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Atmospheric Chemistry and Physics Discussions

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

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Reviewer # 3

We thank the reviewer for his/her useful comments that helped us to improve and clarify several parts of the manuscript. We respond to all the comments in detail below. (Note that we added to the reviewer comments the page and line numbers of the ACPD manuscript as his/her comments obviously referred to the manuscript version before typesetting).

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.

Reviewer comment 1. 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 misunderstand a figure) independently of the text.

Response: We took the reviewer's advice and carefully revised all figure and table captions in order to clarify them and to enable the reader to understand them independently from the text. In addition, we added several more references to tables and figures in the text.

Reviewer comment 2: For example, does k_effupt in eqn 10 explain uptake in the absence of aqueous reactions? Will the readers understand when/how to use this as written?

Response: k_effupt in Eq-10 is a lumped rate constant that represents the combination of uptake and subsequent aqueous phase reactions in the dark experiments. We rewrote Section 3.1 in order to clarify this and also included the definition of keffupt in the new list of parameters added at the end of the manuscript ('Appendix'). We clarify in Figure 1 and in the text (Section 3.1) that keffupt only describes glyoxal reactions in the dark but the detailed scheme will lead to more SOA formation as also photochemical processes are included.

Reviewer comment 3a. Figure 3 is introduced first on line 439 (p. 12390, l. 12), 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.

Response: We realized that the legend in Figure 3b had been wrong. We also changed the figure into a color figure and added headings 'radicals', 'stable oxidation products' and 'recombination products' on top of the figure to clarify the differences between the columns. In addition, we added three text boxes at the left hand side of the figure to highlight the differences of the initialization of the model in each panel. According to that, the figure caption has been clarified as well.

Reviewer comment 3b. Also, in Figure 6f, 6g the units seem to be wrong. Is there really 1000 ug/m3 of SOA formed at night?

Response: The reviewer is right; in the figures f and g, SOA masses are shown in ng m-3 as opposed to the rest of the figure where microg m-3 is used. We clarify this in the caption. In addition, we point out both in the figure caption and in the text that the assumptions made for these model simulations (pH = 7, and instantaneous hydration equilibrium, respectively) might lead to unrealistic results.

Reviewer comment 4. Line 658 (p. 12399, l. 3-5) - where are the second set of simulations shown?

Response: The results of the second set of simulations are discussed in Section 4.2.3. We added the reference to this section in the text.

Other Specific Issues: Reviewer comment 5. There has been considerably more study of acid catalyzed oligomerization than base catalyzed oligomerization. These should both be discussed. The discussion here covers NH4 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 et al., 2007, Perri et al. 2010; Noziere et al. 2010).

Response: We there is a considerable body of literature discussing the formation of organosulfates and other chemical reactions in acidic atmospheric aerosol particles.

However, as the studies by Surratt et al. have shown organosulfates from glyoxal are only formed at the highest aerosol acidity at their experiments (pH ∼ 0). Organosulfates from larger organic molecules are also formed at more moderate pH. The laboratory studies we focus on were performed on particles with more moderate pH (2 < pH < 7) and thus – under those conditions - no organosulfates of glyoxal were identified in dark experiments (cf Noziere et al., 2009; Galloway et al., 2009). In the latter study, however, the formation of glycolic acid sulfate has been observed upon oxidation of glyoxal in ammonium sulfate particles. The efficiency of the reactions of the sulfate radical leading to organosulfates, has been suggested by Noziere et al., 2010 and Perri et al., 2010. However, the competitive reactions suggested by Perri et al.

R(radical) + SO4- -> OrgSulf k = 1e8 M-1 s-1

R(radical) + O2 -> RO2 k ∼ 1e9 M-1 s-1

would require SO4- concentration of ∼1e-5 M in order to compete with the peroxy radical formation. Considering that in cloud water similar concentration levels for OH and SO4- are predicted (∼1e-11 M, Ervens et al., JGR, 2003), it is unclear why the suggested pathway should significantly contribute to organosulfate formation in aerosol water (activity may affect the rate constants somewhat (by a factor <5), or the oxygen concentration in aerosol water is much lower than 10-4 M). We agree with the reviewer that a brief discussion of organosulfates from glyoxal is needed in our manuscript since much discussion of this compound group has come up recently in the literature. We note that we had included some mentioning in Fig 1 of the original manuscript. We now also added further text in the introduction and conclusions sections.

