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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 #2

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This manuscript describes the identification of products from the reaction of methylglyoxal and ammonium sulfate using chemical ionisation mass spectrometry. The authors conclude that nitrogen- and sulfur-containing species are created demonstrating that ammonium sulfate is not just acting as a catalyst but is involved in the chemical reactions. They also observed high-molecular weight products suggestive of oligomers. This reaction system is of considerable interest to the community because of the prevalence of methylglyoxal and its potential for forming secondary organic aerosol (SOA).

However, the conclusions that the authors have drawn from the present work are tentative, and potential implications for the formation/growth of SOA in the atmosphere

are not extended from the laboratory studies. Specifically lacking is the discussion or proposal of any chemical reactions that would lead to the novel nitrogen- and sulfur-containing products. Furthermore, this paper is intended to be a companion to the authors' other manuscript under review in ACPD ("Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 1: Surface tension depression and light-absorbing products," A. N. Schwier, E. L. Shapiro, N. Sareen, and V. F. McNeill, Atmos. Chem. Phys. Discuss., 9, 15541-15565, 2009), but the two papers should be considered as a whole in one complete paper. In my opinion, each of these manuscripts is incomplete on its own, and this is a classic example of splitting a body of work unnecessarily. I recommend that the two manuscripts be combined and reconsidered for publication after the reviewers' comments have been addressed, and this is the primary reason that I suggest rejecting the current manuscript.

Specific comments:

1) The DFT calculations of the stability of I- clusters with several of the products are interesting, but they do not aid in the identification of the products. The authors' conclusions and identifications would hold just as well without these calculations. Also, did the authors consider the I- + X → I-.X reaction for cluster formation in addition to the ligand switching channel?

2) In the I- spectrum, the peaks at 225.2 amu and 227.2 amu are identified with a product of molecular formula C6H11O7S+, but a corresponding peak in the H3O+(H2O)n spectrum is not found. This product is shown in Table 1 as containing two carbonyl and one alcohol functional groups which should make it possible to ionize using proton-transfer from the H3O+(H2O)n ions. The fact that these peaks are missing in the positive spectrum calls into question the validity of assigning the 225.2 amu peak in the negative spectrum to the structure proposed in Table 1.

3) Given the difficulty in assigning peaks in the chemical ionisation mass spectrum with specific products, it seems as if using a complementary method would shed more

light on the identity of the products. For example, have the authors considered using electrospray ionisation with a higher-resolution mass spectrometer, perhaps FTMS?

4) In Table 1, the molecular formulae are given for the ions detected, but the possible structures correspond to the neutral products (not the ions). This should be corrected.

5) How relevant are pH 2.0 conditions to atmospheric aerosol? Under such acidic conditions, how would nitrogen-containing products be formed? Presumably it would have to involve the reaction of NH4+ ions. Is there any precedence for such a reaction?

6) Formation rates for some of the products are estimated, but no attempt is made to relate these to the formation or growth of SOA under atmospheric conditions. Such a calculation would be helpful to illustrate the potential significance of the observed reactions.

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