Secondary organic aerosol formation during evaporation of droplets containing atmospheric aldehydes, amines, and ammonium sulfate:

Supporting Information

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Tables S1 – S2

Figures S1 – S7

Monodisperse droplet drying: concentration dependence

Excess residual particle volumes were shown for t = 1.8 min drying times as a function of aldehyde-methylamine concentrations in Figure 2. Figure S4 shows similar data for aldehyde-AS experiments, in this case for t = 2.0 – 2.5 min drying times, and equimolar concentrations of aldehyde and AS, as before. Higher percent excess residual particle volumes are calculated at low concentrations in all aldehyde-AS experiments. One explanation for these high particle volumes is that the terminal volumes are much smaller for lower concentrations experiments, and small variations in particle sizes can lead to larger errors in this range. Thus, effects that would be subtle at higher concentrations, like aerosol non-sphericity, or drops in aerosol density, would be significant at low concentrations. We attribute the effect, however, to water trapping due to increasing viscosity in the drying aerosol phase as oligomerization progresses. In the case of methylglyoxal, surface coatings may also play a role in trapping water and other volatiles in the dried residual particle.

The middle and bottom panels of Figure S4 indicate that somewhat higher percent excess residual particle volumes are seen at the lowest solute concentrations of aldehyde-amine experiments with methylamine and even with glycolaldehyde alone. The only system that does not exhibit this effect is glyoxal alone. This is consistent with our explanation of oligomerization and water trapping. When a glyoxal-water droplet is dried, the residual particle contains mostly glyoxal trimer dihydrate, and the density and molecular mass of this oligomer compound, including hydrate water, is already used in our calculation. Thus, oligomerization and water trapping is already accounted for, and the apparent larger percent excess residual particle volumes are not observed. In addition, Figure S2 shows that a very slight increase in residual aerosol volume is observed in glyoxal-AS experiments conducted at 2 °C, also consistent with

this explanation, since water diffusion rates in the viscous aerosol phase would be lowered further by the cold temperatures.

TGA

The decomposition of AS (Figure S5) involves several steps that have been previously determined by Kiyoura and Urano (*1*). To summarize, at 100°C, 1 mole of ammonia is lost as AS is converted to ammonium bisulfate. This should have occurred during sample drying (20 min at 105°C). No further reaction occurs until 170°C, at which point ammonium bisulfate begins to lose water to produce sulfamic acid, NH_2HSO_3. Beginning at 200°C, the compounds begin to break down into gases such as H_2, NH_3, SO_3, H_2O and other gases. At our 20°C/min heating rates, this process is not complete until the temperature reaches 400°C, at which point a stable char has been produced. Similar thermal breakdowns are observed beginning at ~180°C for glycine and ~220°C for methylamine (Figures S6 and S7). Due to the presence of pH buffering oxalic acid in these experiments, the methylamine is present as methylaminium oxalate.

Table S1. Aldehyde masses and densities used in calculating % excess residual particle volumes and % excess equilibrium particle volumes.

Aldehyde	*Monomer mass in aerosol (amu)*	*Aldehyde density in aerosol (g cm^{-3})*	*Asphericity correction (1 = spherical)*
Glyoxal	70[a]	1.71 ±0.02[b, c]	1[d]
Methylglyoxal	65[e]	1.9 ±0.1[b, f]	1[g]
Hydroxyacetone	74.08[h]	1.08[i]	1[g]
Glycolaldehyde	60.05[h, j]	1.455[i, k]	1[g]
Acetaldehyde	44.05[h]	0.785[i]	1[g]
Formaldehyde	30.03[j]	0.88[b, i]	1[g]

a: *⅓ × (mass of glyoxal trimer dihydrate)*, the most stable acetal oligomer (*2*, *3*). **b**: Oligomer density. **c**: (Ref (*4*)), equal to glyoxal trimer dihydrate density (Ref (*5*)). **d**: AFM measurement, ref (*4*). **e**: Average mass of oligomer species per monomer, measured by ESI-MS (*4*). **f**: Ref (*4*). **g**: Assumed = *1* (spherical) because mixture of oligomers is not expected to be crystalline. **h**: Molecular mass of aldehyde. Average mass of oligomer species per monomer in aerosol-phase aldol condensation products is expected to be slightly smaller than molecular mass of aldehyde, as observed for methylglyoxal. **i**: manufacturer data. **j**: monomer mass in acetal oligomer. **k**: dimer density

Table S2. Measured equilibrated geometric mean particles sizes and calculated excess equilibrium particle volumes at 75 ±5% RH for equilibrated polydisperse aerosol experiments.

