Supplement for:

Characterization of oligomers from methylglyoxal under dark conditions: A pathway to produce secondary organic aerosol through cloud processing during nighttime

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Table S1: List of control experiments; all experiments were conducted in three different solvents (i.e., methanol, acetonitrile, and acetone).

Experiment	**pH ± 0.15**
MGly Standard (10^{-3} M)	5.3
MGly + H_2SO_4	(3-5)
MGly + $(NH_4)_2SO_4$	5
MGly + Na_2SO_4	5.2
MGly + NaCl	5.2
MGly + $(NH_4)_2SO_4$ + H_2SO_4	(3-5)
MGly + Na_2SO_4 + H_2SO_4	(3-5)
MGly + NaCl + H_2SO_4	(3-5)

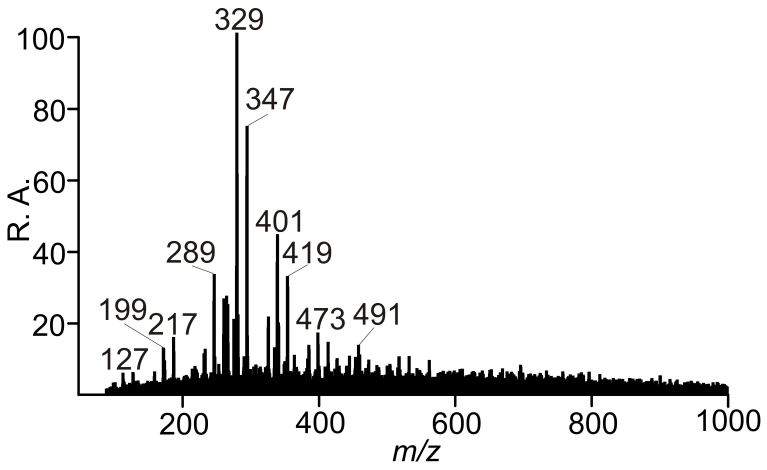


Figure S1. ESI mass spectrum of aldol products (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15°C after zero hour reaction (solvent: acetonitrile). The abundant ions at *m/z* 329 and 401 correspond to the sodiated mono-hydrated forms of 4- and 5-mers, while the ions at *m/z* 347, 419 and 491 correspond to the sodiated di-hydrated forms of 4-, 5- and 6-mers.

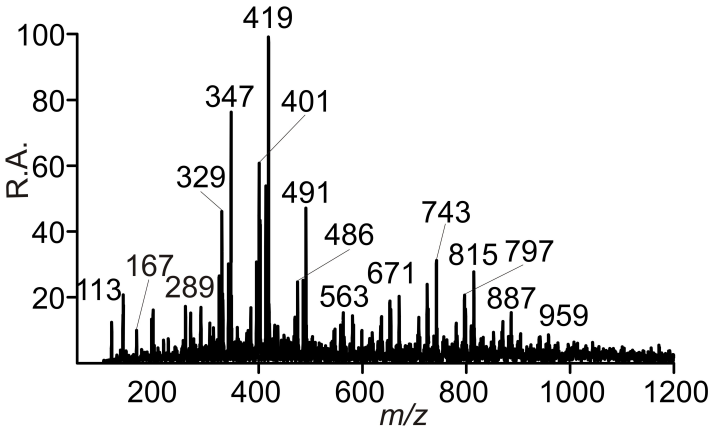


Figure S2. ESI mass spectrum of aldol products (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 4.5 and T = 15 °C after one hour reaction (solvent: acetonitrile). The ions at *m/z* 743 and 815 correspond to the sodiated forms of 10- and 11-mers, showing that the *m/z* pattern compared to that at the onset of the reactions (Fig. S1) changes in time.

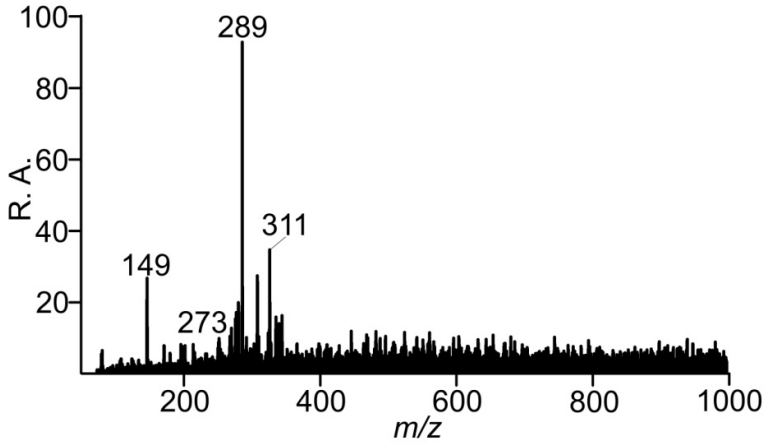


Figure S3. ESI mass spectrum of standard MGly (10^{-3} mol L^{-1}) (positive mode) at pH = 5.3 and T = 15 °C (solvent: methanol). The ion at *m/z* 311 corresponds to the sodiated tetramer (Table 1), indicating that methylglyoxal has the potential of self-oligomerization to a certain extent (the abundant ion at *m/z* 289 could not be assigned and is likely not related to methylglyoxal).

