

Comment on acp-2022-139

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Community 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-CC1>, 2022

Ji et al. performed quantum chemical and subsequent kinetical calculations concerning hydration and oligomerization in the condensed phase of the atmospherically relevant dialdehyde glyoxal. While reading, the following questions arose:

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).

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.?

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?

References

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