Organic matrix effects on the formation of light-absorbing compounds from α-dicarbonyls in aqueous salt solution

Greg T. Drozd, V. Faye McNeill*
Dept. of Chemical Engineering, Columbia University, New York, NY 10027

7 pages
5 figures
2 tables

1. Experimental Methods

A typical product formation experiment consisted of preparing solutions of Gly/mGly and ammonium sulfate, with or without an organic matrix of a simple sugar or sugar alcohol. The initial pH and UV-Vis spectrum were recorded, and then UV-Vis absorption spectra were recorded over a period of ~24 hrs, at which point the final pH was also measured.

Solution Composition and characteristics

All solutions had either 50 or 25 mL total volume and were mixed in 60 mL vials. Solutions were 0.1625 g/mL (1M) AS and 0.325 g/mL (0.78-2.86M) of organic matrix, giving an AS:Organic ratio of 2. The organic matrices were simple carbohydrates (Glucose, Fisher Scientific 98%; Sucrose, Sigma Aldrich 98%), sugar alcohols (Sorbitol, Sigma Aldrich 98%; Maltitol, Sigma Aldrich 99%), and glycerol (BDH, 99%). Solutions had an initial pH of 3; pH was measured using an Accumet 20 pH meter (Fisher Scientific). Glyoxal and methylglyoxal concentrations were kept constant at 0.2M.

The relative viscosities of the solutions were determined following the principle of a Cannon-Fenske viscometer, by measuring the time for a given volume of solution to flow through a capillary. An inverted syringe, with needle attached, was filled with 5mL of solution and the time required for the syringe to fully drain was recorded. The matrix solution viscosities were determined by relating them to measurements for the ammonium sulfate control solution (without the organic matrix). Assuming Hagen-Poiseuille flow[1],

$$\frac{\mu_{sol}}{\mu_{Control}} \cong \frac{\rho_{sol} \times \Delta t_{sol}}{\rho_{Control} \times \Delta t_{Control}} \quad (1)$$

where μ is viscosity, ρ is density, and Δt is the time required for the syringe to drain.

The solutions with an organic matrix present had a viscosity of ~1.78 +/-(0.1) times that of the control solution without an organic matrix, as shown in Table 1. For compounds with data available, these values are consistent with literature values of sugar solutions. As viscosity is directly related to reaction rate[2], this variation in viscosity, among the matrix solutions, should not greatly affect the production of light absorbing products.

The bulk polarities of the matrix solutions are described by their dielectric constants. The dielectric constants for ~20 wt% sugar and sugar alcohol solutions are slightly lower (~6-10%) than for pure water (80.3), ranging from 74.8 for the glycerol matrix to 72.7 for the sorbitol matrix (Table 1). While measurements are not available for the maltitol solution, the small variation for the rest of the matrix compounds with similar structures suggests it falls within this range

UV-Vis Spectroscopy

The formation of products was monitored with UV-Vis spectroscopy. Products from reaction of GLY and AS show peaks at 207nm and 280nm; those for MGLY and AS have a peak at ~200 and 280 nm. An HP 8453 UV-Visible Spectrophotometer was used to measure the UV-Vis absorption spectra of the reaction mixtures in a 1 mm path length quartz cuvette.

Aerosol-CIMS

A custom-built chemical ionization mass spectrometer (CIMS) using $H_3O^+ \cdot (H_2O)_n$ as the reagent ion was used to characterize the organic compounds formed with and without an organic matrix present. This instrument and its operation, as well as its application to detecting the reactions products of GLY and or MGLY+ AS, have been described previously [3]. 5-10ml of the sample solutions were diluted to 250ml in DI water and atomized. The aerosol produced was passed through a steel tube heated to 80-100°C to evaporate particle-phase organics for measurement of the resulting gas-phase organics in the CIMS.