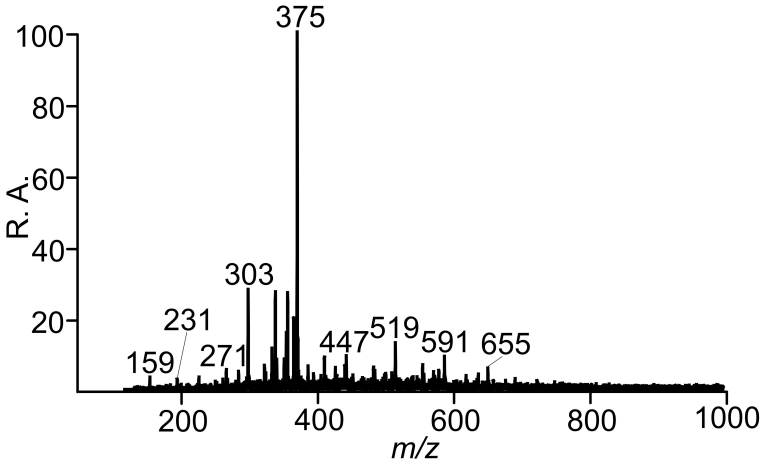


Figure S4. ESI mass spectrum of MGly (10^{-3} mol L^{-1}) (positive mode) at pH = 4.5 and T = 15 °C (solvent: methanol). The abundant ion peaks at *m/z* 303 and 375 correspond to sodiated tri- and tetramers (Table 1), clearly indicating the enhancement in the self-oligomerization of methylglyoxal upon a slight increase in the acidity of the medium.

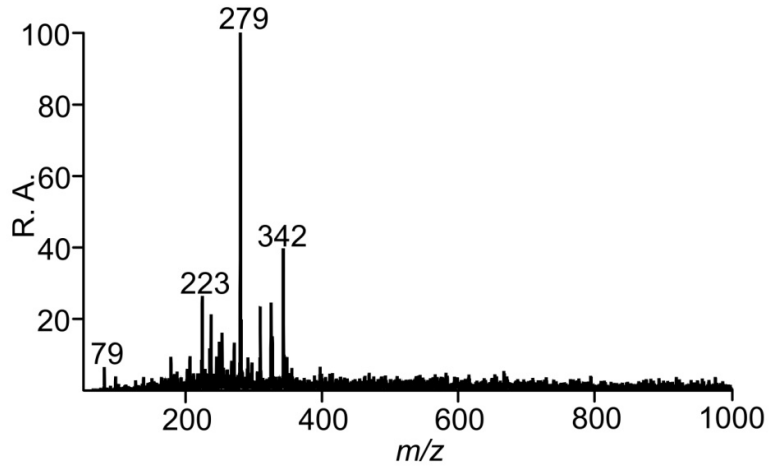


Figure S5. ESI mass spectrum of MGly (10^{-3} mol L^{-1}) (positive mode) at pH = 3.3 and T = 15 °C (solvent: methanol). The abundant ion at *m/z* 342 corresponds to the tetramer formed via acetal formation, supporting that this mechanism has a strict pH limitation; the main peak at *m/z* 279 does not relate to methylglyoxal reactions but could be due to plasticizer contamination with dibutylphthalate.

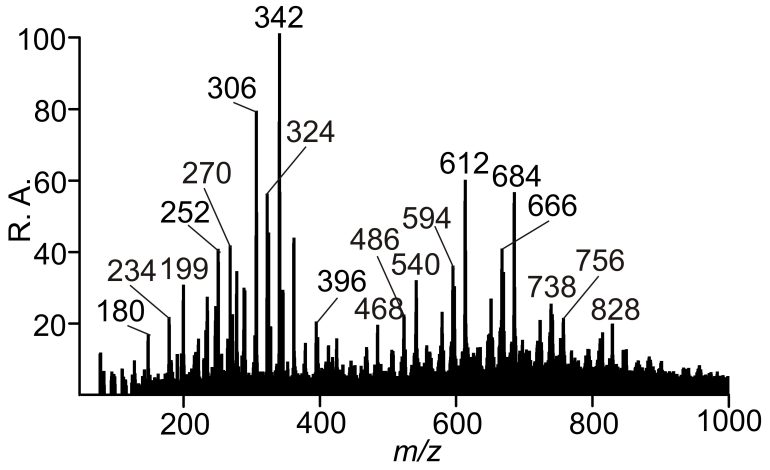


Figure S6. ESI mass spectrum of acetal products (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with sodium sulfate (10^{-4} mol L^{-1}) at pH = 3.2 and T = 15°C after one hour reaction (solvent: methanol). It can be seen that ions at the same even *m/z* values can be detected as in the case of ammonium sulfate (Fig. 2).

