

Radical-initiated brown carbon formation in sunlit
carbonyl – amine – ammonium sulfate mixtures and
aqueous aerosol particles:

Supplemental Information

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Figures S1-S8, Table S1

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Calculations of average N per molecule. Once chemical formulas of product molecules were determined from the exact masses determined by mass spectroscopy, the area of each detected peak was multiplied by the number of N atoms in the chemical formula. These N-weighted peak areas were then summed for all peaks, and this sum was divided by the regular (non-N-weighted) sum of peak areas. The result is the average number of N atoms per detected product molecule, weighted by peak area.

Calculations of average number of conjugated double bonds per molecule. Once chemical structures of product molecules were proposed based on chemical formulas derived from exact masses determined by mass spectroscopy, the area of each detected peak was multiplied by the number of conjugated double bonds in its proposed structure (structures shown in Table 1). These conjugation-weighted peak areas were then summed for all peaks, and this sum was divided by the regular (non-conjugation-weighted) sum of peak areas. The result is the average number of conjugated double bonds per detected product molecule, weighted by peak area.

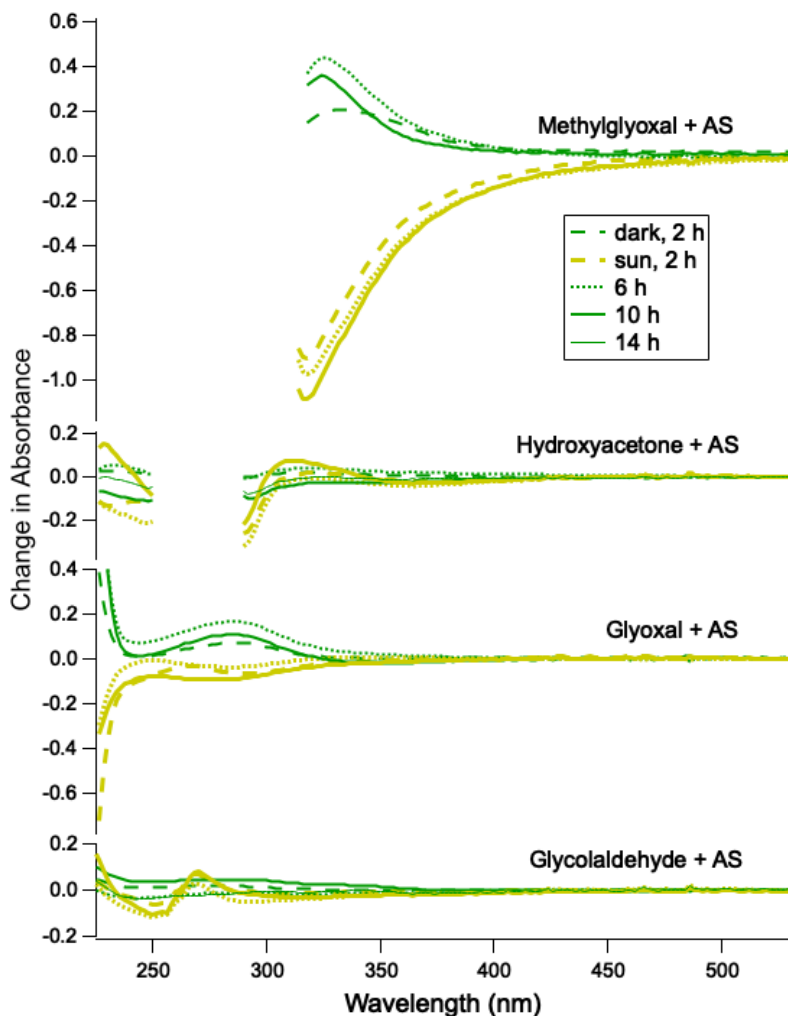


Figure S1: Changes in UV/vis absorption spectra of aqueous reaction mixtures containing 0.25 M carbonyl compound and 0.25 M ammonium sulfate after varying times of dark reaction at 21-28 °C (green lines) or reaction in sunlight at 23-35 °C (gold lines). All data is shown on equivalent vertical scale; gaps in data indicate off-scale

absorption readings, such that $\Delta Absorption$ cannot be calculated accurately. Reaction times are indicated by line type: 2h (dashed line), 6h (dotted line), 10h (thick solid line), and 14h (thin line, GAld and HA only). Color indicates light conditions: sunlight (gold) or dark (green).