Reviewer comment 6a. Eqn 6 K(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.

Response: We added the definition of KH(eff) right after equation 6. In addition, we provided the units for all equations in the text following the equations and added a list of all reaction parameters at the end of the manuscript ('Appendix').

Reviewer comment 6b. Why is SOA formation inversely proportional to LWC in Eqn 10?

Response: The equation had been wrongly written (though correctly applied). We have corrected the equation in the manuscript that reflects now based on the laboratory studies that no dependence on the LWC can be seen and we suggest in the text the possible catalytic role of ammonium sulfate in the observed glyoxal uptake experiments. – We cautioned its general application to other seeds as we cannot evaluate these catalytic processes any further.

Reviewer comment 7. Line 225 and Table 1. (Section 2.5) 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 cm2/cm3 does not agree with the value in the text (line 225 – p. 12381, l. 14)

Response: In Table 1, there are two entries that describe the surface-to-volume ratio of cloud droplets and particles. The first one describes the ratio of the surface to volume of one single cloud droplet or particle, respectively, i.e. it is a function of the particle (droplet) diameter D

pi x Dˆ2 / (Dˆ3 x pi /6).

The second entry 'Surface/Volume' [cm-1 cm-3] includes the number of particles N [cm-3], i.e. it is calculated as

pi x Dˆ2 / (Dˆ3 x pi/6) x N

and thus represents the surface-to-volume ratio of the total aerosol (droplet) size distribution. The entry 'Surface' represents the total surface of the aerosol size distribution

pi x Dˆ2 x N

without including the volume of the particles. In order to clarify this, we have added these equations to the Table. In the text, we compare the two surface-to-volume ratios

of cloud droplets and particles and thus present the (dimensionless) ratio of ∼10ˆ5 – 10ˆ6 and ∼10ˆ11 – 10ˆ13 which is about ∼10ˆ5 – 10ˆ8. We changed the upper limit in the text to reflect the full range of possible ratios.

Reviewer comment 8. 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)?

Response: The reviewer misunderstood the purpose of Figure 3. We do not mean to say that oligomers are hydroperoxides and organic peroxides. Rather, Figure 3 demonstrates that organic RO2 radicals undergo essentially different reaction pathways in concentrated aerosol water, than in cloud water. Radical-radical self reactions become important in aerosol water. There is essentially nothing known about these pathways in concentrated aerosol water, and as such we considered this fact worth highlighting.

Notably, Figure 3h and i show that neither the oxidation products R, R', R" nor the recombination products ROOR and ROOH can fully explain the observed SOA volumes. On the right hand axes in these figures, we displayed the corresponding SOA volumes that only add up to at most ∼ 0.1 micromˆ3 cm-3 after 5 min. However, the observations suggest that within this time scale between 5 – 20 micromˆ3 cm-3 SOA have been formed (cf Figure 4). Thus, our conclusions are that the formed SOA is not mainly composed of oxidation products as predicted by the reaction scheme in Table 4 (i.e. R, R', R", ROOR, ROOH) but other – more efficient - pathways have to occur that are not captured by this reaction scheme but are lumped into the empirical rate constant kphotochem. We added these conclusions more clearly to the text (Section 3.3.1) where Figure 3h and i are described.

Reviewer comment 9. 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?

