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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 #2 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 results from laboratory experiments investigating nighttime oligomer formation through cloud processing of methylglyoxal. Acidity and inorganic salts are added to simulate the conditions in cloud waters. The experiments are an important new contribution to the field and this manuscript will be appreciated by the community. They suggest a variety of reaction mechanisms based on the electrospray ionization mass spectrometry data. The following issues need to be addressed before the manuscript is suitable for publication in Atmospheric Chemistry and Physics. Section 2. More information on the experimental setup is needed. A table with the starting concentrations and resulting pH and ionic strength of each cell would be useful.This table should also include the control experiments which are briefly mentioned, but more detail is required as to what constituted a control experiment. The ESI-MS spectra from the control experiments should also be presented and discussed as it relates to the results. This is a major issue in this paper that needs to be addressed.

Response: A table with conditions of control experiments and resulting spectra for comparison will be provided in the supporting information of the revised manuscript.

There is no mention of any standards being analyzed by the electrospray ionization mass spectrometer (ESI-MS). It is possible that methylglyoxal and the inorganic salts alone could produce a very complex mass spectrum, especially in the positive mode. These standard spectra need to be shown, or at least discussed.

Response: Standard spectra will be provided in the supporting information of the revised manuscript.

The concentration of methylglyoxal (mM) is much higher than that in cloud waters. It is known that oligomerization is concentration dependent. The authors need to justify why this high concentration was chosen as the ESI-MS is capable of much lower concentrations (3 fold at least). This also applies for the concentrations of acid and inorganic salts, the authors need to justify their choices as these concentrations and relative ratios of salts, acid, and organic are not representative of cloud water.

Responses: With regard to the concentrations of methylglyoxal, relatively high concentrations 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. With regard to the choice of the concentrations for acid and inorganic salts, we argue that we could follow the presented reaction mechanisms with the employed catalytic amounts of acid and NH4+ ions.

There is no justification presented for diluting the samples in methanol. One advantage of the ESI-MS is the ability to inject samples without pre-treatment. If the issue is the high starting concentration of methylglyoxal, then either ultrapure water would be better to dilute the samples, or as mentioned above, a more cloud relevant concentration of methylglyoxal would be better suited for these experiments. The addition of methanol unnecessarily introduces adducts and alters the composition of the oligomers formed and thus hinders interpretation of the oligomer system. This is a major issue that needs to be addressed.

Response: Methanol was used for diluting the aqueous samples for different reasons: (1) it is our experience that addition of methanol results in a stabilization of the electrospray signal, and (2) methanol was also selected because it is the most abundant non-methane hydrocarbon in the troposphere (Singh et al., 2001) and it is also well documented that a significant amount of MeOH is present in cloud water (Leriche et al., 2000). Hence, it is believed that if oligomers containing free aldehyde groups are formed in the atmosphere, they could react with methanol and produce acetals and hemiacetals.

The issue raised on page 23000 line 1 need to be addressed in more detail. Sodium and ammonium were added thus to the experiments adduct formation likely dominates the positive mode spectra. This needs to be taken into account while analyzing the ESI-MS data.

Response: The formation of adducts was carefully monitored, and Na+ adducts were detected as presented in the manuscript while ammonium adducts could not be observed.

Page 23000 line 9-10, this sentence mentioning the ability of NH4+ to catalyze oligomerization reactions needs a reference.

Response: Appropriate references will be included in the revised manuscript: Nozière et al., 2009, Sareen et al., 2010.

Page 22998 lines 21-23. The difference between Figures 1 and 2 is not evident from the text. It seems the only difference is the pH, but this is only briefly mentioned in the figure caption. This should be clarified.

Response: The figure captions will be improved in order to reveal the differences between Figures 1 and 2.

Section 3.2.1. This oligomerization pathway is concentration dependent but there is no mention of whether it is likely to happen at cloud relevant concentrations, or whether there is any evidence for this pathway in their data. The relevance of this section needs to be addressed.

Response: We did mention in the manuscript that oligomerization depends on the initial concentration of methylglyoxal. In order to simulate particle formation during cloud evaporation, slightly higher concentrations were selected.

Section 3.3.1. Could the loss of 32u which is attributed to methanol be attributed to the addition of methanol as a solvent and not the presence of a hemiacetal? Is it possible that the loss of 18u attributed to water is actually from an ammonium adduct?

Response: A relatively high collision energy level, i.e., 35%, was needed to fragment the molecular ion species, consistent with a covalent bond as present in a hemiacetal. With regard to the loss of 18 u, it is unlikely that an ammonium adduct was formed since this loss was also observed in the absence of ammonium ions. Moreover, in the case of an ammonium adduct, we would rather expect the loss of ammonia (17 u).

The figure numbering is off throughout the text. Page 23001 line 25 should refer to Figure 3 perhaps? This needs to be addressed throughout the manuscript.

Response: The correction will be made.