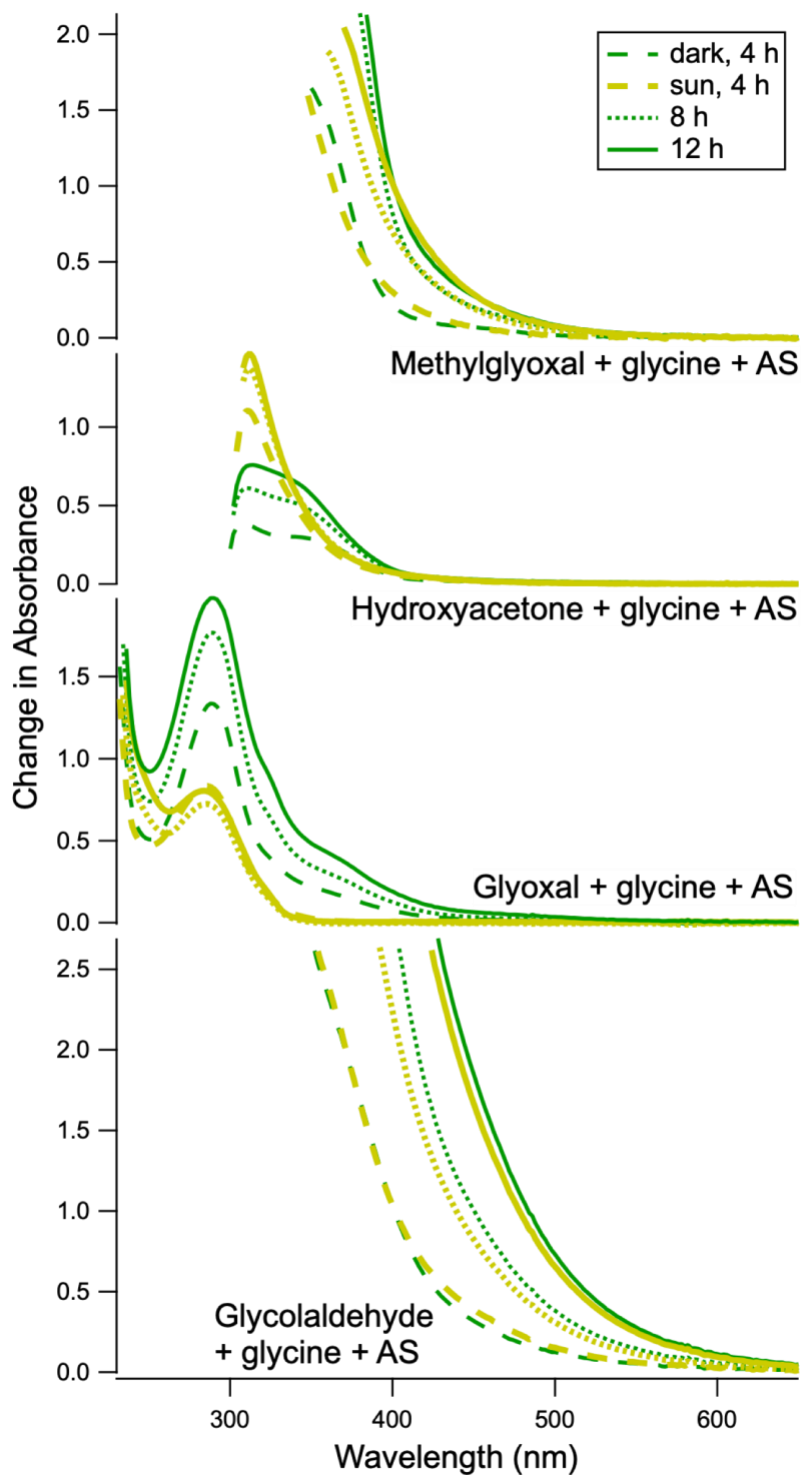


Figure S2: Changes in UV/vis absorption spectra of paired aqueous reaction mixtures containing 0.25 M carbonyl compound, 0.25 M ammonium sulfate, and 0.25 M glycine after varying reaction times in sunlight (gold lines) or dark conditions (green lines). Each sun/dark sample pair was temperature-matched to within 3 °C throughout reaction, except MG, where temperatures diverged by up to 8 °C. All data is shown on equivalent vertical scale; left end of each trace shown indicates off-scale

absorption readings, such that Δ Absorption cannot be calculated accurately. Reaction times: 4 h (dashed line), 8 h (thick dotted line), 12 h (solid line).