Initial diam. (μm)	*Reaction mixture*	*Aldehyde conc. (mM)*	*Amine conc. (mM)*	*Equilib. geom. mean (nm)*	*Excess equilib. particle vol. (%)*
2.1	Water + AS	--	2	106.2	--
2.1	FAld + AS	0.4	2	102.8	-9 ±2[a]
2.1	FAld + AS	1	2	100.3	-40 ±20[a]
2.1	FAld + AS	2	2	104.9	-20 ±30[a]
2.1	GX + AS	0.4	2	106.5	6 ±40
2.1	GX + AS	2	2	108.1	8 ±9
2.1	Water + AS	--	5	144.3	--
2.1	GX + AS	0.2	5	138.4	-12 ±2[a]
2.1	GX + AS	1	5	141.3	-6 ±1a
2.1	GX + AS	5	5	205.0	320 ±70
2.1	Water + Glycine	--	5	141.6	--
2.1	GX + Glycine	0.04	5	136.2	-11 ±2[a]
2.1	GX + Glycine	0.2	5	136.4	-11 ±2[a]
2.1	GX + Glycine	1	5	143.2	25 ±30
2.1	GX + Glycine	5	5	143.3	6 ±7
2.1	MeGly + Glycine	0.2	5	154.2	1300 ±500
2.1	MeGly + Glycine	1	5	152.1	210 ±60
2.1	MeGly + Glycine	5	5	147.8	25 ±9
2.1	Water + MeAm	--	2	61.6	--
2.1	FAld + MeAm	0.4	2	52.1	-40 ±6[a]
2.1	FAld + MeAm	2	2	65.1	7 ±2
2.1	Water + MeAm	--	10	47.2	--
2.1	GX + MeAm	8.6	10	142.9	86 ±2
2.1	MeGly + MeAm	0.4	10	86.8	430 ±70
2.1	MeGly + MeAm	2	10	108.1	180 ±30
2.1	MeGly + MeAm	10	10	131.8	70 ±10
1.2	Water	--	--	33.3	--
1.2	Water + AS	--	1	58.1	--
1.2	FAld + AS	0.5	1	54.9	6 ±60
1.2	FAld + AS	1	1	56.6	50 ±100
1.2	FAld + AS	2	1	57.4	8 ±50
1.2	FAld + AS	3	1	61.6	25 ±30
1.2	FAld + AS	4	1	59.3	6 ±10
1.2	GX + AS	1	1	65.9	130 ±20
1.2	GAld + AS	1	1	56.4	18 ±80
1.2	GAld + AS	2	1	51.3	-30 ±20[a]

Initial diam. (μm)	Reaction mixture	Aldehyde conc. (mM)	Amine conc. (mM)	Equilib. geom. mean (nm)	Excess equilib. particle vol. (%)
1.2	GAld + AS	3	1	52.2	-30 ±20[a]
1.2	Water + Glycine	--	1	56.7	--
1.2	GAld + Glycine	1	1	52.2	-22 ±4[a]
1.2	GAld + Glycine	2	1	73.2	160 ±60
1.2	GAld + Glycine	3	1	51.4	-25 ±4[a]
1.2	FAld + Glycine	1	1	60.5	80 ±100
1.2	FAld + Glycine	2	1	59.6	42 ±100
1.2	FAld + Glycine	3	1	70.0	94 ±7
1.2	Water + Arginine	--	1	71.4	--
1.2	GAld + Arginine	1	1	58.4	-40 ±20[a]
1.2	GAld + Arginine	2	1	69.8	40 ±100
1.2	GAld + Arginine	3	1	67.7	-10 ±30[a]
1.2	FAld + Arginine	1	1	65.8	0.3 ±60
1.2	FAld + Arginine	2	1	63.2	-30 ±10[a]
1.2	FAld + Arginine	3	1	61.8	-30 ±40[a]
1.2	Water + MeAm	--	1	54.1	--
1.2	GAld + MeAm	1	1	52.3	-10 ±2[a]
1.2	GAld + MeAm	2	1	57.1	29 ±70
1.2	GAld + MeAm	3	1	57.5	20 ±10
1.2	FAld + MeAm	1	1	58.1	70 ±30
1.2	FAld + MeAm	2	1	59.1	40 ±30
1.2	FAld + MeAm	3	1	47.6	-30 ±20[a]

Excess equilibrium particle volumes calculated as percentages of aldehydes present. AS, ammonium sulfate. FAld, formaldehyde. GAld, glycolaldehyde. GX, glyoxal. MeAm, methylamine. MeGly, methylglyoxal. **a**: Negative values represent percentage of particle volume (measured in experiment without aldehyde) lost upon addition of aldehyde, eq 3 in text.

