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Title: Elucidating the critical oligomeric steps in secondary organic aerosol and brown carbon formation

The corresponding authors: Prof. Yuemeng Ji and Prof. Taicheng An

Dear Anonymous Referees, Dr. Deming Xia, and Dr. Jan-Hendrik Peters,

Thank you for the helpful and valuable review and comment. We have made careful revisions on the original manuscript according to your kind and helpful comments. The changed sentences have been marked as red color in the revised manuscript. Below is our point-by-point response to your comments:

Anonymous Referee #1

1) Lines 277-278: A little confuse about the statement here: If γ_{GL} used was only suitable for urban condition, estimating other atmospheric conditions should be unreasonable, right? Also, does it mean that there are no available γ_{GL} values for remote and rural conditions from literatures like Liggio (2005)'s study? BTW, "are not" should be "is not".

Response: We are sorry that our expression led to the reviewer's confusion. The γ_{GL} used in our study is more suitable for the urban condition than other conditions, because it was determined at very low relative humidity which is closer to urban condition relative to other conditions (J. Geophys. Res., 2005, 110(D10): D10304). Hence, it suggests that the rate estimated under urban condition is more suitable than those under remote and rural conditions. In addition, there are no available γ_{GL} values, which are explicitly obtained under remote and rural conditions in the previous studies, like Liggio et al. (J. Geophys. Res., 2005, 110(D10): D10304). Hence, for comparative analysis, the same γ_{GL} value is used to estimate the rates under three different conditions. According to the reviewer's helpful comment, to make the expression clearer, the corresponding sentences were modified as following: **"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 287-289)

2) Lines 294-303: Did the authors identify these primary reaction pathways based on their branching ratios?

Response: These primary reaction pathways were determined not only based on branching ratios but also the reaction energies, activation energies, and rate constants.

3) Line 320: please also estimate the mean tau or its ranges for gas-phase processes.

Response: According to the reviewer's suggestion, we added the mean τ in the revised manuscript, which is determined by Liggio et al. (J. Geophys. Res., 2005, 110(D10): D10304).

"Especially, the τ value under urban condition is significantly shorter than the total gas-phase loss (125 min) (Liggio et al., 2005a)." (Please see lines 330-331)

4) Line 28: The full name of SOA is missed.

Response: Thanks to the reviewer's kind reminder. The full name of SOA was supplemented on line 28 of the text.

5) Line 30: "particle" -> "particles"

6) Line 34: "particle-phase and aqueous-phase" -> "particle- and aqueous-phase"

Response: They were modified as suggested. (Please see lines 31 and 34-35)

7) Figure 5: Please describe each circle ring in the caption.

Response: According to the reviewer's suggestion, the following sentences were added to describe each circle ring in the caption of Figure 5 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 571-574)

Dr. Deming Xia's comments:

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.

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)

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)

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 211)

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”.

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 288-289)

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 325-328)

8) TABLE 1: The k_{rate}(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 287-289)

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 571-574)

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”.

Anonymous Referee #3

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)

2) Line 60: “have” should be “has”.

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

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)

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)

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)

6) Line 147: The results show that "the *k* values …are 4.14 × 10^9 M^{-1} s^{-1} and their half-lives ($t_{1/2}$) are lower than ~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 ($t_{1/2}$) of the R_{H+}21-1 and R_{H+}22-1 pathways were calculated using $t_{1/2}=1/(k\times[H^+])$, 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 $t_{1/2}$ was calculated using the formula, $t_{1/2}=1/(k \times [H^+])$, 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)

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)

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)

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 228)

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

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

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 248, 274 and 326)

Dr. Jan-Hendrik Peters's comments:

1) In 2010, Ervens and Volkamer published an article, in which they summarize a large number of experimental data on the kinetics of glyoxal reactions in aqueous aerosol particles that were known at the time. To my surprise, this article has not been referenced in the current work. Can the determined theoretically rate constants in this study be compared to the values given in Ervens and Volkamer 2010? For example, Ji et al. report a *k* value of ~10^9 M^{-1} s^{-1} for dimer and trimer formation (l. 196), which

differs substantially from the values presented by Ervens and Volkamer (k_{dim} ~10^{-2} M^{-1} s^{-1} and k_{olig} ~100 M^{-1} s^{-1} in Table 2).