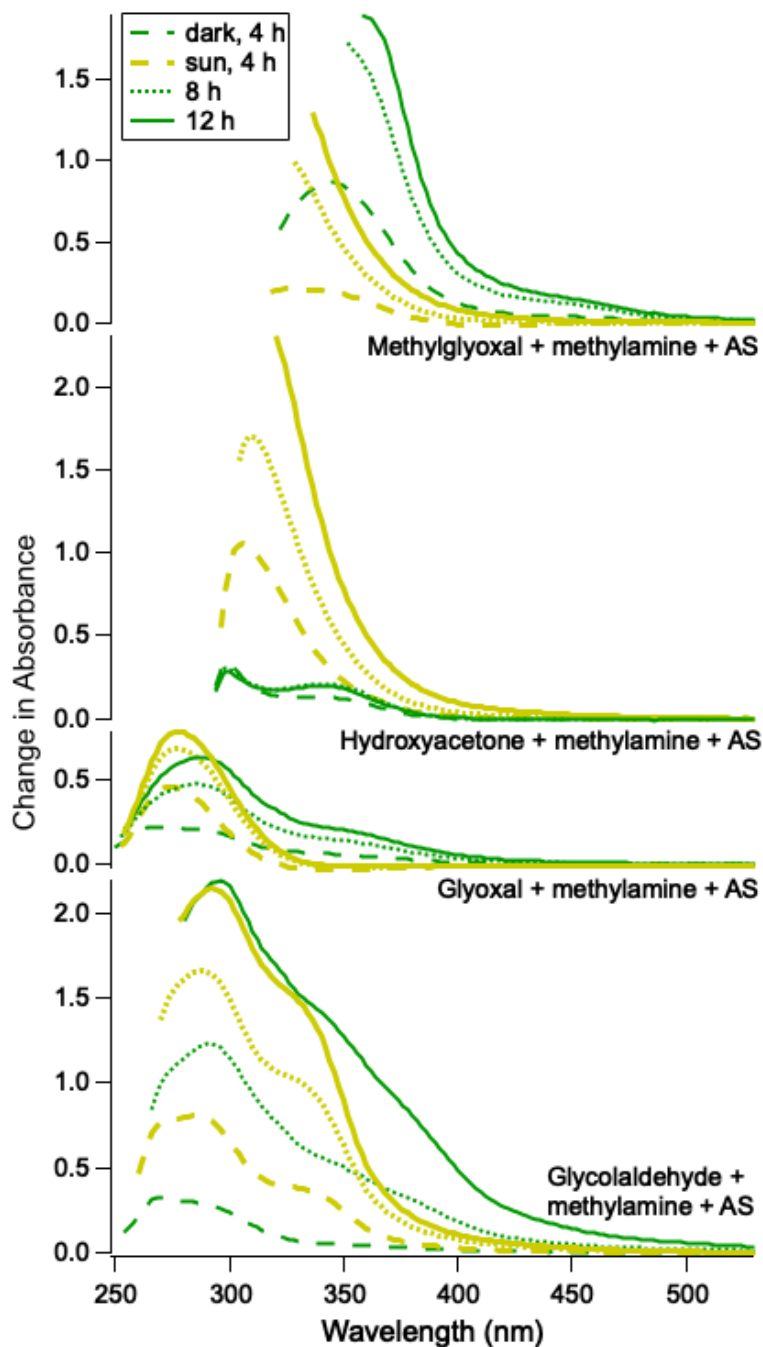


Figure S3: Changes in UV/vis absorption spectra of aqueous reaction mixtures after varying times of dark reaction (green) or reaction in sunlight (gold). Each mixture contained 0.25 M carbonyl compound, 0.25 M ammonium sulfate, and 0.25 M methylamine acidified to pH 4 with sulfuric acid. All data is shown on equivalent vertical scales for comparison; gaps in data on left indicate off-scale absorption readings, such that Δ Absorption cannot be calculated accurately. Reaction times: 4 h (dashed line), 8 h (dotted line), and 12 h (thick solid line).

