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Atmospheric
Chemistry
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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 # 2

We thank the reviewer for his/her comments on our paper. We agree that our model approach by 'extending a cloud model' is a very simplified way to express chemistry in particles. However, we think that this simplicity also bears advantages as it represents an empirical way to describe glyoxal sinks and SOA formation in particles that can be used to reproduce observed SOA formation rates in laboratory experiments.

We highlight the empirical character of our approach stronger throughout the revised manuscript and in our responses below.

General comment This manuscript presents the development of a model for the formation of SOA from glyoxal taking into account the reactivity of this compound in aerosol particles. The justification for this model is very good: there is, indeed, an important gap in current SOA models, which do not take into account the reactivity of organic compounds inside the aerosol particles, and thus a need for such model. The work presented is also quite substantial, as glyoxal is expected to be involved in a large number of reactions in the condensed phase. Considering the large compiling effort involved, the work presented is of good quality. However, some important aspects of the chemistry in concentrated aerosol particles are either not included in the model or not sufficiently discussed in the paper. There are also a few misunderstandings of some recent studies and literature data. My main concern is that this model seems to be based on a cloud chemistry model, thus intended to diluted aqueous media, while the chemistry in concentrated atmospheric particles is fundamentally different (electrostatic interactions with solvent ions, use of activities instead of concentrations, role of Ion Strength on the rate constants: : :). It is thus questionable that a cloud model, even extended with more reactions, gives realistic results for aerosol particles. These aspects are critical for the relevance of the results and of the model itself and need to be carefully addressed before this paper can be published.

Detailed comments Reviewer comment 1. I am uncomfortable with the fact that this model is apparently based on a cloud chemistry model, representing diluted aqueous media, only extended by adding more reactions. Chemistry in concentrated atmospheric particles (ammonium sulfate or other salts) is fundamentally different from diluted media and it is questionable that a cloud chemistry model would give realistic results for aerosol particles. First, electrostatic interactions between the solutes and the solvent ions play important roles in concentrated ionic media, and need to be taken into account as they are in inorganic models, such as the AIM models or Isorropia, which now include organic compounds. Other important aspects of the chemistry in concentrated media are the need to use activities instead of concentrations for the main ions in the calculations, and the potential effect of Ion Strength on the rate constants. Neither of these aspects seems to be addressed in the paper. These effects, which are specific to concentrated ionic media, are likely to play a central role in the enhancement of the SOA yields observed in smog chamber (at least in the dark) and are thus important to include in this model. Radical chemistry in concentrated ionic media is also likely to be very different than in diluted aqueous media: rate constants, products, even the formation of the radicals would be different. It is therefore unclear that the rate constants for the radical reactions used in the model, all obtained from experiments in diluted aqueous media, apply to the chemistry of concentrated particles.

Response: We partially agree with the reviewer. Indeed the occurrence of other – more complex – reactions in the concentrated aqueous phase of particles as compared to the dilute aqueous phase is a central argument supported by our work. It is not the ambition of this paper however to unambiguously establish the reasons for why this is, rather to put empirical bounds to it, and establish the relevance of concentrated aerosol water chemistry. First, we liked to emphasize that dark reactions account only for a very minor fraction of the overall SOA amounts. Also, the fact that rate constants for radical reactions were obtained from experiments in dilute aqueous media is only partially relevant, as this poses an uncertainty only in our “reference case” (cloud chemistry scaled by LWC), and does not affect our parameterization of experiments that studied SOA formation on real aerosols. The reasons listed by the reviewer might help explain the observed discrepancy, but do not necessarily challenge our parameterization. Second, a full thermodynamic model might be able to explain and simulate all individual reaction parameters. However, to our knowledge there is no thermodynamic model that includes aldehydes (such as glyoxal), radicals (such as OH) and organic oxidation products (oligomers etc) that could be used to simulate SOA formation in aqueous particles. Third, even if all these variables were available in thermodynamic models, it does not seem feasible to apply such a model to larger scale SOA models which is ultimately the goal of our exploratory and preliminary model framework. A more empirical model is preferred due to its smaller computational burden. We recognize the issues raised by the reviewer are important, and emphasize now throughout the manuscript the purpose of our work; we have also added a new section (Section 5 ‘Applicability and uncertainties of the model framework’) where we highlight the advantages of our approach (classification of glyoxal reactions; representation of rate constants in unified manner; identification of key parameters), discuss the applicability of the model approach to ambient conditions and future laboratory results, but also list its numerous uncertainties.