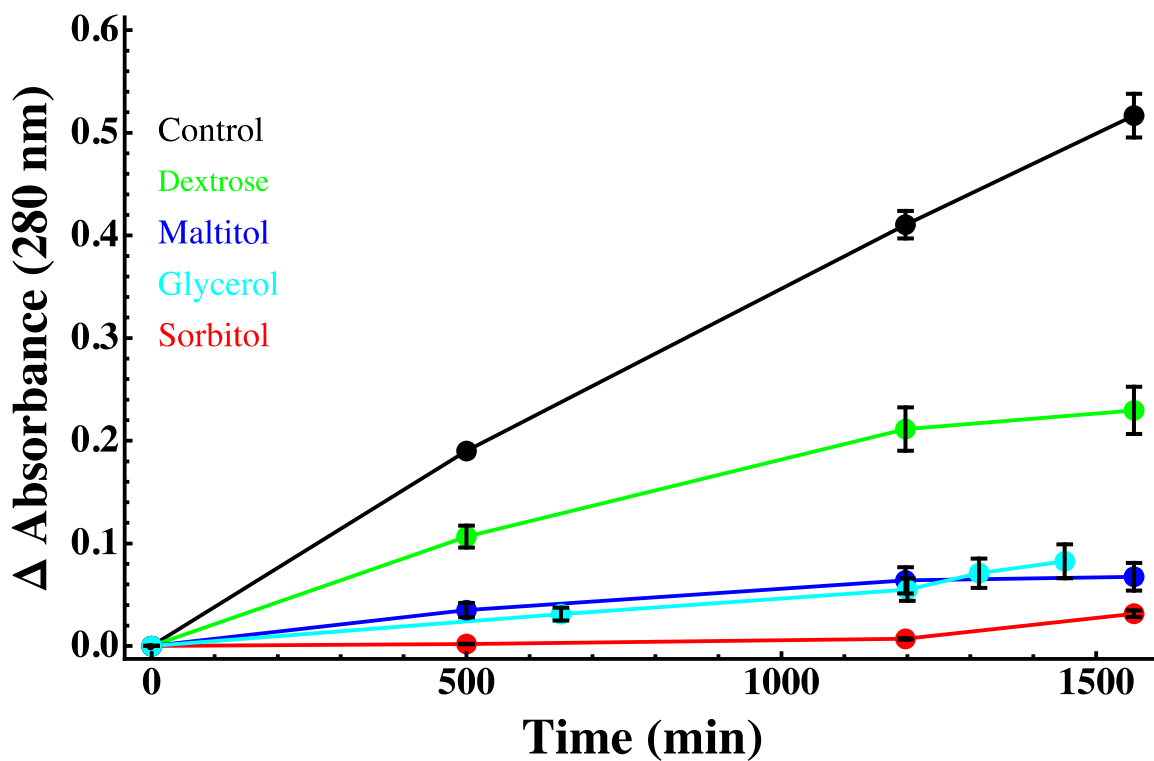## 2. Figures
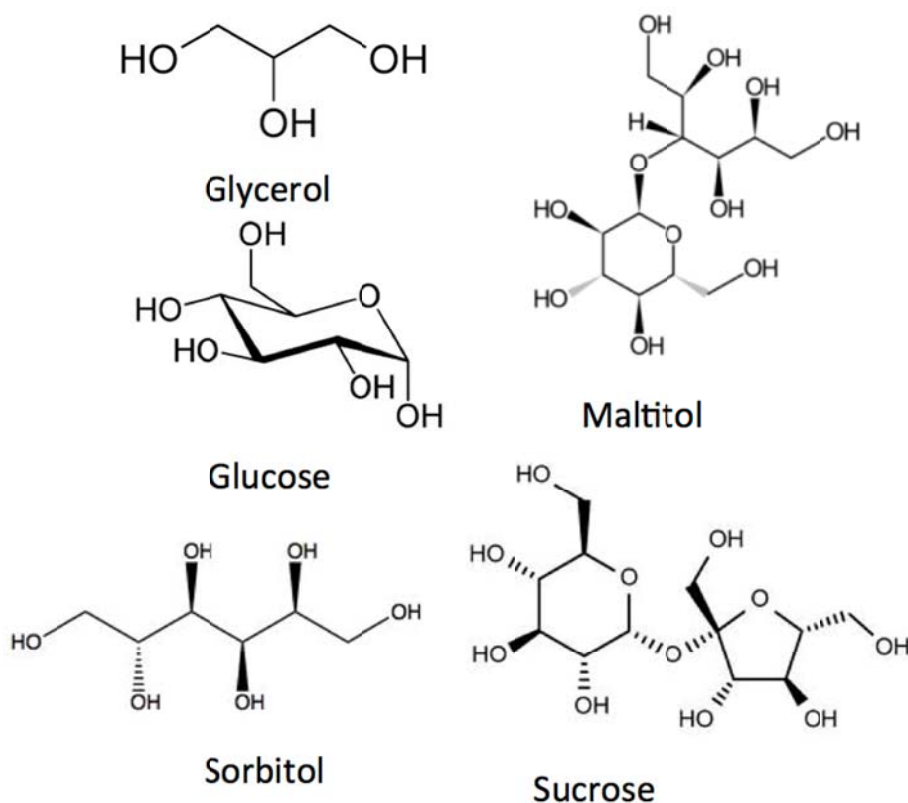
Figure S1. Structures of organic matrices used
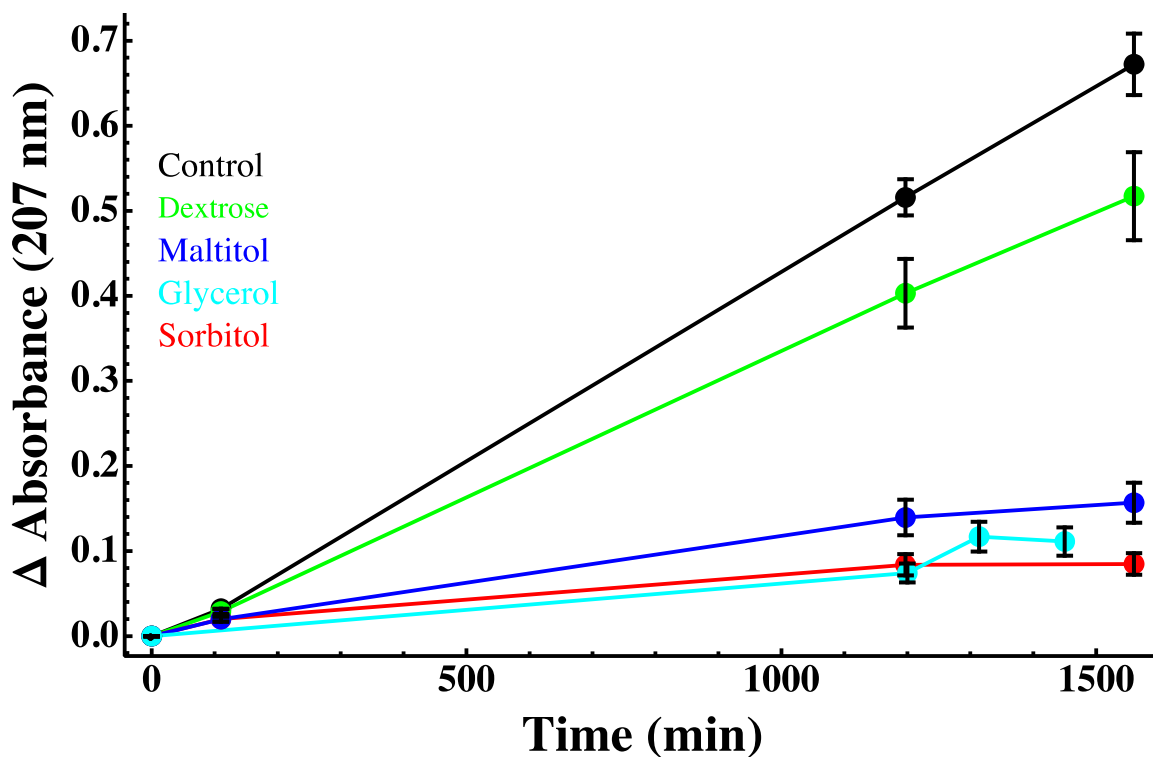
Figure S2. Time-dependent absorbance data for Gly + ammonium sulfate for three representative compounds: dextrose (green), maltitol (blue), glycerol (cyan), and sorbitol (red) over ~24hrs. Δ Absorbance is the increase in absorbance at 207 nm over the initial absorbance at 207nm at t_0 (i.e. background subtracted).

