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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of non-photochemically formed oligomers from methylglyoxal: a pathway to produce secondary organic aerosol through cloud processing during night-time" *by* F. Yasmeen et al.

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We thank Anonymous Referee #1 for constructive comments, which were highly appreciated and helped to improve the manuscript. The comments have been/will be addressed as outlined below:

This paper presents interpreted electrospray ionization (ESI) mass spectra of methylglyoxal oligomers that form in acidified solutions containing ammonium salts. The au-

thors find that aldol condensations are favorable under conditions relevant to clouds in the atmosphere, and that acetal formation is observed at pH = 3.5 but not under less acidic conditions. No organosulfate formation is observed in any experiment, and in the absence of ammonium salts and acid catalyst, no oligomers form. (This important fact is mentioned only once on p. 23001 line 6.)

Response: The pH cut off for acetal formation will be emphasized in the abstract of the revised manuscript. We agree that the absence of organosulfate formation is very relevant taking into account the dark conditions employed and will also emphasize this observation in the revised manuscript.

First, the authors do not appear to be aware of a spate of very recent publications on methylglyoxal oligomer formation chemistry (Schwier et al., 2009; Krizner et al., 2009), two of which contains ESI mass spectra of methylglyoxal oligomers (Sareen et al., 2009; De Haan et al., 2009).

Response: It is noted that this manuscript was in the process of submission when the cited articles were published; these recent articles will be properly cited in the revised manuscript.

some of the ESI-MS data interpretations in this work are very speculative, but are not presented as such. For example, the aldol structures presented are often examples of many possible isomeric structures that could be formed and would fragment similarly in the ion trap, but this is not usually made clear. The authors also repeatedly claim that they have structurally characterized acetal oligomers with five-membered rings that are analogous to glyoxal oligomers. The only structural data presented in this work, however, is the repeated loss of 18 and 72 amu in the ion trap, which again could come from a wide variety of methylglyoxal oligomer structures, not just the ones shown.

Response: We do agree that there is a possibility of several isomeric aldol structures. Hence, we will carefully use the term "selected tentative structures" in the revised manuscript. We will further revise the structures taking into account the fragmenta-

tion behavior and the free energy landscape presented by Krizner et al. (2009), and will include the most reasonable tentative structures. A more complete list of possible structures will be provided in the supporting information. With regard to fragmentation behavior, we only mentioned neutral losses of 18 and 72 Da because they are structurally informative: by definition of oligomerization the repetition of monomer units (72 Da) is very relevant, while the loss of H2O (18 Da) is quite logical for hydrophilic oligomers that are formed by hydration with water being present in the medium.

The authors detect several significant ion peaks with masses 1 amu less than expected, which they attribute to radical cations of the five-membered-ring acetal oligomers. While the authors themselves exhibit a healthy skepticism towards this explanation, it seems to this reviewer that nitrogen incorporation could more easily explain such peaks. The manuscript fails to address this possibility.

Response: There is no doubt that nitrogen incorporation can very well explain even mass ions. However, we have confirmed that these molecular ion species with even mass are generated in the absence of nitrogen-containing species in the reaction mixture. The only explanation that can be provided for the formation of radical molecular cations is that easily oxidizable organic compounds can be ionized by removal of one electron, via redox reactions in the electrospray ionization (ESI) source, which competes with acid/base reactions and coordination with ionic species. The extent to which these processes occur depends on a combination of factors, such as proton affinity and redox potential, as well as experimental parameters (flow rate of the solution in the capillary). Under well-defined conditions (compounds with low redox potential and low proton affinity and a low solvent flow rate), the ESI source can behave as a controlled-current system of electrons to form open-shell molecular radical cations by an electrochemical oxidation process that is inherent to positive-ion mode ESI (Blades et al., 1991; Vessecchi et al., 2007). Furthermore, such radical ions have been observed by Hastings et al. (2005) for five-membered ring structures while studying hydration and oligomer formation of glyoxal.

Specific Comments

p. 22996 lines 20 – end: This list of chemical mechanisms should be expanded to include dicarbonyl oligomerization via aldol condensation, as proposed by several groups.

Response: The list will be expanded in the revised manuscript.

p. 22997 line 22: This sentence implies that 1 mM methylglyoxal was used in the experiments in order to simulate cloud conditions. However, this concentration is 1 to 4 orders of magnitude higher than measured cloud concentrations for this compound.

Response: Relatively high concentrations of methylglyoxal were employed in order to simulate the reaction processes occurring during cloud evaporation. Upon cloud evaporation, low volatility compounds are concentrated and result in new SOA particle formation.

p. 22998 line 2: Can the authors provide a justification for their choice of methanol as a dilution solvent?