Temperature matching between sun and dark samples was achieved for all samples except methylglyoxal, where the temperature of the sunlit sample exceeded the dark sample by as much as 8 C, causing extra brown carbon formation.

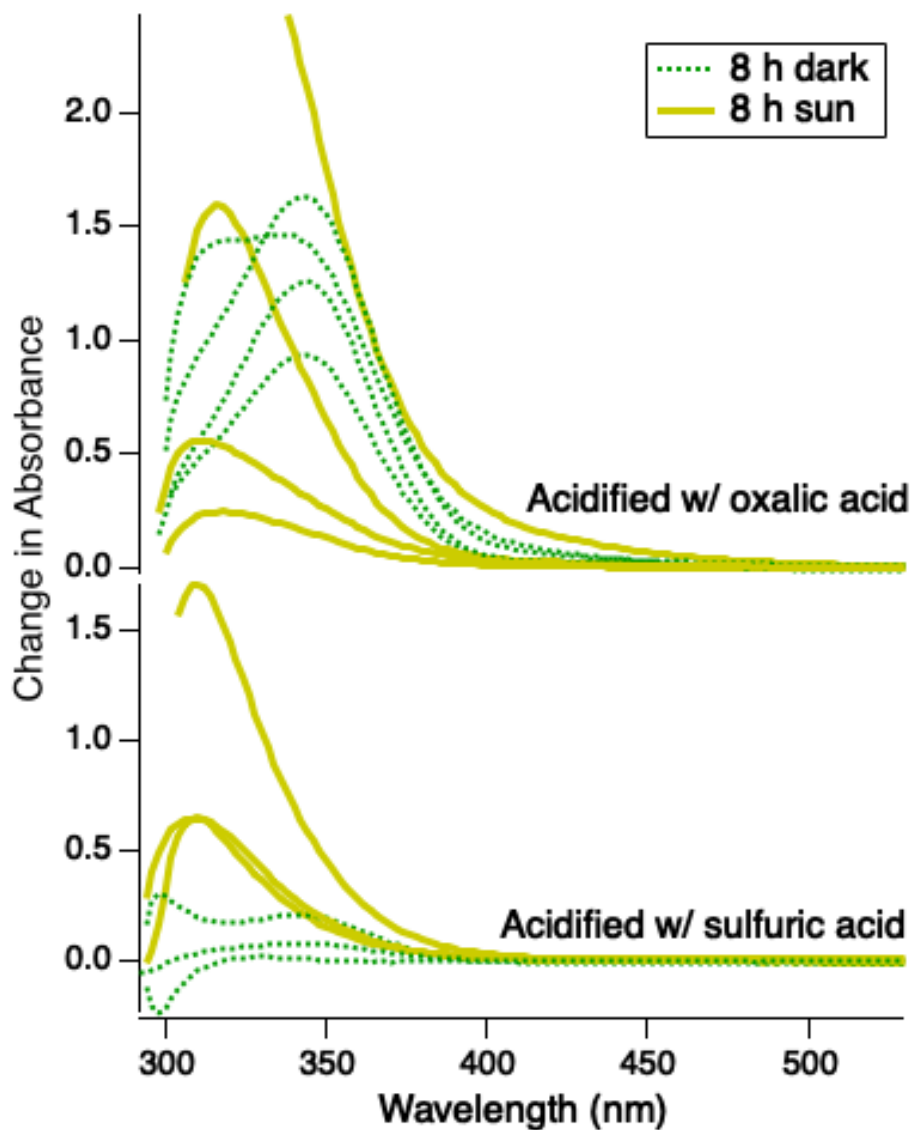


Figure S4: Changes in UV/vis absorption spectra after 8 h reaction of replicate aqueous mixtures containing 0.25 M each hydroxyacetone, methylamine, and ammonium sulfate, mixed and run on different days in sunlight (gold) or dark (green). Methylamine was acidified to pH 4 with oxalic acid (top panel) or H_2SO_4 (bottom panel).