Page 23002 lines 3-5. This point about methylglyoxal and sodium adducts should be addressed with a standard mixture that includes both components. Throughout this section the authors occasionally invoke the presence of sodium adducts but this issue needs to be addressed. What is their logical reasoning for only some ions being adducted with sodium and others not?

Response: We have observed Na+ adducts for oligomers formed by aldol condensation; we think the reason for the behavior of this type of oligomer molecules to form complexes with Na+ is that they have a free rotation in space and can chelate Na+ at multiple sites. In contrast, five-member ring structures as found in oligomers of the acetal/hemiacetal type are rigid and do not allow for chelation of Na+ ions; hence, they will appear as protonated molecules or radical cations.

Page 23002 line 16 does not seem to refer to Figure 7.

Response: The correction will be made; this explanation refers to Figure 2.

Page 23002 lines 23-25. This statement is a major issue in this paper. There is no reasoning given for the formation of radical cations and there is no reference to any other ESI-MS literature that might support this claim. It is highly unlikely that these compounds would form and the authors need to revise this entire argument, or provide strong evidence supporting the presence of these compounds.

Response: This issue was also raised by reviewer #1; see our detailed responses to the comments of this reviewer.

In general, in this section the masses and their fragmentation patterns could have multiple explanations and the authors do not provide strong enough evidence supporting their proposed pathways. The difference in 72u is exactly the same difference seen in Altieri et al., 2008 which the authors cite as a mechanism not contributing in this work.

Response: We have explored different possibilities considering the reaction conditions

and possible mechanisms (Krizner et al., 2009) have been proposed in the revised manuscript. As mentioned in the manuscript, the photooxidation mechanism proposed by Altieri et al. (2008) does not apply because we use dark conditions.

The losses of 32 u and 18 u are very common for many functional groups on many molecules and are not conclusive for the proposed structures. This needs to be addressed.

Response: (1) Dilution with solvents other than methanol does not produce acetal formation (loss of 32 u), supporting that this loss of 32 u is due to MeOH; (2) There was no observation of a satellite peak at two units higher than the parent mass; hence, the presence of S was ruled out; (3) The loss of 18 u (as a neutral) can only be due to H_2O. In the case of an NH_4^+ adduct species, we would rather expect the loss of NH_3 (17 u). Moreover, the presence of ammonium adduct species was ruled out by control experiments in which MGly was introduced in a medium containing other salts (Na_2SO_4 and NaCl) and a similar oligomerization and loss of 18 u were observed.

Section 3.3.2 The detection of aldols in the negative mode is unusual for ESI-MS. The authors should verify this with standard compounds. If they are not aldols, it is possible that other types of compounds were formed that are detected in the negative mode. How many of the negative mode masses can be accounted for by taking the positive mode compounds and subtracting the proton or sodium ion?

Response: A possible explanation is that aldol structures in which the enol form is resonance-stabilized can be deprotonated and detected in negative ion ESI-MS.

Table 1 needs a more descriptive caption. Are these the compounds that are suggested to form at the higher pH? The same is true for Table 2, although the likelihood of these radical cations is very suspect.

Response: The legends to Table 1 and 2 will be revised. With regard to the occurrence of molecular radical cations, see our detailed response to the comments of reviewer 1.

Figure 3 is unclear. The labeling needs to be improved as does the figure caption. It is not obvious what the n=4, etc. are referring to, nor which panels the di-acetals and di-hydrates are referring to. The parent ions need to be identified in a clear manner. The presence of the three arrows under the circled masses is unclear.

Response: The Figure legend will be improved following the suggestions; the three arrows under the circled mass is symbolic and denotes fragmentation of the parent molecular ion species with the circled m/z value.

Figure 5 is not referred to in the manuscript.

Response: The correction will be made; P 23002 line 28 refers to Figure 5

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

Krizner, H. E., De Haan, D. O., and Kua, J.: Thermodynamics and kinetics of methylglyoxal dimer formation: A computational study, J. Phys. Chem. A, 113, 6994-7001, 2009.

Leriche, M., Voisin, D., Chaumerliac, N., Monod, A. and Aumont, B.: A model for tropospheric multiphase chemistry: application to one cloudy event during the CIME experiment, Atmos. Environ., 34, 5015-5036, 2000.

Nozière, B., Dziedzic, P., and Cordova, A.: Products and kinetics of the liquid-phase reaction of glyoxal catalyzed by ammonium ions (NH4+). J. Phys. Chem. A, 113, 231-237, 2009.

Sareen, N., Schwier, A. N., Shapiro, E. L., Mitroo, D., and McNeill, V. F.: Secondary organic material formed by methylglyoxal in aqueous aerosol mimics, Atmos. Chem. Phys., 10, 997-1016, 2010.

Singh, H., Chen, Y., Staudt, A., Jacob, D., Blake, D., Heikes, B., and Snow, J.: Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds, Nature, 410, 1078–1081, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 22993, 2009.