**Atmospheric
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Light-absorbing secondary organic material formed by glyoxal in aqueous aerosol mimics

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Abstract

Light-absorbing and high-molecular-weight secondary organic products were observed to result from the reaction of glyoxal in mildly acidic (pH=4) aqueous inorganic salt solutions mimicking aqueous tropospheric aerosol particles. High-molecular-weight (500–600 amu) products were observed when ammonium sulfate (($NH_4)_2SO_4$) or sodium chloride (NaCl) was present in the aqueous phase. The products formed in the $(NH_4)_2SO_4$ solutions absorb light at UV and visible wavelengths. Substantial absorption at 300–400 nm develops within two hours, and absorption between 400–600 nm develops within days. Pendant drop tensiometry measurements show that the products are not surface-active. The experimental results along with ab initio predictions of the UV/Vis absorption of potential products suggest that an aldol condensation mechanism is active in the glyoxal-$(NH_4)_2SO_4$ system, resulting in the formation of pi-conjugated products. If similar products are formed in atmospheric aerosol particles, they could change the optical properties of the seed aerosol over its lifetime.

1 Introduction

Although secondary organic aerosol (SOA) formation has been the subject of study for many years, recent field measurements have revealed significantly more SOA than predicted by state-of-the-art atmospheric chemistry models (Heald et al., 2005; Volkamer et al., 2006). This suggests the existence of SOA precursors or mechanisms which have not yet been identified, or pathways which are known but not currently represented well in models. For example, the abundant biogenic VOC isoprene was recently identified as a major SOA source which was previously not included in models (Heald et al., 2005; Henze and Seinfeld, 2006; Kroll et al., 2006). It has also been suggested that SOA formation in urban areas from anthropogenic VOCs is underrepresented in models (Volkamer et al., 2006), and that the heterogeneous uptake of glyoxal (CHOCHO) by aerosols could be a significant source of unaccounted-for OA (Volkamer

et al., 2007).

Glyoxal is a first-generation gas-phase oxidation product of many biogenic and anthropogenic VOCs (Tuazon et al., 1984, 1986, 2005; Volkamer et al., 2001, 2005; Baker et al., 2005). Volkamer et al. (2007) observed glyoxal concentrations in Mexico City which were significantly lower than expected based on model predictions. After testing three scenarios with their model, they concluded that the missing sink of glyoxal was most likely irreversible heterogeneous uptake to aqueous inorganic aerosols with a reactive uptake coefficient of $\gamma \approx 0.0037$. They linked this missing sink to the 15–25% of observed SOA mass which was unaccounted for by models during the same Mexico City case study (Volkamer et al., 2006). The irreversible uptake of glyoxal by cloud droplets followed by dehydration is another likely pathway for SOA formation (Ervens et al., 2004, 2008; Carlton et al., 2007; Fu et al., 2008).

Glyoxal uptake to laboratory-generated aerosols has been studied by several groups (Jang and Kamens, 2001; Kroll et al., 2005; Liggio et al., 2005a, b; Hastings et al., 2005; Loeffler et al., 2006; Corrigan et al., 2008; Volkamer et al., 2008). It has been suggested that, for aqueous seed aerosols, uptake is followed by hydration and ester oligomer formation (Jang and Kamens, 2001; Hastings et al., 2005; Liggio et al., 2005a; Loeffler et al., 2006; Tong et al., 2006; Kua et al., 2008). Organosulfate products have also been observed (Liggio et al., 2005b). Some groups suggest the oligomerization process is acid-catalyzed (Jang and Kamens, 2001; Liggio et al., 2005). However, other laboratory and field studies do not support this mechanism (Kroll et al., 2005; Loeffler et al., 2006; Peltier et al., 2007; Volkamer et al., 2007). Oligomerization reactions may enhance the gas-particle partitioning of glyoxal to aqueous aerosols beyond what is predicted based on Henry's Law (Volkamer et al., 2007, 2008; Corrigan et al., 2008).

Laboratory and field studies provide further evidence for gas-phase VOC oxidation as a source of humic-like substances (HULIS) and oligomeric material in continental aerosols, with glyoxal being a potential reaction intermediate (Kalberer et al., 2004; Gao et al., 2006; Gomez-Gonzalez et al., 2008; Muller et al., 2008). Note that the terms "oligomer" and "HULIS" are both used in the literature to refer to moder-

ately large (~300–600 Da) organic molecules resulting from accretion reactions of smaller monomer species, and HULIS is sometimes also attributed with some additional properties of terrestrial humic or fulvic acid, such as aromaticity and light absorption. (Graber and Rudich, 2006) There is evidence that HULIS are surface active (Facchini et al., 1999; Kiss et al., 2005; Salma et al., 2006), although it has also been suggested that aggregate phases formed by HULIS and other large organic molecules may scavenge organic material from the aerosol surface (Tabazadeh, 2005).

