

Interactive comment on “Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 2: Product identification using Aerosol-CIMS” by N. Sareen et al.

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We thank Referee 3 for his or her review of the manuscript. We address the referee's specific comments below.

Detailed comments:

1 - Typical concentration of methylglyoxal in aerosols. *It could be interesting to have some estimates of the concentration of methylglyoxal in aerosols to justify the relevance of the conditions studied in this work. Are there any values in the literature or is it possible to make some estimates?*

Kawamura and coworkers have measured methylglyoxal monomer and related compounds (glyoxal, ketocarboxylic acids, and dicarboxylic acids) in ambient aerosols (Sempere and Kawamura, 1994; Kawamura et al., 1996; Kawamura and Yasui, 2005; Ho et al., 2007; Kundu et al., 2009). Methylglyoxal was found to comprise roughly 0.005–0.05% of aerosol mass in urban environments (Kawamura and Yasui, 2005; Ho et al., 2007). However, since methylglyoxal is highly reactive, this value underestimates the total methylglyoxal taken up by the particles. Assuming that all pyruvic acid, glyoxylic acid, and oxalic acid in the aerosol was formed via methylglyoxal oxidation (Carlton et al., 2006) provides a rough upper bound for methylglyoxal uptake of 2% of aerosol mass (Kawamura and Yasui, 2005; Ho et al., 2007). Assuming a particle density of 1 g cm^{-3} this corresponds to an in-particle initial methylglyoxal concentration range of 0.7 mM to 0.28 M.

2 - pH of the solutions. *As also noted by other reviewers, a pH of 2 for non-buffered solutions of ammonium sulfate or sodium chloride is very surprising, even with 25% wt of methylglyoxal. My guess is that the solutions were right but the measurement technique was flawed: pH paper? pH paper is notorious for not aging well, and is probably not even accepted as a measurement technique in scientific publications anymore. Please, use a digital pH-meter, which, at least, can be calibrated and gives a precision of 0.5 (or 0.1) units on the measurement, necessary here. A pH between 4 (for ammonium sulfate) and 7 (for NaCl) should be more likely for these solutions.*

More accurate digital pH measurements were used to confirm the pH values previously measured using pH paper. The pH value of 2 for these solutions is attributed to trace amounts of pyruvic acid in the methylglyoxal stock solution. Pyruvic acid is a relatively strong organic acid, with $\text{pK}_a = 2.49$. Therefore, the fact that our stock solution is $\text{pH} = 2$ corresponds to a very small (0.07%) impurity of pyruvic acid in the methylglyoxal stock solution.

3 - Validation of the product analyses with the instrument. *My understanding is that this aerosol CIMS instrument is presented here for the first time and, therefore,*

that the main objective of this paper is to demonstrate its applicability to the identification of organic compounds in aerosol particles. Such a validation can only be made by comparing the ions obtained with known initial products or by studying known reactions. Among other things, it has to be shown that known organic compounds produce mostly one ion (and potentially clusters), as fragmentation should be minimal with CIMS, and that no spurious products are created by the hot inlet, or by recombination of the ions in the CDC or in the chamber. This is essential because the discussion of the products reported in this paper (Tables 1 and 3) and of their potential importance for the chemistry can not be made before these products are shown to be real. For this, it would be indispensable to study the ions obtained with standard compounds. The paper mentions that succinic acid was used for calibration, but more compounds, similar to the reaction products expected here, also need to be tested. These tests should also include salt/organic mixtures such as those studied here. Alternatively, known reactions (i.e. for which the products have been characterized by other techniques previously) could also be studied before to study the reaction of methylglyoxal.

Aerosol-CIMS was first introduced by Hearn and Smith (Hearn and Smith, 2004a). CIMS, the analytical technique for detecting gas-phase species that Aerosol-CIMS is based on, is very well-established and its application to atmospheric measurements has a long history (Huey et al., 1995; Huey, 2007). The Aerosol-CIMS system used here is similar to the University of Washington instrument used in McNeill et al. (2006, 2007, 2008) and the University of Georgia instrument of Hearn and Smith. The application of the Aerosol-CIMS technique to the study of organic aerosols of known and unknown composition has been validated extensively (Hearn and Smith, 2004a,b, 2005, 2006a,b, 2007; Hearn et al., 2005, 2007; Renbaum and Smith, 2009a,b; McNeill et al., 2007, 2008). That is to say, the reviewer's suggestion that "*Alternatively, known reactions (i.e. for which the products have been characterized by other techniques previously) could also be studied. . .*" has already been performed by us and others previously.

The gas-phase ion chemistry of organic species with I^- and H_3O^+ is well-known (Slusher et al., 2004; McNeill et al., 2007, 2008; Blake et al., 2009) and we supplemented the literature here with DFT calculations demonstrating the favorability of clustering reactions for detecting the proposed compounds with I^- . Succinic acid was chosen as a representative compound for calibration due to its structural similarity to the anticipated product compounds. The use of Aerosol-CIMS to study organics in mixed inorganic/organic aerosols has been previously established by McNeill et al. (2007, 2008).

4- Characterization of the chemistry. *If the intention of this paper is to provide fundamental information on the products of methylglyoxal in salt solutions, then the work to be done is much more demanding because these products have to be characterized by techniques that are recognized as unambiguous in chemical sciences, ideally NMR or at least GC or LC/MS, where compounds are characterized by retention times. At the minimum, the expected reaction products should be compared with standard compounds – especially those of particular interest, such as the nitrogen-containing intermediates or organosulfates. As pointed out by the other reviewers, the ions identified here are interesting but still leave out different possibilities as for the initial compounds.*

The discussion of this chemical system is especially difficult as reactions between organics and NH_4^+ in aerosols (catalytic or not) have only be discussed very recently, and little fundamental information is available on them. As pointed out in some comments, it therefore important to discuss (and, of course, quote) previous literature supporting the existence of the condensation and catalytic pathways by information that can not be obtained in this work (NMR identification of products, reaction rates showing the relevance under atmospheric conditions. . .).

We see the reviewer's point. Note that, upon the suggestion of the reviewers and the Editor, we have combined the two manuscripts into one, so the Aerosol-CIMS study now has a supporting role rather than being a stand-alone manuscript. More discussion of the products, mechanism, and previous literature is included in the com-

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bined manuscript. More detailed product characterization as suggested by the reviewer would be interesting for future work.

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