Response: Experiments were performed with acetonitrile, acetone and methanol. Oligomerization was observed with all three solvents. Spectra obtained from samples diluted with acetonitrile will be provided in the supporting information of the revised manuscript. Methanol was selected because it is the most abundant non-methane hydrocarbon in the troposphere (Singh et al., 2001). Moreover, it is also well documented that a significant amount of methanol is present in cloud water (Leriche et al., 2000; Laj et al., 2009). Hence, it is believed that if oligomers containing free aldehyde groups are formed in the atmosphere, they can react with methanol and can produce acetals and hemiacetals.

p. 23000 line 15: How would the formation of UV-absorbing molecules promote the formation of cloud condensation nuclei (CCN), since organics often make poor CCN relative to the inorganic salts with which they mix?

Response: the sentence will be rephrased as follows: “The UV-visible absorbing properties of these conjugated molecules could change the optical properties of aerosols and as such influence the earth’s radiation budget, while their hydrophilic properties could increase their capacity to act as cloud condensation nuclei (Novakov et al., 1993; Andracchio et al., 2002; Kerminen et al., 2005)”.

Line 22: This pH cut off for acetal formation is an important result and should be highlighted by very specific language in the abstract.

Response: We will emphasize this finding in the abstract of the revised manuscript.

p. 23001: The discussion of Figure 4 should emphasize that the molecules shown are examples of structures that are consistent with the data. The data does not prove that these particular structures are correct.

Response: We will clarify that the proposed structures are consistent with the MS data. The discussion will be modified as follows: “We observed two consecutive losses of two molecules of methanol (32 Da x 2) from the molecular ion species of the first series to produce the molecular ion species of the third series. The molecular ion species of the third series fragment by loss of one monomer unit (72 Da) to yield the oligomer of the lower series.”

p. 23004 line 17: This “first” statement should be revisited in light of the very recent publications cited earlier. Table 1 and Figure 4: The methyl acetal derivatives shown in columns 2 and 3 in Table 1 (and in columns 1 and 2 in Figure 4) should be identified more clearly as artifacts of sample dilution in methanol.

Response: We did mention that formation of the double hemiacetal can be explained by addition of methanol (i.e., the solvent used in ESI to dilute the sample) to the carbonyl functions (P23001 line 15).

Table 2: The random switching between radical cation and protonated species for structurally similar molecules shown in the table seems very unlikely. It seems more likely

that the apparent radical species are actually oligomers that have incorporated nitrogen, since the mass of an NH group is one less than an oxygen atom. Can the authors rule this out? In any case, this possibility should be discussed in the manuscript.

Response: The presence of nitrogen was ruled out by observing oligomerization in the absence of ammonium sulfate.

Figure 3: It would be helpful to clearly label this figure as the aldol condensation products. The description is confusing because the “corresponding acetals” are not obtained from the reaction mixture per se but are artifacts of the use of methanol to dilute the reaction samples.

Response: The correction will be made.

Figure 5: These fragment measurements are consistent with five-membered ring structures but are also consistent with many other oligomer structures – they are not structurally specific. The structures shown could well be incorrect. The authors should provide a more nuanced discussion. Do the authors have a suggestion for the structure of the m/z 199 ion?

Response: There are indeed several possible structures and only selected tentative structures have been presented here. We are very well aware that the presented structures should be regarded as tentative, since the structure characterization is only based on the interpretation of MS data. Some of the structures presented in the original manuscript will be revised taking into account the fragmentation behavior. The m/z 199 ion can in our opinion be explained by loss of 90 u (or hydrated methylglyoxal) from the m/z 289 ion through a rearrangement reaction in the left part of the precursor ion; since this loss cannot be explained with the ion structure given in Figure 5, more reasonable ion structures for m/z 289 and its product ion m/z 199 will be proposed in the supporting information of the revised manuscript.

Technical Corrections

p. 23004 line 1: A comma is needed between “uptake” and “irradiated.”

Response: Correction will be made

Table 2: The water complex of the doubly hydrated monomer has a mass that is 20 Da larger than the doubly hydrated monomer. The difference should be 18 amu.

Response: Correction will be made.

Additional References (to be included in the revised version):

Andracchio, A., Cavicchi, C., Tonelli, D., and Zappoli, S.: A new approach for the fractionation of water-soluble organic carbon in atmospheric aerosols and cloud drops, Atmos. Environ., 36, 5097-5107, 2002.

Blades, A. T., Ikonomou, M. G., and Kebarle, P.: Mechanism of electrospray mass spectroemtry – electrospray as an electrolysis cell, Anal. Chem., 63, 2109–2114, 1991.

Hastings, W. P., Koehler, C. A., Bailey, E; L., and De Haan, D. O.: Secondary organic aerosol formation by glyoxal hydration and oligomer formation: Humidity effects and equilibrium shifts during analysis, Environ. Sci. Technol., 39, 8728-8735, 2005.

Kerminen, V. M., Lihavainen, H., Komppula, M., Viisanen, Y. and Kulmala, M.: Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation, Geophys. Res. Lett., 32, L14803, 2005, doi:10.1029/2005GL023130

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