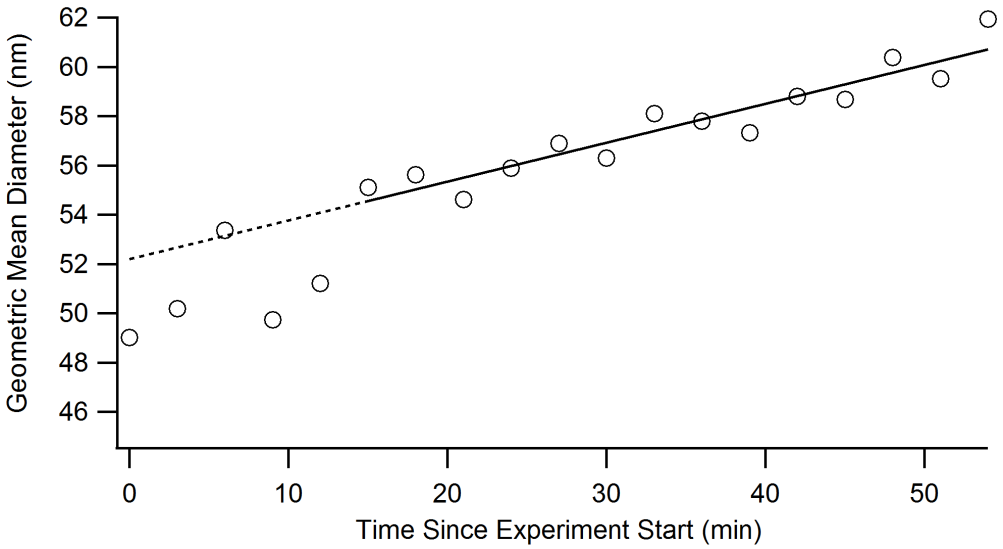


Figure S1: Typical particle diameter data for 1 mM glycine + 1 mM glycolaldehyde (open circles). Mixing occurs in the chamber for the first 15 minutes, so data are fit to the geometric mean diameter from 15-60 minutes (solid line) and extrapolated back to zero (dotted line) to determine the initial geometric mean diameter for each experiment.