Response: We are sorry that the reference published in *Atmos. Chem. Phys.* by Ervens and Volkamer was not cited in the current manuscript because it presents the kinetic results about the direct oligomerization of glyoxal. According to the calculated results obtained by Kua et al. (J. Phys. Chem. A, 2008, 112, 66-72), the direct oligomerization of glyoxal, such as the reaction between glyoxal and glyoxal or glyoxal and glyoxal hydrates, proceeds a large activation barrier with more than 20 kcal mol^{-1} to form dimer. In addition, our recent theoretical and experimental studies (Li et al., 2021; Ji et al., 2020) also revealed that the protonation-initiated cationic oligomerization of small α-dicarbonyl compounds is more favorable in the atmosphere to form dimers and oligomers. Hence, in this study, we mainly focus on the mechanism of protonation-initiated cationic oligomerization of glyoxal and its role in the formation of secondary organic aerosol (SOA) and brown carbon (BrC). Our calculated rate constants from the protonation-initiated cationic oligomerization are ~10^9 M^{-1} s^{-1}, which represents the diffusion-limited rate constant as explanation in the original manuscript (please in lines 113-114): "The *k* values of the pathways without TSs are controlled by the diffusion-limit effect and thereby equal to the diffusion-limited rate constants". That is, according to the results obtained by our current study, the dimer and trimer formation is dominated by the barrierless processes, and the diffusion-limited rate constants are therefore taken as the rate constants for the barrierless processes. The above results are consistent with those of the recent study published in *Environ. Sci. Technol.* (Li et al., 2021). On the other hand, using the *k* value of ~10^9 M^{-1} s^{-1}, the predicted rate of glyoxal aqueous heterogeneous reaction agrees with the experimental result obtained by Liggio et al. (J. Geophys. Res., 2005, 110(D10): D10304). As for the reference published in *Atmos. Chem. Phys.*, the k_{dim} for dimer formation with ~10^{-2} M^{-1} s^{-1} and k_{olig} for oligomer formation with ~100 M^{-1} s^{-1} are from the direct nucleophilic addition between glyoxal and glyoxal or glyoxal and glyoxal hydrates (Ervens and Volkamer, 2010). Therefore, the rate constants for dimer and trimer formation are different because two studies depended on the different mechanism and therefore measured the rates constants of the different reactions. It may be the main reason for the difference of the results for our work with *Atmos. Chem. Phys.* by Ervens and Volkamer. According to the comment, the corresponding reference (Ervens and Volkamer, 2010) was cited and the following statements were added in the revised manuscript: "**It should be pointed out that the rate constants of dimer and trimer formation obtained from our theoretical calculations are distinct from those previously investigated by Ervens and Volkamer (Ervens and Volkamer, 2010). The rate constants in this previous study are obtained to be ~10^{-2} and ~100 M^{-1} s^{-1} for dimer and trimer formation based on the direct nucleophilic addition between GL and GL or GL and GL hydrates. Our protonation-initiated cationic oligomerization involves nucleophilic addition of diol/tetrol to carbenium ions, which is fast and barrierless. Hence, the formation of various ring-opening/cyclic dimers and trimers is initiated by protonation and subsequently propagated via the electrostatic attraction, with the rate constants of ~10^{9} M^{-1} s^{-1}, ultimately contributing to SOA formation.**" (Please see lines 204-210)

2) The ratios of different glyoxal species (e.g. monomers, dimers, trimers and higher oligomers) in aqueous glyoxal solution are highly dependent on the total glyoxal concentration in solution or within an aqueous aerosol particle (Whipple 1970, Kliegman 1972 and Chastrette 1983). For higher glyoxal concentration, comparable with a glyoxal-containing aerosol particle passing through dryer air layers, the chemical equilibrium shifts from monomeric towards oligomeric species. How could this affect the results presented by Ji et al.?