Reviewer comment 2. In general, the rate and equilibrium constants used in this model are somewhat incomplete, especially concerning the ionic chemistry and the partitioning and oligomerization of glyoxal. There is, of course, nothing that the authors can do about it, more laboratory investigations are just needed to complete these data for different solutions compositions, concentrations, pH. But this has to be kept in mind when using this model to estimate SOA yields in the atmosphere. For instance, the oligomerization rate and equilibrium constants in ammonium sulfate used in the model, which are responsible for the strong enhancement of the SOA yields in the dark, are estimated from smog chamber results. These results might not apply to all types of aerosols in the atmosphere and could lead to important errors when estimating SOA yields in the atmosphere.

Response: We agree with the reviewer that our study only represents a limited model of glyoxal reactions and equilibria in aqueous particles. However, we feel that this framework will prove useful as it (i) is 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) will guide future laboratory studies, e.g. the systematic investigation of composition (pH) effects as this parameter has shown to be important, and (iii) suggests different reactions 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. We added a section to the manuscript (new Section 5) (following a suggestion by Reviewer #3) where we summarize these points. As for the applicability in the atmosphere, similar points could be raised also for other simulation chamber experiments that probe SOA formation from partitioning of semivolatile vapors. The difficulty to extrapolate simulation chamber data to the atmosphere prevails after more than a decade of experimental research on semivolatile partitioning, and can hardly be regarded a particular complication with parameterizing SOA from glyoxal.

Reviewer comment 3. There seems to be some misunderstanding of some of the recent studies of the glyoxal reactivity. For instance, the reaction of glyoxal with NH4+ reported by Noziere et al., (2009) is one step of the oligomerisations responsible for the enhanced SOA yields obtained in smog chamber by Kroll et al., (2005). This was established by the product analysis in that paper, reporting mostly oligomers. The discussion of this chemistry should thus not be treated separately but included in section 3.2.3. The overall oligomerisation rate for glyoxal in ammonium sulfate is nontheless better estimated from smog chamber experiments, where SOA yields were monitored directly, than from the bulk study, where only one specific reaction step was monitored (hence the very different rates). This does not change the results of the model but is conceptually important since the Noziere paper establish that NH4+ is directly involved in the oligomerisation of glyoxal. And this chemistry is obviously not negligible since it is responsible for the enhancement of the SOA yields by several orders of magnitude. Concerning the formation of imidazoles, it is well established in the literature that these products represent a small yield of the reaction of glyoxal with NH3 or NH4+ compared to the oligomerisation (see for instance Wikipedia/ imidazole). Since there are already many unknowns in the model, it is important that the relative importance of different reactions assumed in the model does not, at least, contradict the literature.

Response: The reviewer is right that our presentation of the results by Noziere et al was not fully clear in the manuscript. We have clarified in the text that in NH4+ solution, glyoxal mainly forms the same oligomers as we have discussed in Section 3.2.3. In

addition, we changed the text in Section 3.3.2 (‘Glyoxal reaction with the ammonium ion’) and repeated ammonium’s catalytic role in oligomer formation there and point out that C-N compounds are only a minor fraction of the identified products.

Reviewer comment 4. Concerning the reactions with amino acids: the concentrations of amino acids reported in aerosol are extremely small (nM to mM). It seems thus that reactions including these compounds should be extremely slow and negligible, and probably not indispensable in the model. But I guess the results of the model would confirm this anyway.

Response: As shown in Figure 7, the contributions of the amino acid reactions usually do not exceed 0.01% of the total predicted SOA mass under dark conditions (Note that under photochemical conditions, these relative contributions will be even smaller). We have added the absolute predicted SOA masses to the legend in Figure 7 which highlights that a contribution of the amino acid reaction of a few % only translates into SOA mass formation rates on the order of < 5 ng m-3/ 12 hours.

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