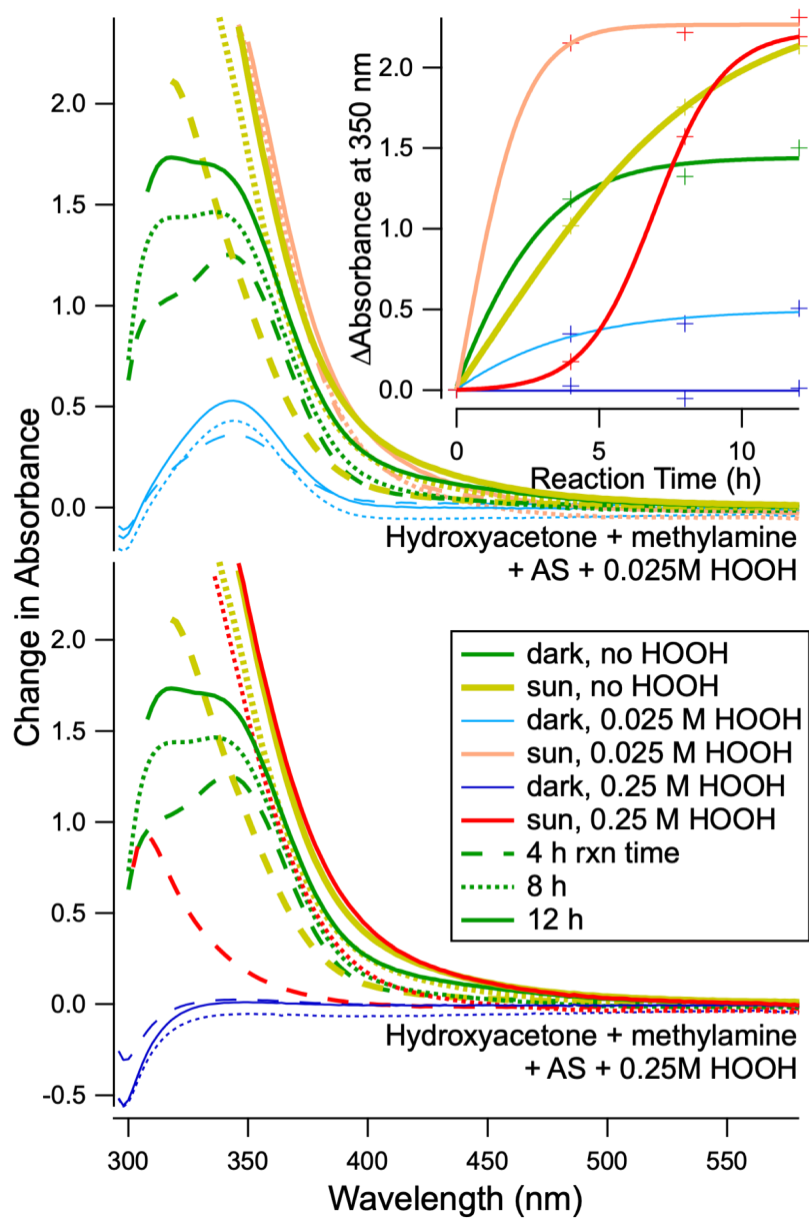


Figure S5: UV/vis absorption spectra of reaction mixtures containing 0.25 M HA, methylamine, and AS in sunlight (gold), dark (green), sunlight with HOOH (red), or dark with HOOH (blue). Top panel: Spectra of solutions with and without 0.025 M HOOH after 4 h (dashed lines), 8 h (dotted lines) and 12 h (solid lines) reaction times. Bottom panel: Effects of 0.25 M

HOOH (dark blue and dark red). Inset: Change in absorption at 350 nm vs time, using same color code. For parallel experimental data measured with glycine instead of methylamine as the amine species present, see Figure S8.