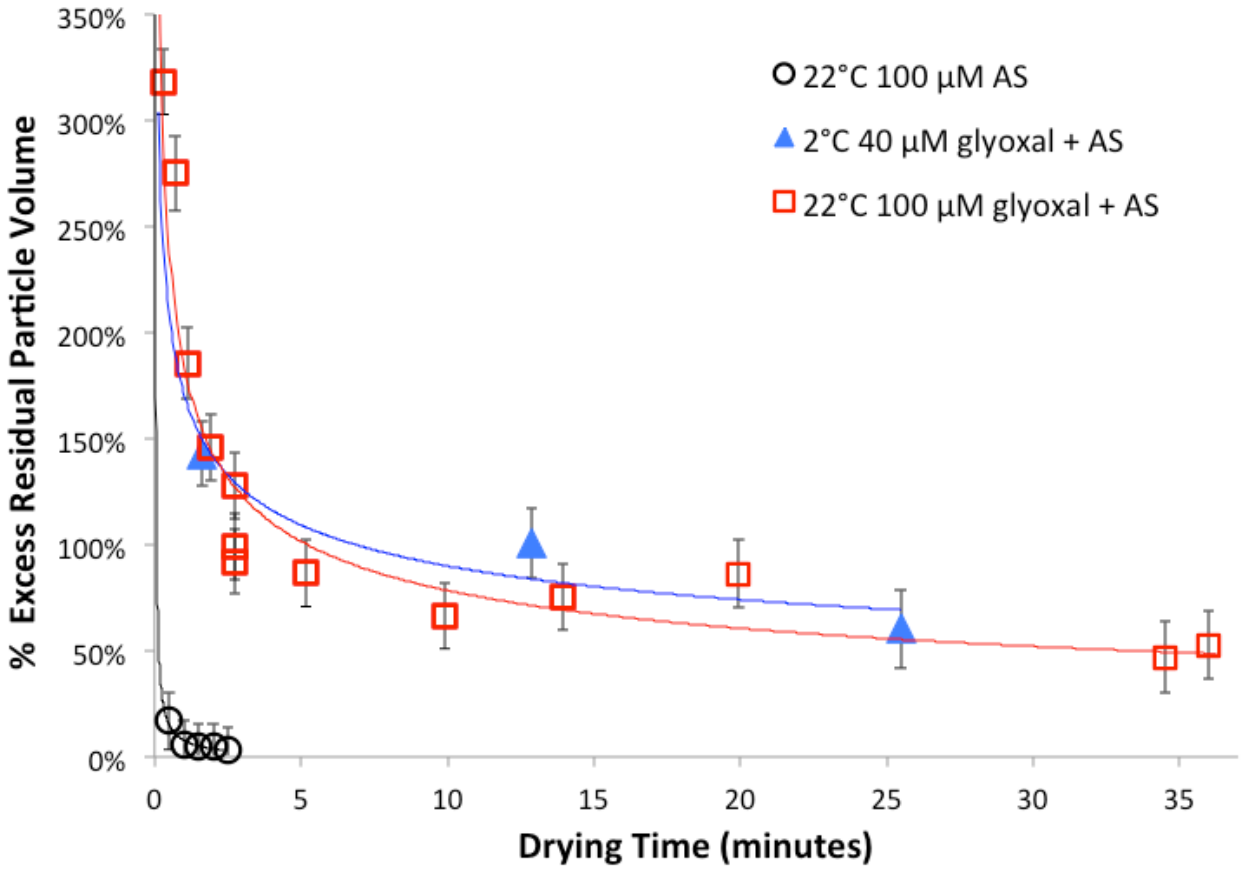


Figure S2: Excess residual particle volumes (expressed as percentages of total aldehyde volumes present in original droplet) measured out to long drying times for indicated concentrations of AS and glyoxal-AS at two different temperatures. Volumes equivalent to 0% of the aldehyde present are equal to 100% of the AS present in the original droplet. Data are fit to y-offset power law equations to show rapid decrease in particle size as aqueous droplets are mixed with dry air at $t = 0$.

