

We thank the reviewers for careful reading and helpful comments that improve the quality of our manuscript. Reviewer comments have been copied followed by our responses in bold.

Anonymous Referee #3)

This paper describes a detailed model of the aqueous-phase oxidation of glyoxal and methylglyoxal. Main improvements over a previous glyoxal oxidation model have to do with simulating laboratory experiment conditions better, namely the attenuation of the photolysis beam by HOOH absorption. In addition, tetraperoxy compound decomposition rates were allowed to vary by an order of magnitude (staying within published limits) in order to better fit the data. However, in order to make the simulations match the data, two additional adjustments were made. First, glyoxylic acid photolysis rates and product ratios were adjusted away from published measurements. Second, the absorption of unknown product molecules was added in. There is reasonable justification for at least the latter adjustment. Most of these adjustments were only needed for the highest concentration runs, in any case. The model, once validated in this way, was used to calculate overall SOA yields for glyoxal and methylglyoxal oxidation in the aqueous phase. A variety of concentrations were used, in order to produce data relevant to both atmospheric clouds and aqueous aerosol particles. The model predicts mass-based aerosol yields near 100% for the aqueous phase oxidation of glyoxal and methylglyoxal, despite the potential for evaporation of some of the semivolatile products. However, the product gas/particle partitioning values used in the model come from atmospheric measurements, so all is believable. This paper represents an advance in our understanding of SOA formation in the aqueous phase, especially from methylglyoxal.

Specific Comments

R3C1) To avoid confusion the authors should restate the sentence in the abstract: “Oligomerization of unreacted aldehydes during droplet evaporation could enhance yields,” The statement is true inasmuch as these accretion reactions are another competing pathway to SOA formation, and could increase SOA mass; however, as they do not depend on OH oxidation, their SOA-forming contribution cannot be numerically added to the measured yields of this study in a meaningful way.

Response: Although OH radical reactions occur in the cloud droplet, we expect there still remain “unreacted aldehydes.” Their amount will be significant in the CSTR system. We now have added this to the abstract:

During droplet evaporation oligomerization of unreacted methylglyoxal/glyoxal that did not undergo aqueous photooxidation could enhance yields.

R3C2) p. 8 line 16: The paragraph should make clear that this is how aqueous SOA can form in the model. There are certainly other possible mechanisms in the atmosphere.

Response: Now it reads:

The following atmospheric processes are needed to model aqSOA: ...

R3C3) p. 8 last sentence: Can the authors give some examples of atmospheric conditions / precursors present when a given assumption might be appropriate? Readers will not know what to make of this statement otherwise.

Response: We add following examples to the paper:

For example, a batch approximation would be appropriate if the dominant methylglyoxal precursors were toluene. The gas-phase lifetime of toluene due to OH (when [OH] in the gas phase is $2 \times 10^6 \text{ molecule cm}^{-3}$; Finlayson-Pitts and Pitts, 2000) is ~ 1 day ($k = 5.63 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; Atkinson and Arey, 2003) and it produces $\sim 20\%$ methylglyoxal (Nishino et al., 2010). This methylglyoxal can dissolve in cloud/fog waters and react with OH radicals with the lifetime of 4.3 hrs (when [OH] in the aqueous phase is assumed to be $1 \times 10^{-13} \text{ M}$). A batch approximation is appropriate since in this case the gas-phase production of methylglyoxal is slower than the aqueous-phase OH oxidation of methylglyoxal. In contrast, a CSTR approximation would be more appropriate if the production of methylglyoxal were dominated by compounds like 1,3,5-trimethylbenzene (which produce $\sim 50\%$ methylglyoxal; Nishino et al., 2010). This is because the gas-phase lifetime of 1,3,5-trimethylbenzene due to OH radicals is 2.5 hrs. Thus, in this case the gas-phase production of the methylglyoxal precursor is now faster than its aqueous oxidation.

R3C4) p. 11 line 27: Could the authors list specifically which runs of the model allowed radical-radical reactions to occur, and which runs had them turned off? If the radical-radical reactions are turned off, what is the main sink for radicals in the model?