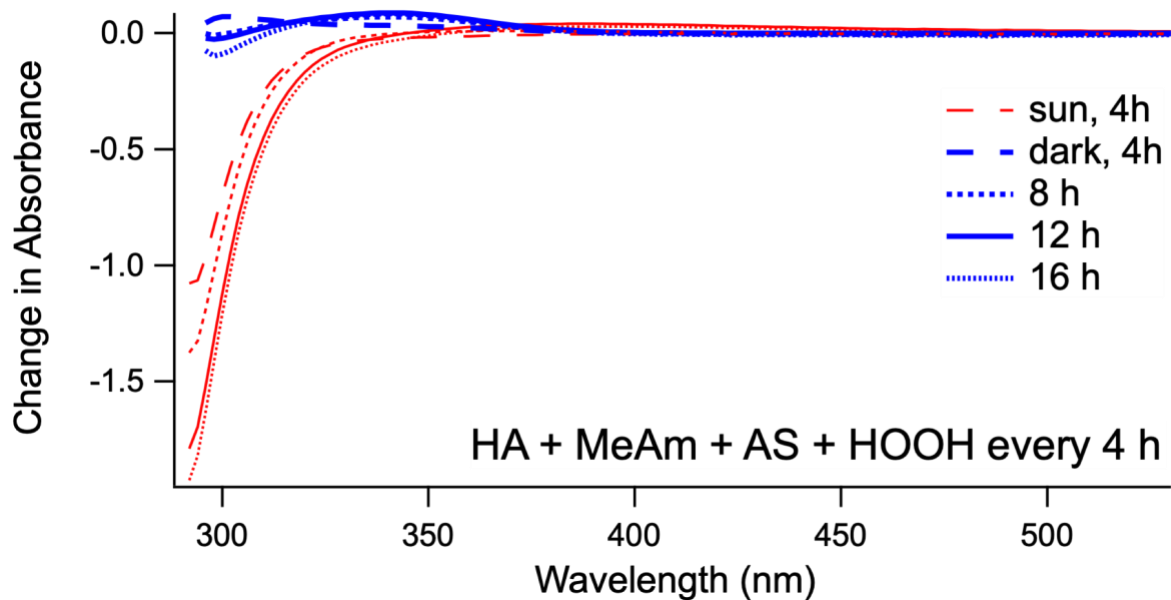


Figure S6: Changes in UV/vis absorption spectra during reaction of replicate aqueous mixtures containing 0.25 M each hydroxyacetone, methylamine, and ammonium sulfate, in sunlight (red) or dark (blue). Methylamine was acidified to pH 4 with H₂SO₄. All solutions had 0.25 M HOOH added at t = 0, 4, 8, and 12 h.