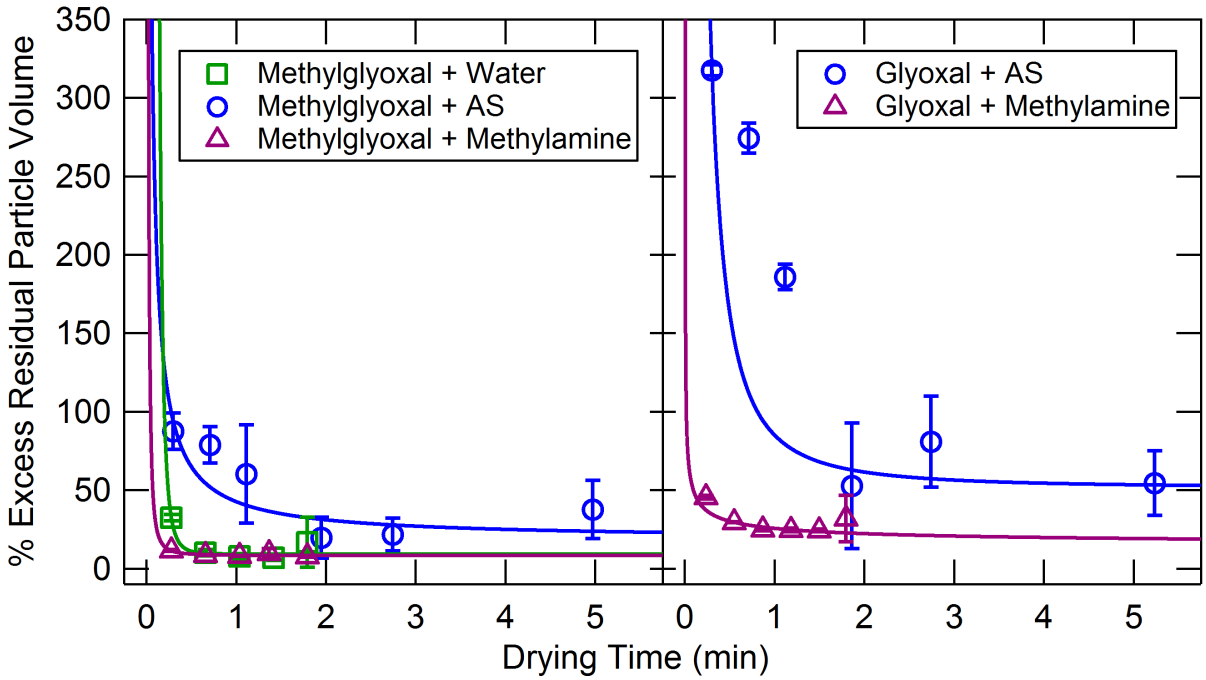
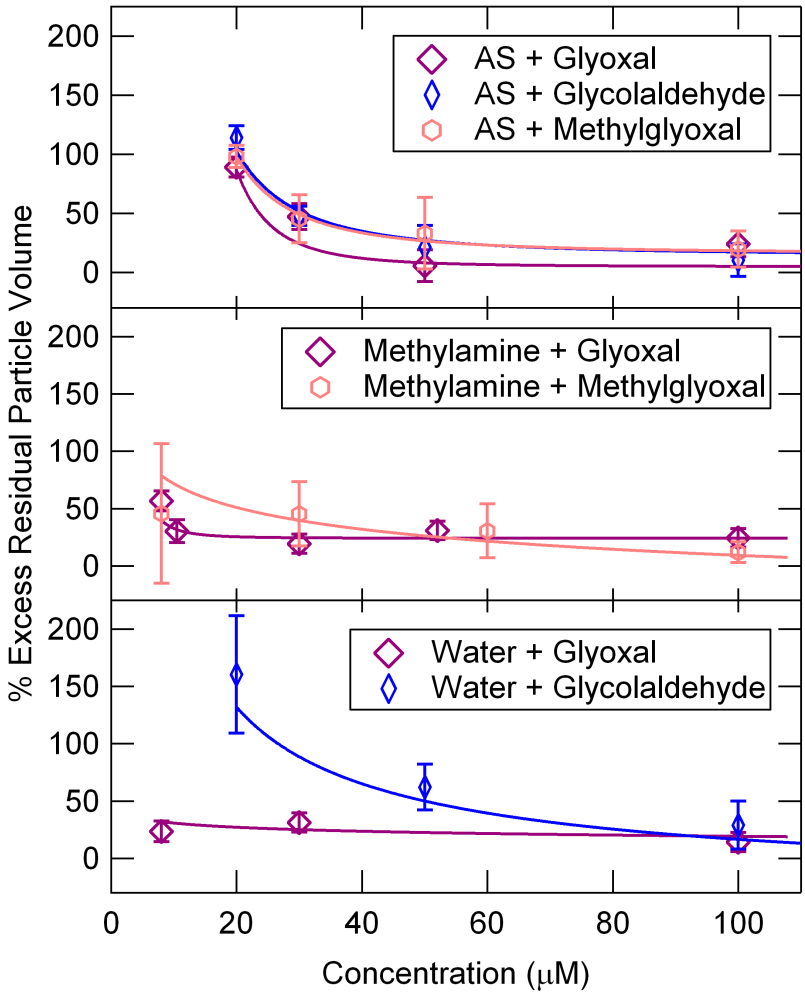


Figure S3. Excess residual particle volumes (expressed as percentages of total volume of organic compounds present in original droplet) as a function of drying times for 100 mM concentrations of aldehydes and methylamine (purple triangles) or aldehydes alone (green squares).. Aldehyde + AS data from Figure 1 (blue circles) shown for comparison. Power law fits are shown. Excess volumes are calculated by subtracting AS-only residual volumes (AS experiments) or water-only residual volumes (non-AS experiments).



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95 **Figure S4:** Excess residual particle volumes after 2.0 – 2.5 min drying time (expressed as
96 percentages of total volume of organic compounds present in original droplet) as a function of
97 concentration of 1:1 molar ratio mixtures of aldehydes and AS (top), aldehydes and methylamine
98 (middle) or aldehydes only (bottom). For top panel, excess volumes are calculated by
99 subtracting AS-only residual volumes. For middle and bottom panels, water-only residual
100 volumes were used. Fit lines are to guide the eye.