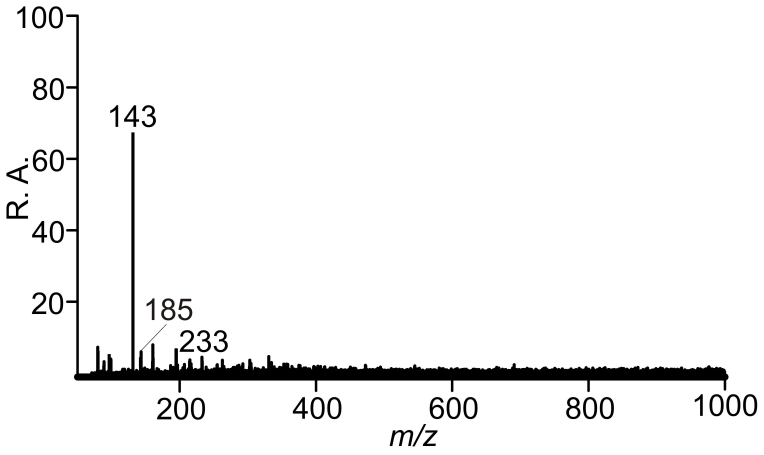


Figure S7. ESI mass spectrum of MGly (10^{-3} mol L^{-1}) (negative mode) at pH = 5.3 and T = 15 °C (solvent: methanol). The abundant ion at *m/z* 143 corresponds to the protonated methylglyoxal dimer.

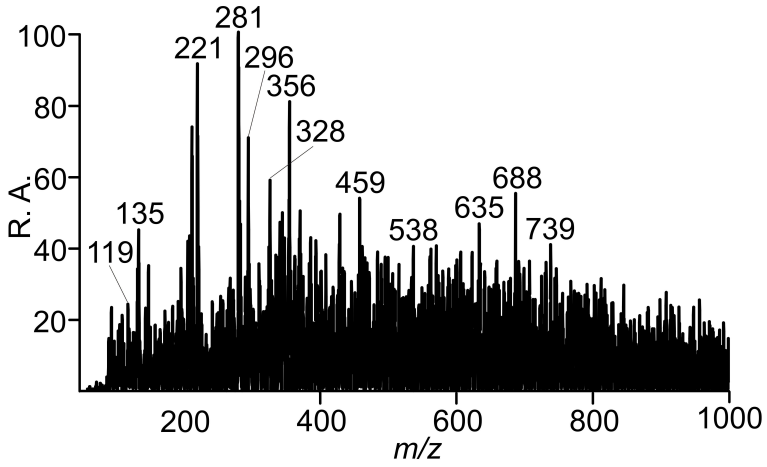
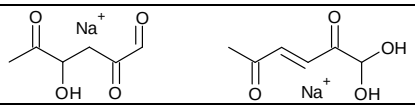
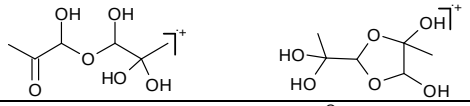
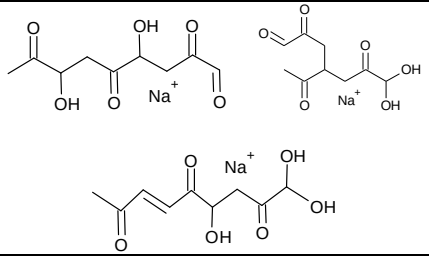
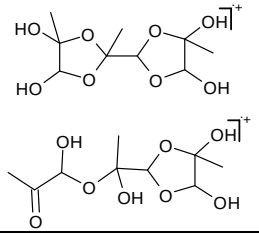
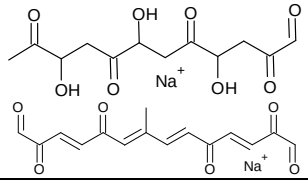


Figure S8. ESI mass spectrum (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH = 5 and T = 15 °C after one hour reaction (solvent: methanol). A very noisy and complex spectrum was obtained, with peaks just appearing above background, indicating that these conditions are not favorable for oligomer formation.

Table S2: Possible ion structures attributed to selected reaction products of methylglyoxal under simulated cloud conditions on the basis of interpretation of ESI mass spectra.

m/z molecular ion or sodiated molecule	molecular formula	possible structures
167	$C_6H_8O_4$	
180	$C_6H_{12}O_6$	
239	$C_9H_{12}O_6$	
252	$C_9H_{16}O_8$	
311	$C_{12}H_{16}O_8$	
324	$C_{12}H_{20}O_{10}$