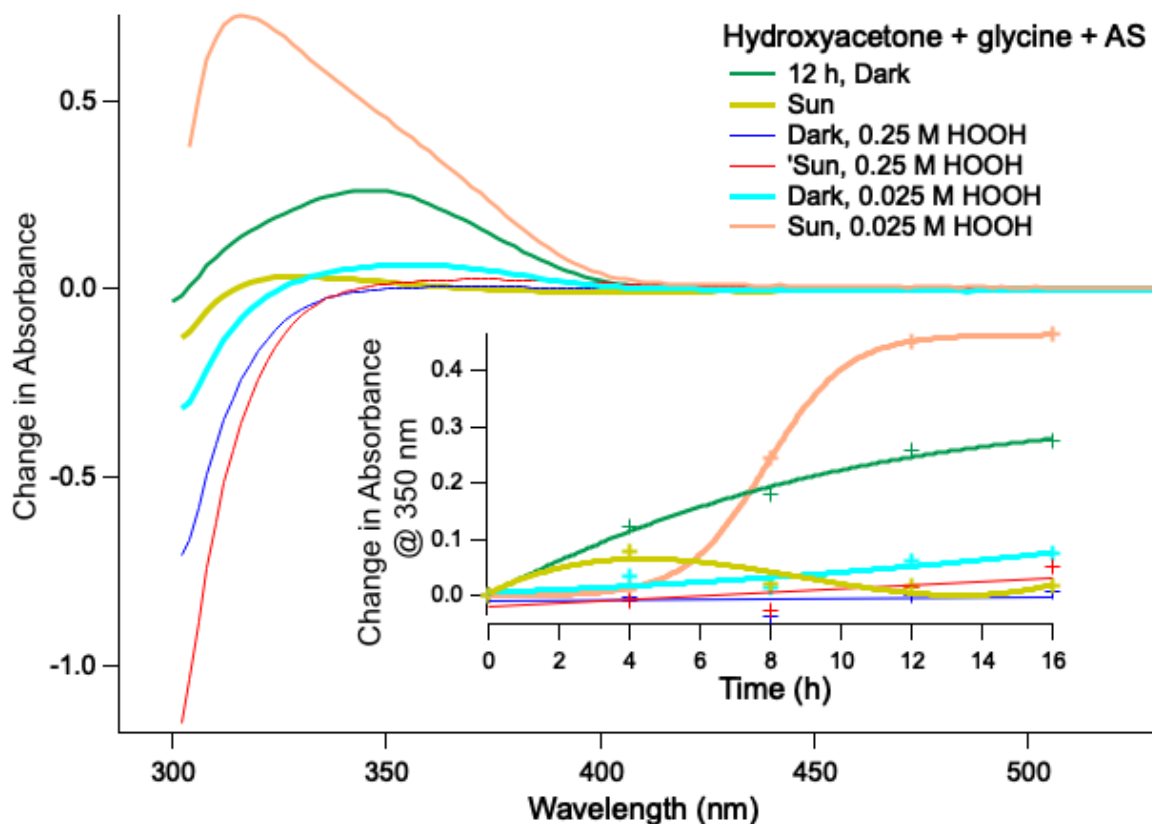


Figure S7: Changes in UV/vis absorption spectra during reaction of aqueous mixtures containing 0.25 M each hydroxyacetone, glycine, and ammonium sulfate after 12 h, in sunlight (gold) or dark (green), or with additional 0.25 M HOOH in sunlight (red) or dark (dark blue), or with 0.025 M HOOH in sunlight (orange) or dark (light blue). Inset: changes in absorption at 350 nm observed as a function of time.