Response: Organic radicals react with O_2 and other radicals in all simulations. However, reactions with O_2 dominate at cloud conditions and organic radical-radical reactions dominate at wet aerosol conditions. Our kinetic model includes both reactions and the dissolved O_2 concentration is set to be maintained by Henry's law equilibrium with the gas-phase O_2 . Both organic radical- O_2 reactions and organic radical-radical reactions are always "turned on" in the model. We do not turn off organic radical-radical reactions for cloud conditions. At cloud conditions, organic precursor concentrations are low; therefore, organic radical concentrations are low. Consequently, organic radical- O_2 reactions are dominant because O_2 concentrations are much higher than organic radical concentrations. But as we increase organic precursor concentrations (toward aerosol relevant conditions), organic radical concentrations are high enough that organic radical-radical reactions are competing with organic radical- O_2 reactions. Our model simulation results are consistent with experimental results, which were performed with 30 – 3,000 μM of initial glyoxal or methylglyoxal.

To clarify, we add the following in the text (end of Section 3.1):

Note that organic radical-radical reactions for all organic species except acetic and pyruvic acid are always "turned on" in the model. At low concentrations, organic radical- O_2 reactions are dominant, whereas at high concentrations, organic radical-radical reactions are important.

R3C5) p. 15 line 22: The work of Barbara Noziere et al. on aldol condensation reactions forming brown carbon in aerosol particles could be appropriately cited here.

Response: We now add Noziere et al., Phys. Chem. Chem. Phys., 2010 as reference.

R3C6) p. 16 line 8: An explanation / justification is needed for the assumption that all dissolved, water-soluble organics in an aerosol particle will have the same ability to form oligomers as glyoxal. As mentioned on p. 11, the authors showed in a recent publication that acetic acid, for example, cannot form oligomers under these conditions.

Response: Water-soluble organic constituents in wet aerosols are poorly understood. We knows their total concentrations are as high as ~ 10 M based on field measurements of water soluble organic mass concentrations and the amount of liquid water. Glyoxal (or methylglyoxal) has been extensively studied as a water soluble organic compound that could contribute SOA formation via aqueous chemistry. Using glyoxal (or methylglyoxal) as a water soluble organic surrogate is reasonable way to start investigating aqueous chemistry leading to SOA formation. It is true that acetic acid does not form oligomers as glyoxal (or methylglyoxal) does. However, aldehydes and alcohols are prominent water soluble organic precursors (Blando and Turpin, 2001). They are reactive to OH radical reactions in the aqueous phase (lifetime is ~1e1 min) and undergo similar chemistry by forming oxalates at cloud conditions and oligomers via radical-radical reaction at wet aerosol conditions. Having said all this, we think it is reasonable to provide a caveat to recognize the complexity and uncertainty in aerosol chemistry.

To achieve this, we add the following in the Simulation Results Section:

It should be recognized that the chemistry in wet aerosols is complex and poorly understood. It is unlikely that all dissolved, water-soluble organics in an aerosol particle will have the same ability to form oligomers. However, glyoxal or methylglyoxal are reasonable surrogates for dissolved water-soluble organics because 1) aldehydes and alcohols are the major known water soluble organic precursors (Blando and Turpin, 2001); 2) they are remarkably reactive to OH radicals in the aqueous phase; 3) and they are expected to have similar oxidation mechanisms.

R3C7) Fig 1: Is an ROO + NO pathway relevant in the aqueous phase?

Response: No. Although ROO + NO is common pathway in the gas phase, in the aqueous phase little NO is available because NO is not water soluble ($H = \sim 2e-3 \text{ M/atm}$).

R3C8) Fig 8: For comparison, this figure should show a model result when using literature values for pyruvic acid photolysis. Since this is the most questionable adjustment made to the model, readers should be able to see how important its effect is in achieving decent fits to experimental data.

Response: In Fig. 8A, we have now added the simulation of oxalate when the literature value for pyruvic acid photolysis is used (i.e., $\text{Pyruvic Acid} + \text{UV} \rightarrow 0.45 \text{ Acetic Acid} + 0.55 \text{ CO}_2$; $k = 5e-4 \text{ s}^{-1}$) and the result when neglecting pyruvic acid photolysis entirely. Since there is little difference between the model results using an “adjusted” pyruvic acid photolysis expression and the results obtained without correction for pyruvic acid, we have removed the “adjusted” model results. In the plot, the legend for this is “This Work (w/ PYRAC + UV)” and “This Work (w/o PYRAC + UV),” respectively.

R3C9) p. 15 last line: The initial phrase of this sentence is confusing. Do the authors mean “For the batch reactor runs...”?

Response: It has now been corrected.

For the batch reactor runs, 10^{-7} – 10 M of glyoxal/methylglyoxal ...