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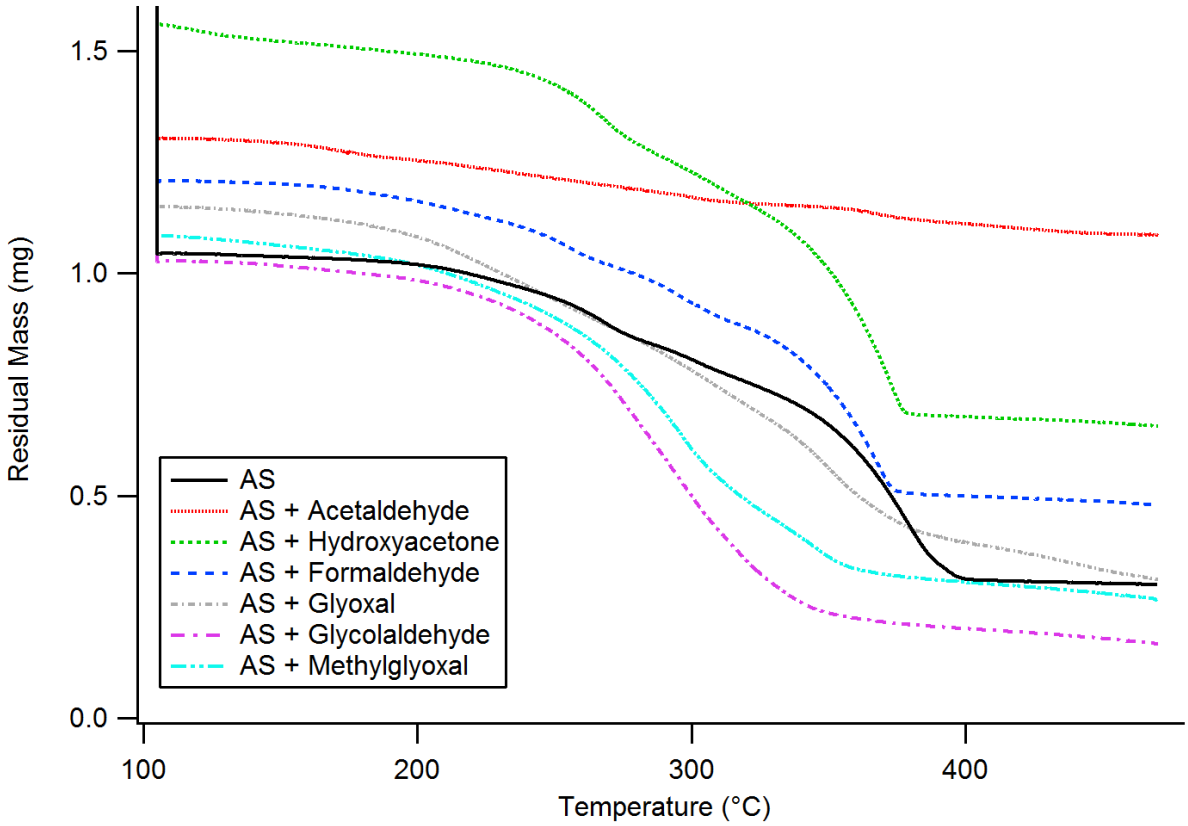

Figure S5: Thermal gravimetric analysis traces of AS (solid black) and carbonyl-AS mixtures (dashed lines) during and after 20 min. evaporation at 105°C of 15 µL 0.5 M samples. Red: acetaldehyde; green: hydroxyacetone; dark blue: formaldehyde; gray: glyoxal; light blue: methylglyoxal; violet: glycolaldehyde. Scan rate: 20°C / min. Data for Figure 5 taken from beginning of temperature ramp beyond 105°C.

