

Atmos. Chem. Phys. Discuss., author comment AC4  
<https://doi.org/10.5194/acp-2022-139-AC4>, 2022  
 © Author(s) 2022. This work is distributed under  
 the Creative Commons Attribution 4.0 License.

## Reply on CC1

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-AC4>, 2022

---

**Dear Dr. Jan-Hendrik Peters,**

Thank you for the helpful and valuable community comment. Below is our point-by-point response to your 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  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for dimer and trimer formation (l.196), which differs substantially from the values presented by Ervens and Volkamer ( $k_{\text{dim}} \sim 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{\text{olig}} \sim 100 \text{ M}^{-1} \text{ s}^{-1}$  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<sup>-1</sup> 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  $\alpha$ -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  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , 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  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , 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  $\sim 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{olig}$  for oligomer formation with  $\sim 100 \text{ M}^{-1} \text{ s}^{-1}$  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  $\sim 10^{-2}$  and  $\sim 100 \text{ M}^{-1} \text{ s}^{-1}$  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  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , 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 focused 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). Under 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 revealed 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  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  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.

## References

- Cerqueira, M. A., Pio, C. A., Gomes, P. A., Matos, J. S., and Nunes, T. V.: Volatile organic compounds in rural atmospheres of central Portugal, *Sci. Total Environ.*, 313, 49-60, [https://doi.org/10.1016/s0048-9697\(03\)00250-x](https://doi.org/10.1016/s0048-9697(03)00250-x), 2003.
- Corrigan, A. L., Hanley, S. W., and Haan, D. O.: Uptake of glyoxal by organic and inorganic aerosol, *Environ. Sci. Technol.*, 42, 4428-4433, <https://doi.org/10.1021/es7032394>, 2008.
- Cramer, C. J. and Truhlar, D. G.: Implicit solvation models: equilibria, structure, spectra, and dynamics, *Chem. Rev.*, 99, 2161-2200, <https://doi.org/10.1021/cr960149m>, 1999.
- Ervens, B. and Volkamer, R.: Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles, *Atmos. Chem. Phys.*, 10, 8219-8244, <https://doi.org/10.5194/acp-10-8219-2010>, 2010.
- Gao, Y., Ji, Y., Li, G., and An, T.: Mechanism, kinetics and toxicity assessment of OH-initiated transformation of triclosan in aquatic environments, *Water Res.*, 49, 360-370, <https://doi.org/10.1016/j.watres.2013.10.027>, 2014.

Gomez, M. E., Lin, Y., Guo, S., and Zhang, R.: Heterogeneous chemistry of glyoxal on acidic solutions. An oligomerization pathway for secondary organic aerosol formation, *J. Phys. Chem. A*, 119, 4457-4463, <https://doi.org/10.1021/jp509916r>, 2015.

Ji, Y., Shi, Q., Li, Y., An, T., Zheng, J., Peng, J., Gao, Y., Chen, J., Li, G., Wang, Y., Zhang, F., Zhang, A. L., Zhao, J., Molina, M. J., and Zhang, R.: Carbenium ion-mediated oligomerization of methylglyoxal for secondary organic aerosol formation, *Proc. Natl. Acad. Sci. U. S. A.*, 117, 13294-13299, <https://doi.org/10.1073/pnas.1912235117>, 2020.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, 110, D23207, <https://doi.org/10.1029/2005jd006004>, 2005.

Kua, J., Hanley, S. W., and Haan, D. O. D.: Thermodynamics and kinetics of glyoxal dimer formation: A computational study, *J. Phys. Chem. A* 112, 66-72, <https://doi.org/10.1021/jp076573g>, 2008.

Lawson, S. J., Selleck, P. W., Galbally, I. E., Keywood, M. D., Harvey, M. J., Lerot, C., Helmig, D., and Ristovski, Z.: Seasonal in situ observations of glyoxal and methylglyoxal over the temperate oceans of the Southern Hemisphere, *Atmos. Chem. Phys.*, 15, 223-240, <https://doi.org/10.5194/acp-15-223-2015>, 2015.

Li, Y., Ji, Y., Zhao, J., Wang, Y., Shi, Q., Peng, J., Wang, Y., Wang, C., Zhang, F., Wang, Y., Seinfeld, J. H., and Zhang, R.: Unexpected oligomerization of small alpha-dicarbonyls for secondary organic aerosol and brown carbon formation, *Environ Sci Technol*, 55, 4430-4439, <https://doi.org/10.1021/acs.est.0c08066>, 2021.

Liggio, J., Li, S., and McLaren, R.: Reactive uptake of glyoxal by particulate matter, *J. Geophys. Res.*, 110, D10304, <https://doi.org/10.1029/2004jd005113>, 2005.

Munger, J. W., Jacob, D. J., Daube, B. C., Horowitz, L. W., Keene, W. C., and Heikes, B. G.: Formaldehyde, glyoxal, and methylglyoxal in air and cloudwater at a rural mountain site in central Virginia, *J. Geophys. Res. Atmos.*, 100, 9325-9333, <https://doi.org/10.1029/95jd00508>, 1995.

Peters, J. H., Dette, H. P., and Koop, T.: Glyoxal as a potential source of highly viscous aerosol particles, *ACS Earth Space Chem.*, 5, 3324-3337, <https://doi.org/10.1021/acsearthspacechem.1c00245>, 2021.

Qian, X., Shen, H., and Chen, Z.: Characterizing summer and winter carbonyl compounds in Beijing atmosphere, *Atmos. Environ.*, 214, 116845, <https://doi.org/10.1016/j.atmosenv.2019.116845>, 2019.

Turro, N. J., Ramamurthy, V., and Scaiano, J. C.: Modern molecular photochemistry of organic molecules, University Science Books: Sausalito, Calif., 2010.

Volkamer, R., Molina, L. T., Molina, M. J., Shirley, T., and Brune, W. H.: DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air, *Geophys. Res. Lett.*, 32, L08806-L08809, <https://doi.org/10.1029/2005gl022616>, 2005.