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***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 #2**

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This paper presents results from laboratory experiments investigating night time 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.

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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. 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.

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.

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.

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

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Page 23000 line 9-10, this sentence mentioning the ability of  $\text{NH}_4^+$  to catalyze oligomerization reactions needs a reference.

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.

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.

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?

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. 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?

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

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.

In general in this section the masses and their fragmentation patterns could have mul-

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

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.

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.

Figure 5 is not referred to in the manuscript.

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