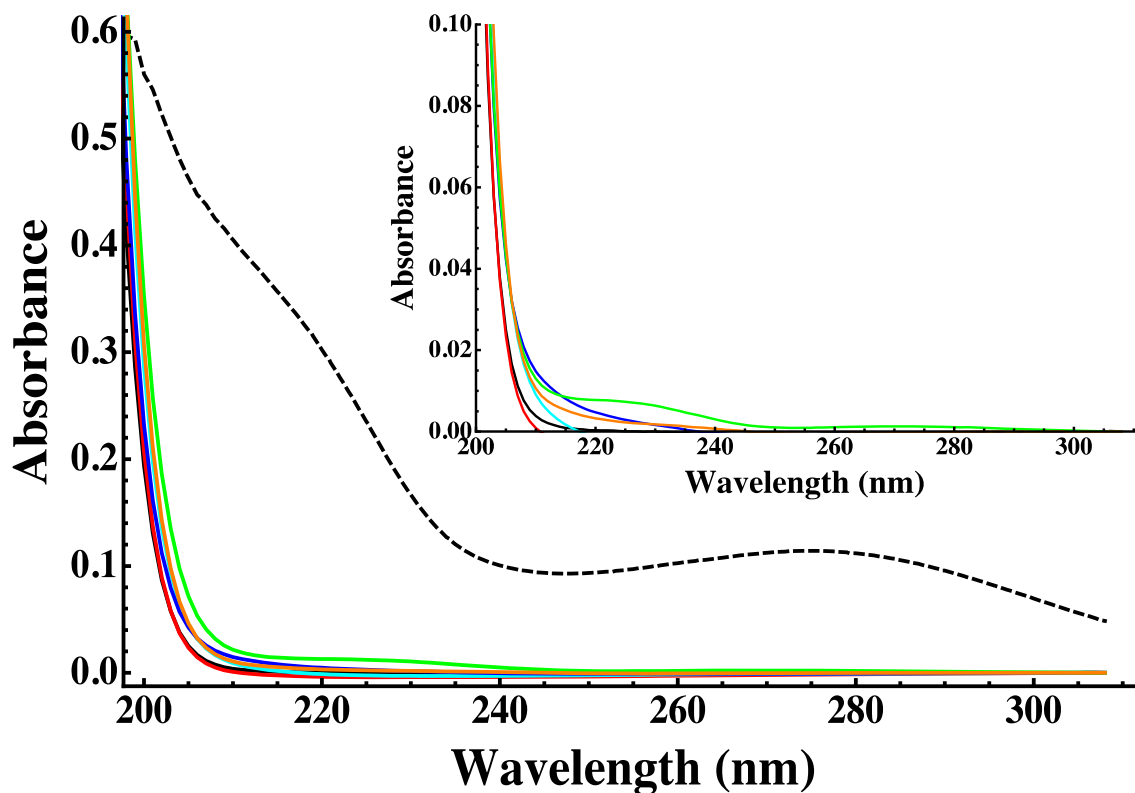Figure S3. Time-dependent absorbance data for mGly + ammonium sulfate for three representative compounds: dextrose (green), maltitol (blue), glycerol (cyan), and sorbitol (red) over ~24hrs. Δ Absorbance is the increase in absorbance at 280nm over the initial absorbance at 280nm at t_0 (i.e. background subtracted).