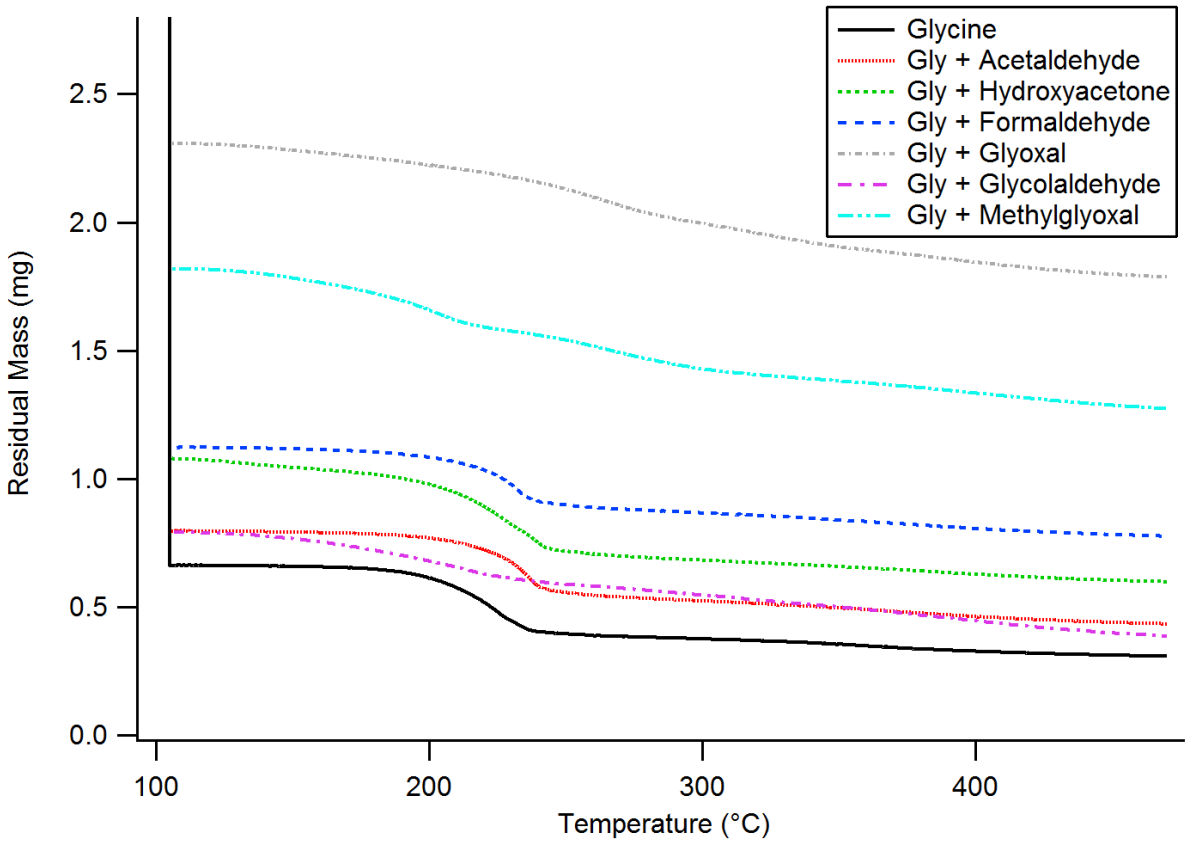

Figure S6: Thermal gravimetric analysis traces of glycine (solid black) and carbonyl-glycine mixtures (dashed lines) during and after 20 min. evaporation at 105°C of 15 μL 0.5 M samples. Red: acetaldehyde; green: hydroxyacetone; dark blue: formaldehyde; gray: glyoxal; light blue: methylglyoxal; violet: glycolaldehyde. Scan rate: 20°C / min. Data for Figure 5 taken from beginning of temperature ramp beyond 105°C.