Response: The conversion of glyoxal and oligomeric species may connect with glyoxal concentration, but the mechanism is not affected by glyoxal concentration. First, in this study, we mainly focus on the mechanism of the aqueous-phase reaction of glyoxal in the absence and presence of ammonia and amines as well as its role in SOA and BrC formation. Hence, Peters stated that "for higher glyoxal concentration, comparable with a glyoxal-containing aerosol particle passing through dryer air layers, the chemical equilibrium shifts from monomeric towards oligomeric species" do not affect the aqueous-phase mechanism we proposed. Secondly, to assess the role of the aqueous-phase mechanism of glyoxal in the SOA and BrC formation, we calculated the growth rate according to the rate constant, the glyoxal concentration, and the uptake coefficients of glyoxal in three atmospheric conditions. Herein, the rate constant is obtained from the aqueous-phase mechanism by this work and not relative to the concentration. The glyoxal concentration and the uptake coefficient of glyoxal are from the references (Cerqueira et al., 2003; Lawson et al., 2015; Qian et al., 2019; Munger et al., 1995; Liggio et al., 2005). In three atmospheric conditions (urban, remote, and rural), the concentration of glyoxal is not more than 2.0 ppb even in urban condition, which corresponds to the largest glyoxal concentration in three studied conditions (Qian et al., 2019; Volkamer et al., 2005). On the other hand, the uptake coefficient is closely relative to the type and concentration of aqueous aerosol, relative humidity, acidity and ionic strength of the aerosol (Ervens and Volkamer, 2010; Corrigan et al., 2008; Liggio et al., 2005; Kroll et al., 2005; Gomez et al., 2015). Hence, we think that the comment stated that "The ratios of different glyoxal species (e.g. monomers, dimers, trimers and higher oligomers) in aqueous glyoxal solution are highly dependent on the total glyoxal concentration in solution or within an aqueous aerosol particle" can reflect in the uptake coefficients of glyoxal. It indicates that the questions stated in the comment have an influence on the concentration and the uptake coefficient of glyoxal, thereby affecting the estimation of the growth rate. In our study, our predicted growth rate agrees with the experimental result obtained by Liggio et al. (J. Geophys. Res., 2005, 110(D10): D10304). Because we were aware of the impact for the concentration and the uptake coefficient of glyoxal in the assessment of SOA and BrC formation, in this study, we specifically stated that the uptake coefficient of glyoxal used here is more suitable for urban condition (please see lines 289-290). However, it is worth noting that the questions stated in the comment do not affect our results about the mechanism of aqueous oligomerization of glyoxal. Finally, we are grateful to the comment of Peters because the comment will help us to better understand the aqueous oligomerization of glyoxal in the future study. We will consider and cover his/her suggestion in the future.

3) The authors observed diffusion-limitation effects for some of the reactions. In a

recent publication, highly viscous or even glassy phase states were observed for aerosolized samples of dried aqueous glyoxal solutions (Peters 2021). This may imply moderate to high viscosity of glyoxal-containing aerosol particles. In addition, reasonably long equilibration times (with a strong temperature dependence) were observed upon dilution of glyoxal solution. Can those experimental observations be connected to the mentioned diffusion-limited processes?

Response: Thanks for the community comment of Peters. Our results reveal that the protonation-initiated cationic oligomerization of glyoxal is fast and barrierless, and the *k* values are therefore limited by aqueous-phase diffusion effect. Previous studies have pointed out that the rate constant of bimolecular reaction is controlled by the diffusion-limit effect when it is up to 10^{10} M^{-1} s^{-1} in solution (Gao et al., 2014; Cramer and Truhlar, 1999). That is, the diffusion-limited effect is related with water (Turro et al., 2010). However, the diffusion-limit effect in the comment is mainly connected to the high particle viscosities, which may be affected by the concentration of glyoxal, relative humidity and temperature (Peters et al., 2021). Hence, two diffusion-limit effects are fundamentally different. It indicates that the diffusion-limit effect mentioned in our study cannot be connected to that resulted from high viscosity of glyoxal-containing aerosol particles.

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