

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.

Anonymous Referee #1

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General Comments

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

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the absence of ammonium salts and acid catalyst, no oligomers form. (This important fact is mentioned only once on p. 23001 line 6.) The quality of the experiments is high, but the choice of methanol to dilute the reaction samples seems unfortunate and unjustified, since this needlessly complicates the mass spectra with methyl acetal artifact peaks. This manuscript will be of significant interest to atmospheric chemists.

There are a few issues that should be addressed. 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). Second, 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. 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.

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.

p. 22997 line 22: This sentence implies that 1 mM methylglyoxal was used in the

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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.

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

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?

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

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.

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.

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.

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.

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? The m/z 217 structure shown (which should be labeled as such) does not look as if it could easily lose another water molecule.

Technical Corrections

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

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

References

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Krizner, H. E., De Haan, D. O., and Kua, J.: Thermodynamics and kinetics of methylglyoxal dimer formation: A computational study, *Journal of Physical Chemistry A*, 113, 6994-7001, 10.1021/jp903213k, 2009.

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