pd) basis set more "flexible" than the /6-311G(d,p) basis set?

Response: Relative to 6-311G(d,p) basis set, three reasons indicate that the 6-311+G(3df,3pd) basis set is more "flexible": First, it is a heavy-augmented basis set and provides one s- and p- diffuse function to heavy atoms, to improve the radial distribution of tracks; Secondly, it also provides three sets of polarization d- and one set of polarization f- functions to heavy atoms, and three sets of polarization p- and one set of polarization d- functions to H atom, to describe the deformation properties of atomic orbitals; Thirdly, it further improves the polarization relative to the 6-311G(d,p) basis set. In summary, the 6-311+G(3df,3pd) level can provide stricter SCF convergence and more accurate results than the 6-311G(d,p) basis set.

Question 2) LINE 97: What is the "M06-2X//M06-2X" level? Is it means that M06-2X/6-311+G(3df,3pd)//M06-2X/6-311G(d) level?

Response: It means the M06-2X/6-311+G(3df,3pd)//M06-2X/6-311G(d,p) level in this study. For clarify, the explanation of M06-2X//M06-2X was added in the revised

manuscript as "**For simplicity, hereinafter they were denoted as the X//Y, i.e., M06-2X//M06-2X level, where Y is a SPE calculation at the M06-2X/6-311+G(3df,3pd) level and X is the geometry optimized at the M06-2X/6-311G(d,p) level.**" (Please see lines 98-99)

Question 3) LINES 98 and 123: Please add citation of the methods CCSD(T) and NBO.

Response: According to the reviewer's suggestion, the corresponding references were supplemented. (Please see lines 101-102 and 127)

Question 4) LINES 153 and 200: The sub-title "3.2" is the same as "3.3". I guess that the "3.3" should be written as: Oligomerization mechanisms with methylamine/ammonia.

Response: We are very grateful to the reviewer's attention on this detail. The sub-title "3.3" was corrected as "**Oligomerization mechanisms with methylamine/ammonia**". (Please see line 207)

Question 5) LINES 265 ~ 293: Some contents here belong to "Methods" rather than "Results and Discussion".

Response: We are very grateful to the reviewer's suggestion. These contents about how to deduce the heterogeneous GL reaction rates and growth rates to SOA and BrC were not put into "Method" because it isn't only method. That is, some formulas are obtained by our own derivation. Hence, we think it should belong to "Results and discussion".

Question 6) LINES 278 ~ 279: The sentence is hard to understand.

Response: According to the reviewer's comment, the corresponding sentence was modified to improve the quality as: "**The lower values under remote and rural conditions are explained by the γ_{GL} used here, which is more suitable for the urban condition (Liggio et al., 2005a).**" (Please see lines 284-285)

Question 7) LINES 315 ~ 316: It is relatively arbitrary to judge the importance of heterogenous loss of GL in urban regions only based on the simulated lifetime. Urban regions may have more competing loss pathways of GL, compared with other regions. Therefore, more discussion should be supplemented to support the view "a more important role of heterogeneous reaction of GL in urban air quality compared with other conditions".

Response: We are very grateful to the reviewer's comment. We think our vague expression make the reviewer mistaking that it is relatively arbitrary to deduce this conclusion. Firstly, the reviewer queried our conclusion because it obtained "only based on the simulated lifetime". Our simulated lifetime is in agreement with that of experimental data, suggesting that our simulated lifetime is suitable. Hence, the conclusion based on our simulated lifetime should be suitable and no relatively arbitrary. Secondly, we compared the lifetime under three conditions and found the lifetime under urban

conditions is very faster than those under rural and remote conditions. We agree with the reviewer's statement of "Urban regions may have more competing loss pathways of GL, compared with other regions.". Hence, we deduce that it is a more important role only compared with rural and remote conditions rather than it is a more important role under urban condition. To avoid the misunderstanding, the following sentences were modified as: "**Using our predicted heterogeneous GL reaction rates, the aqueous heterogeneous lifetime (τ) of GL is estimated to be 3.60 min under urban condition, somewhat smaller than that of experimental data (5.0 min) (Liggio et al., 2005a). However, the τ values are 89 and 61 min under rural and remote conditions due to low GL level, respectively (Liggio et al., 2005a). It indicates a more important role of aqueous heterogenous reaction of GL in urban air quality relative to other conditions.**" (Please see lines 321-324)

Question 8) TABLE 1: The krate(total) and GR in rural regions calculated by the authors are higher than the experimental ones by one order of magnitude (1.85×10^{-3} vs 1.90×10^{-4} and 0.57 vs 0.032). Please add more discussion.

Response: According to the reviewer's helpful suggestion, the additional discussion was added to the revised manuscript, to indicate why the values in rural regions are higher than the experimental ones as: "**The k_{rate} value under urban condition almost agrees with that of the experimental data and is slightly larger than those of the experimental data under other conditions (Liggio et al., 2005a). The lower values under remote and rural conditions are explained by the γ_{GL} used here, which is more suitable for the urban condition (Liggio et al., 2005a).**" (Please see lines 283-285)

Question 9) Figure 5: Please explain the (I), (II), and (III) in the caption.

Response: We have explained the (I), (II), and (III) in conclusion of the original manuscript. The explanation is too long to be added to the caption, and thus the detailed explanation was left in original place in the revised manuscript. According to the reviewer's suggestion, a concise caption was added to the Figure 5's caption as: "**The inside circle ring represents the ion-mediated initial reaction of GL to yield DL, TL and 1st-CBs; The middle circle ring corresponds to the formation of RODs and 2nd-CBs; The outer circle ring denotes the formation and propagation of ROTs from the association reactions of 2nd-CBs with DL/TL.**" (Please see lines 559-562)

Question 10) Variables are recommended to be expressed in italics.

Response: According to the reviewer's comment, all variables were expressed in italics in the revised manuscript, such as "τ" to "τ".