Figure S4. Background absorbance data for 1M ammonium sulfate with: water (black), and 6.5g/25mL glucose (red), sucrose (cyan), maltitol (orange), sorbitol (green), and glycerol (blue). The black, dashed line shows the absorbance of 1M ammonium sulfate with 0.2M methylglyoxal immediately after mixing; this spectrum has been divided by 6 to more clearly show all the spectra on the same axes. Absorption or scattering by all matrices appears negligible compared to the reaction mixture with mGly.
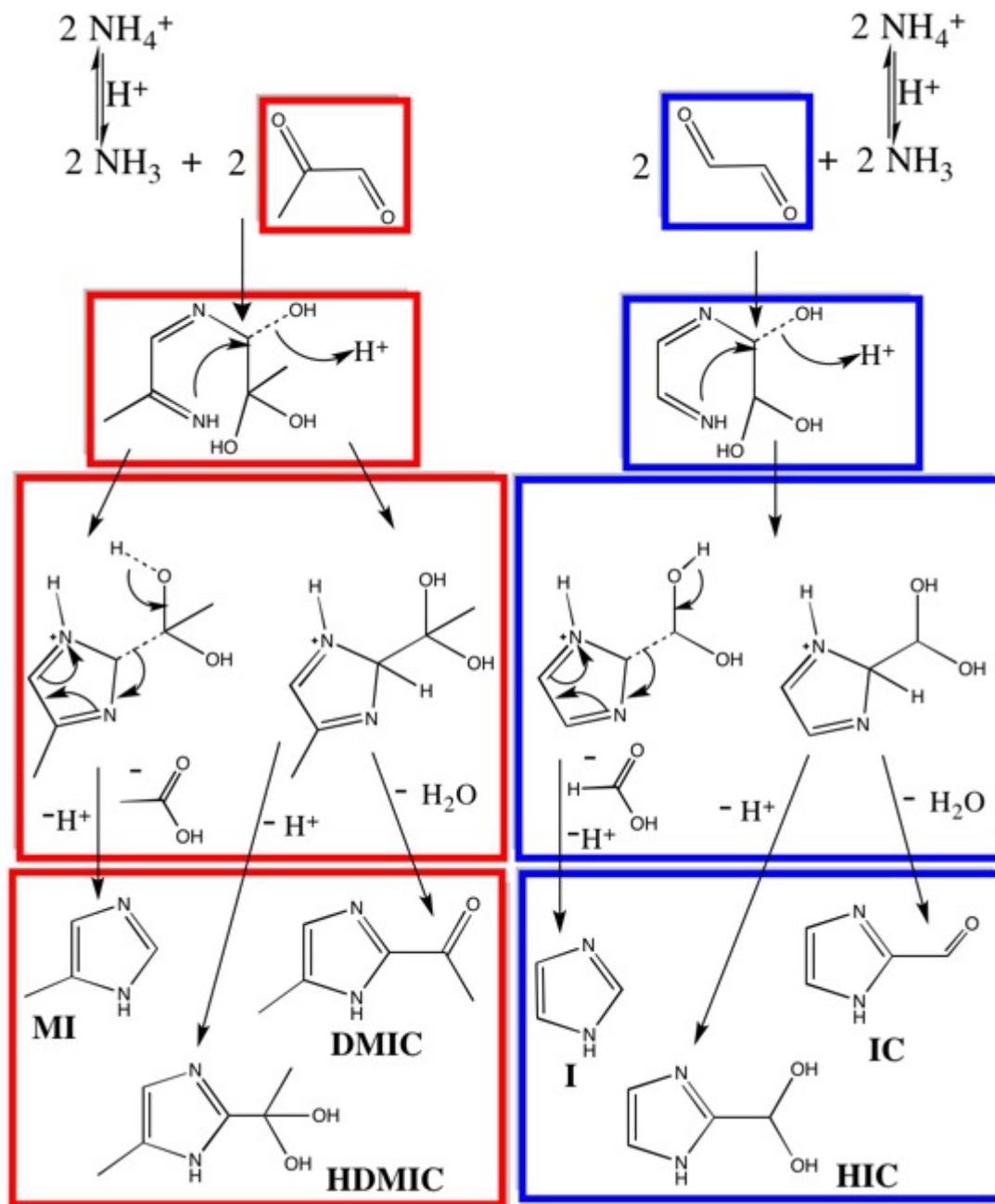
Figure S5. Mechanism of Gly and analogous mechanism for mGly reaction in concentrated ammonium sulfate solution.[4, 5] The first set of stable products are shown, with previous studies showing further addition of Gly (mGly) units occurring.[4] Oligomers of both Gly and mGly from condensation reactions have also been proposed and may also contribute to UV-Vis absorption.[3, 6-10]