Response: The assumptions that underlie estimates of OH and HO2 have been listed in Section 3.3.1 of the manuscript where the model conditions are described that lead to the results in Figure 3. We do not initialize HO2 in the gas phase but set an initial OH gas phase concentration and thus all HO2 forms in the aerosol water, and all OH is taken up from the gas phase. The predicted OH and HO2 concentrations in both dilute (cloud droplets) and concentrated (particles) aqueous phase are shown in Figure 3a, d, and g. Even though we only use a very limited chemical mechanism (i.e. only chemical processes in the aqueous phase and prescribed gas phase glyoxal and OH concentrations), the predicted concentrations of OH and HO2 agree well with those in a previous model study with full gas and aqueous phase chemistry ('CAPRAM', Ervens et al., JGR, 2003). This comparison seems sufficient to justify the limited reaction mechanism for the purposes of our study where all HO2 is formed in the aqueous phase. To our knowledge – no direct measurements of OH and HO2 in cloud water (and even less so, in aqueous particles) are available. However, multiphase mechanisms have been applied to explain observations of several (organic and inorganic) compounds in cloud water which would have probably not been as successful if the OH and the linked HO2 concentrations were systematically wrong. We feel that an extensive discussion of such multiphase models will exceed the scope of our paper. In aerosol water, the OH levels might be significantly different than in clouds as shown in Figure 3; however, since the peroxy radical chemistry in concentrated solutions is very uncertain (as pointed out in our discussion of Figure 3), we can only speculate about the realistic OH and HO2 levels in aerosol water.

Reviewer comment 10a. 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.

Response: The only reason why we used linear correlations for the two data sets of AmmSulf and AmmSulf/FA is their higher number of experiments compared to the other seeds. It seems that linear fit for all data except AmmSulf/FA might also lead to a reasonable correlation. However, as this point, there is too few data in order to reasonable quantify the composition effect of the seed on SOA yields, we rather prefer to only show separate correlations for each seed. If more laboratory data become available, these trends will be revisited in order to identify more robust trends. Based on the sparse data set, we cannot systematically evaluate the composition effect for seeds other than ammonium sulfate and ammonium sulfate/fulvic acid on SOA formation as pointed out in Section 3.3.1 (Simulation B). We state the need for more laboratory studies to establish clearer correlations with composition in the new section 5 ('Applicability and uncertainties of the developed model framework').

Reviewer comment 10b. (by the way, the red line does not seem to be fit to the data) We noticed this error already in the typesetting stage of the manuscript and have corrected it for the version that is published in ACPD.

Reviewer comment 11. Line 689 (p. 12400, l. 9/10) 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.

Response: We clarified this paragraph. Indeed, our model studies suggest that the aqueous phase reaction of OH + glyoxal only contributes to < 1% to the total predicted SOA mass if all other processes (kNH4+, kphotochem,kamine, kaminoacid) are included. Nearly 100% of all SOA shown in Fig 6 a – e is formed by the photochemical process(es) kphotochem. We point out here – and also make clearer in the text (Section 3.3.1 'Simulation B') – that this process is not the direct photolysis of glyoxal but kphotochem represents an empirical rate constant for (an) additional photochemical process(es) that is/are not captured by the simple reaction of OH + glyoxal based on rate parameters that are determined in dilute aqueous conditions, but lead to the excess SOA under photochemical conditions as depicted in Figure 4. At this point we can only speculate that these lumped processes include additional radical formation and oxidation processes that lead to accelerated SOA formation rates in particles.

Reviewer comment 12. 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.

Response: There seems to be a misunderstanding in the interpretation of Figure 4. The lines represent linear fits to the data and are not the 1:1 lines. The x-axis shows a range up to 0.0012 microm^3 cm-3 whereas the y-axis shows data on a range up to 25 microm^3 cm-3. A diagonal in this plot would represent a slope (and thus ‘underestimate due to cloud chemistry’) of ~2000. We changed the scaling on the x-axis to clarify this and refer in the figure caption to Table 5 where the slopes and correlation parameters are summarized.

Reviewer comment 13. Near the end of the paper, there should probably be a separate section describing the strengths and limitations of the paper. 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?

