

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 #2

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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

C4235

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

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.

C4236

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.

2. In general, the rate and equilibrium constants used in this model are somewhat incomplete, especially concerning the ionic chemistry and the partitioning and oligomerisation 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 oligomerisation 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.

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 nonetheless 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

C4237

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.

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.

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C4238