m/z	Assigned compound	Molecular Formula	Ion Formula
81	BI[a]	$C_6N_4H_6$	$C_4N_2H_4(H^+)$
95	Hydrated Gly	$C_2O_4H_6$	$C_2O_4H_6 (H^+)$
97	IC[a,b]	$C_4O_1N_2H_4$	$C_4O_1N_2H_4(H^+)$
109	BI[a]	$C_6N_4H_6$	$C_4N_4H_4(H^+)$
115	GHIC[a]	$C_4O_2N_2H_6$	$C_4O_2N_2H_6(H^+)$
133	GHIC[a]	$C_4N_2O_2H_6$	$C_4O_2N_2H_6(H_3O^+)$
145	GI[a,b]	$C_5O_2N_2H_6$	$C_5O_2N_2H_6(H_3O^+)$
145	HGI[a,b]	$C_5O_3N_2H_8$	$C_5O_2N_2H_8(H^+)$
153	BI[a]	$C_6N_4H_6$	$C_6N_4H_6(H_3O^+)$
153	Gly Oligomers[b]	$C_4O_5H_6$	$C_4O_5H_6 (H_3O^+)$
163	GI[a,b]	$C_5O_2N_2H_6$	$C_5O_2N_2H_6(H_2O) (H_3O^+)$
163	HGI[a,b]	$C_5O_3N_2H_8$	$C_5O_2N_2H_8(H_3O^+)$
181	HGI[a,b]	$C_5O_3N_2H_8$	$C_5O_2N_2H_8(H_2O) (H_3O^+)$