Response: We added a new section 5 to the manuscript where we discuss the advantages and disadvantages, together with the uncertainties, associated with our simplified model approach. Issues in this section include the discussion of - the assumption of ideal solutions in particles, - uncertainties with the resulting SOA mass (molecular weight, density etc) - uncertainties in the applicability to ambient aerosols since the ‘composition effect’ cannot be quantified based on the current study - processes that are likely missing or not fully captured due to our empirical approach (e.g., k(photochem)) The advantage of our framework is that it provides (i) the first comprehensive review of all glyoxal studies on particles that highlights common features in a numerical way (i.e. by deriving rate constants), (ii) guidance for future laboratory studies, e.g. to explore in a systematic way compositions (pH) effects as this parameter has shown to be important, and (iii) the classification of glyoxal reactions into different categories (dark/light, reversible/irreversible, surface/bulk etc) that can be used not only for glyoxal but also to classify and compare reactions of similar compounds.

Details: Reviewer comment 14. The text reads like 10-100% from line 76 (p. 12375, l. 2) is being compared to 30-90% from line 85 (p. 12375, l. 11). I don’t think that was the authors’ intent.

Response: Indeed the cited studies suggest that the fraction (amount of the species in the aqueous phase / total amount of species (gas + aqueous phase)) of glyoxal, glycolaldehyde and methylglyoxal in cloud droplets is about 10-100% whereas in aqueous particles this fraction is ~30-90%. While this is not intuitive due to the drastically different liquid water contents, it suggests that in particles these species are present as oligomers and thus shift the partitioning equilibrium towards the particle phase. Routine analytical methods cannot distinguish between oligomers and monomers which leads to this apparent enhanced partitioning (exceeding thermodynamic equilibrium) in particles. We added a few sentences to the text to make this clearer.

Reviewer comment 15. Line 110 (p. 12376, l. 1) and 117 (p. 12376, l. 17) are redundant

Response: These lines are not redundant as they refer to the SOA predictions for clouds and particles, respectively. They summarize the findings by Fu et al. (2008) and Stavrakou et al. (2009) who included SOA formation in both cloud droplets and aqueous particles in their model simulations and provided ranges of predicted SOA from glyoxal for both aqueous phases. We added to the text ‘in clouds’ and ‘in particles’ to make these differences more obvious.

Reviewer comment 16. typos line 147 (p. 12378, l. 21) (irts) and 148 (l. 21) (particles should be singular)

Response: Both typos have been corrected.

Reviewer comment 17. Line 351 (p. 12386, l. 24) provide reference for density = 2 (seems high)

Response: We use a density of 2 g cm-3 in order to be consistent with the data in the study by Volkamer et al., 2009 who derived this number based on calculations of contributions of glyoxal and water in a glyoxal solution. We agree that this number is probably an upper limit as in the meantime the density of the glyoxal trimer has been determined to be in the range of 1.67 – 1.71 g cm-3 (DeHaan et al., 2009). However, since oligomers like the trimer that form under dark conditions make up a very minor fraction of the glyoxal related SOA mass, it is not clear to what degree the density of the trimer would be a better proxy for glyoxal SOA density than the rounded number of 2. We discuss in the new section 5 ‘Applicability and uncertainties of the developed model framework’ this uncertainty and point out that with lower densities our obtained kphotochem might be lower, and that the density of glyoxal SOA is currently not known. Future studies will show whether the density of glyoxal-SOA may in fact depend on the experimental conditions used to produce glyoxal SOA in the first place.

Reviewer comment 18. Words "simulation A, B, C" should show up in the appropriate figure captions.

Response: We added ‘Simulation A’ to the caption of Figure 4 and ‘Simulation B’ and ‘Simulation C’ to the results in Table 6.

Reviewer comment 19. Line 582 (p. 12395, l. 28) - the caution about the constants in Table 6 provided on line 582 should also be a footnote in Table 6

Response: We extended the table header to Table 6 and point out that kphotochem have been derived for high OH/hïĄő and are likely to be smaller at lower concentrations.

Reviewer comment 20. Line 688 (p. 12400, l. 8) - not sure why figure 6a is mentioned here.

Response: We removed the reference to Figure 6a.

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