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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #3

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General comment:

This paper presents a characterization of reaction products of methylglyoxal in ammonium sulfate and sodium chloride mixtures, using a newly built aerosol CIMS. This is generally an interesting paper, especially as an illustration of the performances of the aerosol CIMS, which could be a valuable instrument for analyzing atmospheric aerosols. However, the authors have chosen to study a chemical system that is not well known and, as a result, both the identification of the ions obtained with the instrument and the characterization of the reaction are incomplete and require additional work before publication. It might not be indispensable to achieve both to make the pa-

per publishable, but at least one of these aspects need to be completed by performing the additional experiments detailed below- and the authors can chose between different options.

I am not convinced either that the content of this manuscript and of the companion paper (Schwier et al.) justify two separate papers, but this is a question that I am addressing to the editor of this manuscript.

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 ?

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.

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 or-

ganic 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.

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 NH4+ 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 show-

ing the relevance under atmospheric conditions. . .).

However, I am not sure that the main application of this new instrument should be the fundamental investigation of chemical reactions, as many other techniques (NMR, GC and LC/MS. . .) are much more adequate for this and do not require to aerosolize the solutions. Again, my understanding is that the main interest of this aerosol CIMS is future application to atmospheric aerosols, in which case the authors should probably focus on validating its performances, as discussed above.

In summary, if this paper presents this instrument for the first time, then a more complete validation of the analyses is necessary, including, at least the characterization of ions obtained with standard compounds and the demonstration that no artificial products or ions are formed in any part of the system. If the objective of the paper is to present fundamental new information on the reaction studied, the products need to be characterized by unambiguous techniques such as NMR and GC or LC/MS. And even more work would be necessary to obtain quantitative information on the importance of the different reaction pathways in atmospheric aerosols, such as yields or reaction rates.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 15567, 2009.