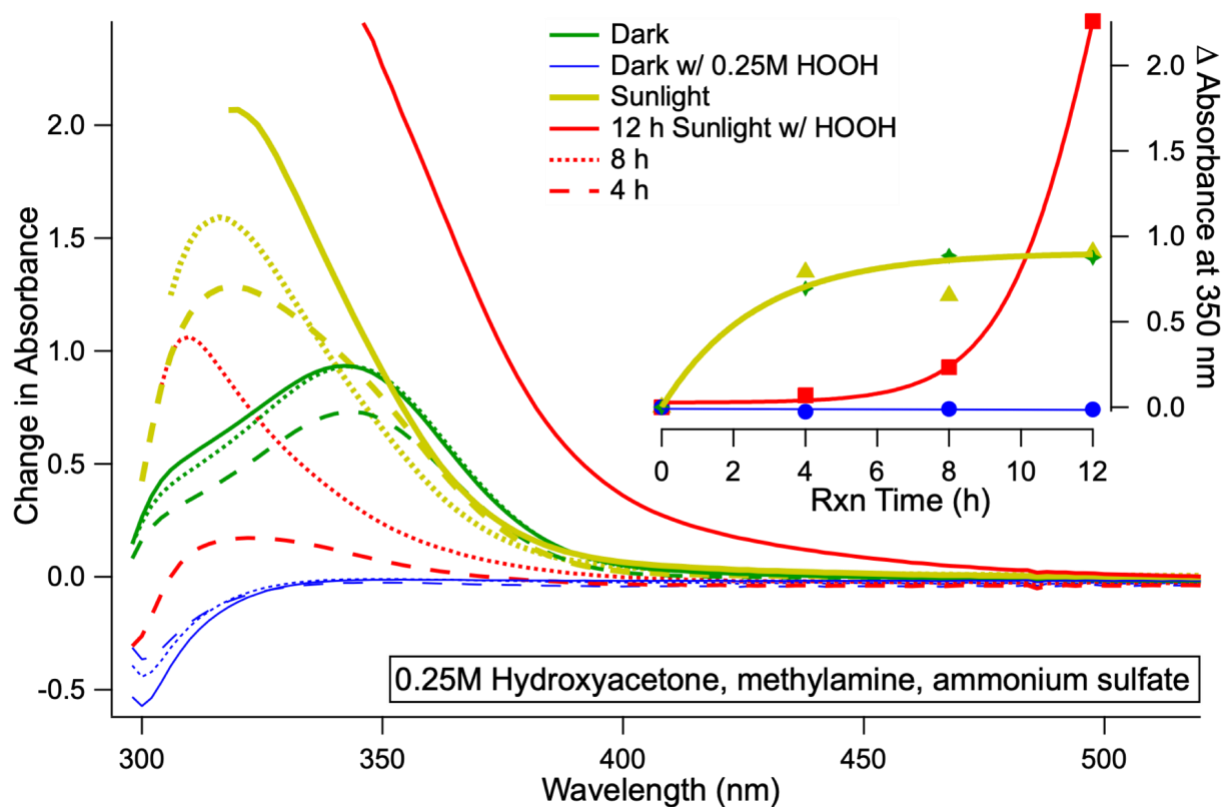


Figure S8: UV/vis absorption spectra of reaction mixtures containing 0.25 M hydroxyacetone, methylamine, and AS in sunlight (gold) with 0.25 M HOOH (red) and at same temperature in dark (green) with HOOH (blue) after 4 h (dashed lines), 8 h (dotted lines) and 12 h (solid lines) reaction times. Inset: Change in absorption at 350 nm vs time, using same color code.

Table S1: Summary of Large Chamber Conditions Used to Generate Aerosol for LC-ESI-MS Analysis

Expt	Seed type and amount ($\mu\text{g}/\text{m}^3$)	[MeAm] _g (ppm)	Oxid.	Aerosol mass on filter, (μg)	ESI-MS ions increased after chamber exposure: <i>m/z</i> and formula	Lights on?	Cloud events	RH range (%) ^a	Temp (°C)
1	Dry AS / glycine ^b	<0.05 (control)	O ₂	38	154.0526 C ₇ H ₇ NO ₃ (also in AS blank)	Yes	1 dark	<5-ss	18-22
2	Dry AS ^c	1.0	O ₂	30	none	No	1 dark	<5-ss	17-19
3	AS / MeGly ^d	2.0	O ₂	31	311.2191 C ₁₄ H ₂₆ N ₆ O ₂ 198.1477 C ₁₁ H ₁₉ NO ₂ 217.0500 C ₁₀ H ₁₀ O ₄ Na ⁺ 267.1928 C ₁₂ H ₂₂ N ₆ O 214.1188 C ₉ H ₁₅ N ₃ O ₃ 368.2410 C ₁₆ H ₂₉ N ₇ O ₃ 301.1410 C ₁₃ H ₂₀ N ₂ O ₆	Yes	1 sun	47-ss	14-17
4	MeGly ^e	2.0, then 1.0	O ₂	58	301.1410 C ₁₃ H ₂₀ N ₂ O ₆ 263.0555 C ₁₁ H ₁₂ O ₆ Na ⁺ 218.1140 C ₈ H ₁₅ N ₃ O ₄ 268.1769 C ₁₂ H ₂₁ N ₅ O ₂	No	1 dark	79-ss	15
5	MeGly ^e	2.0	H ₂ O ₂	31	214.1188 C ₉ H ₁₅ N ₃ O ₃ 202.1802 C ₁₁ H ₂₃ NO ₂ 161.0924 C ₆ H ₁₂ N ₂ O ₃ 243.1453 C ₁₀ H ₁₈ N ₄ O ₃	Yes	2 sun	72-ss	16

Notes: Expts. 1-2 are controls without methylglyoxal present. Expts. 3-5 explored chemical modification of AS/methylglyoxal and methylglyoxal seed particles upon exposure to methylamine gas, cloud processing, and simulated sunlight (in Expts. 3 and 5 only). **a:** All experiments reached supersaturation (ss) during cloud events. **b:** Solution containing 1.2 mM AS and 5 mM glycine atomized to form aerosol. **c:** Atomized from 1.85 mM AS solution. **d:** Solution containing 10 mM AS and 30 mM methylglyoxal atomized without drying into chamber at 52% RH. **e:** 100 mM methylglyoxal solution atomized without drying into chamber at 80% RH.