Table S1. Mass assignments for mass spectra from Gly + NH_4^+. Abbreviations and references are given in the main text. [a] Kampf et al.[4] ;[b] Yu et al.[5] ; [c] Noziere et al.[8]

m/z	Assigned compound	Molecular Formula	Ion Formula
95	mGly Oligomer[a]	(oligomer fragment)	$C_2O_4H_6 (H^+)$
97	DMI[b]	$C_5N_2H_8$	$C_5N_2H_8 (H^+)$
101	4MI; 5-MI[b]	$C_4N_2H_6$	$C_4N_2H_6 (H_3O^+)$
109	mGly Hydrate[a]	$C_3O_2H_8$	
125	1,4-DMIC ; 1,5-DMIC[b,c]	$C_6O_1N_2 H_8$	$C_6O_1N_2H_8(H^+)$
126	Oligomer[a]	$C_6O_2N_1H_7$	$C_6O_2N_1H_7(H^+)$
143	1,4-DMIC ; 1,5-DMIC[b,c]	$C_6O_1N_2 H_8$	$C_6O_1N_2H_8(H_3O^+)$
143	HDMIC[c]	$C_6O_2N_2 H_{10}$	$C_6O_2N_2 H_{10} (H^+)$
144	mGly Oligomer[a]	$C_6O_3N_1H_9$	$C_6O_3N_1H_9(H^+)$
144	mGly Oligomer[a]	$C_6O_2N_1H_8$	$C_6O_2N_1H_8(H_3O^+)$
163	mGly Oligomer[a,d]	$C_6O_5H_{10}$	$C_6O_5H_{10}(H^+)$
165	mGly Oligomer[a]	$C_6O_4H_9$	$C_6O_4H_9(H_3O^+)$
181	mGly Oligomer[a,d]	$C_6O_6H_{12}$	$C_6O_6H_{12}(H^+)$
181	mGly Oligomer[a,d]	$C_6O_5H_{10}$	$C_6O_5H_{10}(H_3O^+)$

Table S2. Mass assignments for mass spectra from mGly + NH_4^+. Abbreviations and references are given in the main text. [a] Sareen et al.[3] ; [b] DeHaan et al.[11] ; [c] Analogous to Kampf et al.[4] ; [d] Nemet et al.[12]

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