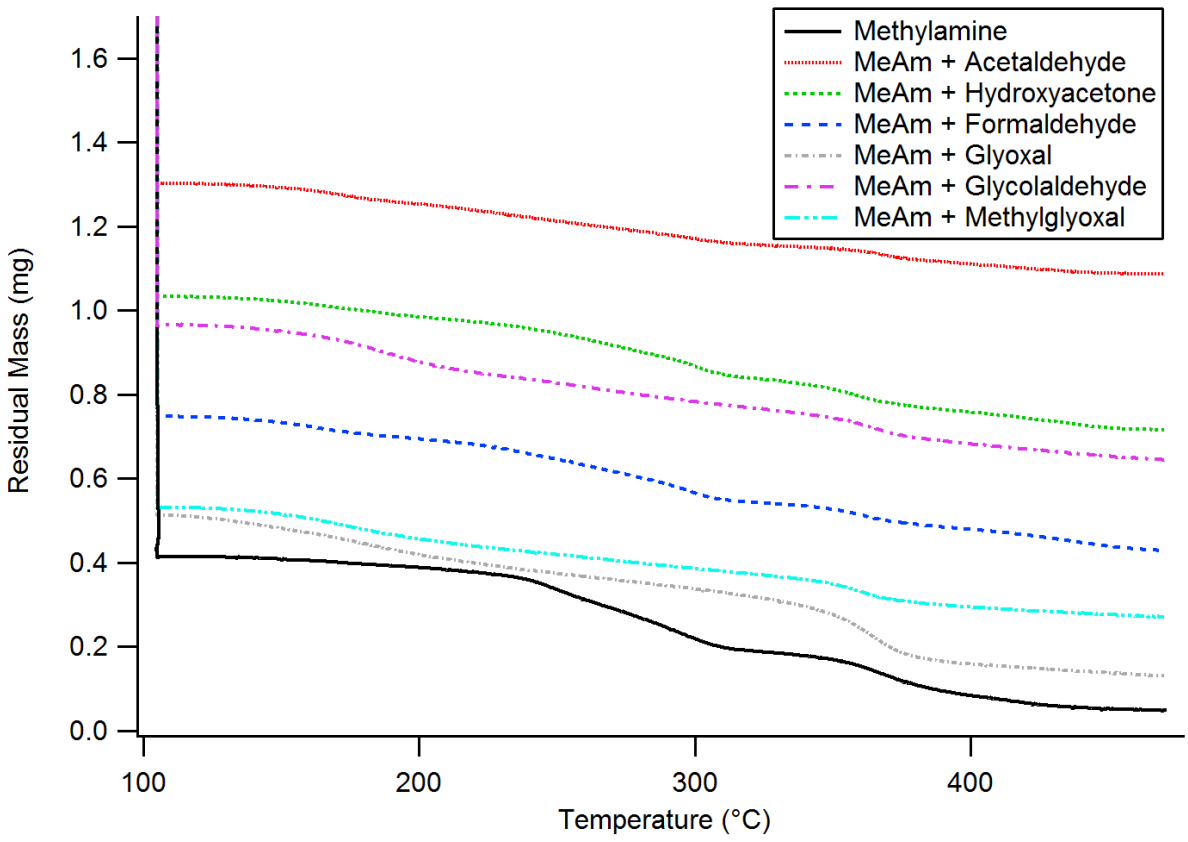

Figure S7: Thermal gravimetric analysis traces of methylamine (solid black) and carbonyl-methylamine mixtures (dashed lines) during and after 20 min. evaporation at 105°C of 15 µL 0.5 M samples. Red: acetaldehyde; green: hydroxyacetone; dark blue: formaldehyde; gray: glyoxal; light blue: methylglyoxal; violet: glycolaldehyde. Scan rate: 20°C / min. Data for Figure 5 taken from beginning of temperature ramp beyond 105°C.

ABBREVIATIONS

AS, ammonium sulfate; TGA, thermogravimetric analysis;

126 REFERENCES

127 1. Kiyoura, R.; Urano, K., Mechanism, kinetics, and equilibrium of thermal decomposition
128 of ammonium sulfate. *Ind. Eng. Chem. Process Des. Develop.* **1970,** *9*, (4), 489 - 494.
129 2. Kua, J.; Hanley, S. W.; De Haan, D. O., Thermodynamics and kinetics of glyoxal dimer
130 formation: a computational study. *J. Phys. Chem.* **2008,** *112*, (1), 66-72.
131 3. Whipple, E. B., The structure of glyoxal in water. *J. Am. Chem. Soc.* **1970,** *92*, (24), 7183-
132 7186.
133 4. De Haan, D. O.; Corrigan, A. L.; Tolbert, M. A.; Jimenez, J. L.; Wood, S. E.; Turley, J. J.,
134 Secondary organic aerosol formation by self-reactions of methylglyoxal and glyoxal in
135 evaporating droplets. *Environ. Sci. Technol.* **2009,** *43*, (21), 8184-8190.
136 5. Galloway, M. M.; Chhabra, P. S.; Chan, A. W. H.; Surratt, J. D.; Flagan, R. C.; Seinfeld, J. H.;
137 Keutsch, F. N., Glyoxal uptake on ammonium sulphate seed aerosol: reaction products
138 and reversibility of uptake under dark and irradiated conditions. *Atmos. Chem. Phys.*
139 **2009,** *9*, 3331-3345.

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