

Interactive comment on “Glyoxal processing outside clouds: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles” by B. Ervens and R. Volkamer

Anonymous Referee #3

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The authors of this paper have taken on a difficult task. They are parameterizing the formation of SOA from glyoxal in water-containing particles for use in models making use of available knowledge about the kinds of processes that occur, without considering the detailed chemistry. It would be easy to criticize this type of exercise. However, this type of approach is probably needed to move the modeling forward at this time.

Having said that, the paper is thick enough that the reader can easily lose their place. The information provided in figures and tables need to be linked better to each other and to the text. The reader needs to be able to understand a figure (and not misunder-

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stand a figure) independently of the text. For example, does k_{eff} in eqn 10 explain uptake in the absence of aqueous reactions? Will the readers understand when/how to use this as written? Figure 3 is introduced first on line 439, but it is really hard to understand what is being shown in each section of the figure. For example, what is the difference between Fig 3a and Fig 3b? This type of information is either needed in the figure caption or the figure caption must tell you where to find it. Also, in Figure 6f, 6g the units seem to be wrong. Is there really 1000 $\mu\text{g}/\text{m}^3$ of SOA formed at night? Line 658 - where are the second set of simulations shown?

Other Specific Issues:

1. There has been considerably more study of acid catalyzed oligomerization than base catalyzed oligomerization. These should both be discussed. The discussion here covers NH_4 only. Agreed - in the absence of oxidation/photolysis reactions - these should be reversible. Considerable effort has been made to include formation of imidazoles, but organosulfates have not been mentioned. There is some evidence that they form more readily from acidic sulfate than from ammonium sulfate (Surratt, Perri 2010; Nozriere 2010).
2. Eqn 6 $K(\text{eff})$ has not been defined in the paper, only K^* What does it mean? What units does it have? Do the units in Eqn 6 work?? In fact, this is a concern for Eqn 10 too. All terms and units in all equations need to be provided. Why is SOA formation inversely proportional to LWC in Eqn 10?
3. Line 225 and Table 1. There seem to be 3 different entries for surface to volume ratio in Table 1. this I do not understand. The one with units of cm^2/cm^3 does not agree with the value in the text (line 225)
4. The authors seem to be representing the oligomers as being organic hydroperoxides and organic peroxides. Is there any evidence supporting this? Does this process create series of oligomers with mass difference similar to those observed by others (e.g. Tan 2010)?

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5. Many others would like to know what the concentrations of OH and HO₂ are in atmospheric aerosol water. To what degree can the modeled values be trusted? What assumptions go into their calculation? What percentage of the aqueous HO₂ is formed in the aqueous phase?
6. A lot of energy is expended trying to explain how results depend on the starting seed composition especially considering the modest number of experiments, but the differences between seeds do not seem to have a plausible explanation. Given this, what should we conclude? With the exception of AmmSulf/FA, Figure 4 does not show distinct differences between seeds - it mostly shows scatter. I doubt that the data from these different seeds are statistically different. (by the way, the red line does not seem to be fit to the data)
7. Line 689 says the contribution of OH reaction is <1%. I think most readers will interpret this to mean that the vast majority of SOA is formed either by direct photolysis of glyoxal or by dark reactions. But this contradicts what the authors have said elsewhere.
8. I agree that the chemistry in aerosol water is much more complicated than in clouds. However, the conclusion that cloud chemistry falls short in explaining SOA seems unsupported by Figure 4. In figure 4, some of the data fall above and others below the 1:1 line.
9. Near the end of the paper, there should probably be a separate section describing the strengths and limitations of the paper.
10. Undoubtedly in an effort of this type the chemistry will only be partially correct. To what extent does that matter?? Can the authors can provide some sense of the uncertainties that will result from use of this approach?

Details:

The text reads like 10-100% from line 76 is being compared to 30-90% from line 85. I don't think that was the authors' intent.

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Line 110 and 117 are redundant

typos line 147 (irts) and 148 (particles should be singular)

Line 351 provide reference for density = 2 (seems high)

Words "simulation A, B, C" should show up in the appropriate figure captions.

Line 582 - the caution about the constants in Table 6 provided on line 582 should also be a footnote in Table 6

Line 688 - not sure why figure 6a is mentioned here.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12371, 2010.

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