Further laboratory studies are needed in order to evaluate the relative importance of glyoxal as a precursor of SOA material and HULIS in atmospheric aerosols, and how the uptake of glyoxal may affect the physical properties of the seed aerosol. To this end, we studied the formation of secondary organic products by glyoxal in mildly acidic (pH=4) aqueous inorganic salt mixtures. We used UV/Vis spectrophotometry, pendant drop tensiometry, and matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) to characterize the reaction products, and the kinetics of product formation were investigated. When ammonium sulfate ($(NH_4)_2SO_4$) is present in the aqueous phase, we find evidence of high-molecular-weight (up to 600 amu) products, and the mixtures absorb light at UV and visible wavelengths (300–600 nm). If these products are formed in atmospheric aerosol particles, they could change the optical properties of the seed aerosol over a period of hours to days.

2 Experimental

2.1 Sample preparation

Sample solutions were prepared using commercially available chemicals (Fisher Scientific, VWR, Alfa Aesar) and ultrapure water (Millipore) in batches of 100 mL or 250 mL. With the goal of mimicking a range of conditions relevant to aqueous atmospheric aerosols to the extent possible in a bulk system, solutions were made to be saturated in the inorganic salt of interest ($(NH_4)_2SO_4$, NaCl, Na_2SO_4) (Tang and Munkelwitz, 1994;

ACPD

9, 59–80, 2009

Light-absorbing SOA from glyoxal

E. L. Shapiro et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Tang et al., 1997). Glyoxal-containing solutions were prepared using 40 wt% aqueous glyoxal (Fisher Scientific). Solutions were initially composed of 3.11 M $(NH_4)_2SO_4$, 5.1 M NaCl, or 1.18 M Na_2SO_4, and glyoxal concentrations ranging from 0 M–2.21 M. In order to achieve a pH relevant to tropospheric aerosols (Keene et al., 1998; Keene and Savoie, 1998; Fridlind and Jacobson, 2000; Keene et al., 2002, 2004; Pszenny et al., 2004), dilute HNO_3 was added to the prepared salt stock solution dropwise until the mixure read pH=4 ($\pm$1) when tested with pH paper. Since the aqueous glyoxal stock solution itself was mildly acidic, in many cases no additional HNO_3 was necessary to acheive pH 4. Basic control solutions were prepared in an analogous manner using dilute NaOH.

2.2 UV/VIS spectrophotometry

UV/VIS absorption of the samples was characterized using an HP 8453 UV/Visible Spectrophotometer in the Columbia University Materials Research Science and Engineering Center (MRSEC) facility. A 10 mm open-top quartz cuvette (Agilent Technologies) was used in order to minimize interference below 200 nm. All measurements were taken at room temperature and ambient pressure.

2.3 MALDI-MS

A Voyager-DE MALDI mass spectrometer was used in order to test for the presence of high-molecular-weight products. The MALDI-MS was used in positive ion mode at 25 000 V. 2,5-dihydroxybenzoic acid (DHB) was used to make the matrix for all solutions following Karas et al. (1993). Briefly, 1 mg of DHB was added to 100 µL of a 9:1 water to ethanol mixture and 1 µL each of the sample and matrix mixture. The mixture was allowed to dry for ten minutes before analysis. Spectra of the matrix mixture alone were taken as a background reference.

2.4 Surface tension measurements

Pendant drop tensiometry (PDT) was used to measure surface tension. The PDT apparatus used in this study is similar to that described by Anastasiadis et al. (1987). Full experimental details are available in the supplementary material (http://www.atmos-chem-phys-discuss.net/9/59/2009/acpd-9-59-2009-supplement.pdf).

2.5 Ab initio calculations

To aid in the interpretation of the UV/Vis spectrophotometry data, Jaguar 6.0 (Schrödinger, Inc.) was used for ab initio predictions of the UV/Vis absorption of potential products. Geometries were optimized and vibrational frequency calculations were performed using density functional theory (DFT) with the B3LYP functional and the cc-pVTZ(-f) basis set (Kendall et al., 1992). Configuration interaction singles (CIS) calculations were then used for the excited states, again with the cc-pVTZ(-f) basis set (Foresman et al., 1992). Calculations took minutes to hours when performed on an Intel Core 2 Duo 3.16 GHz PC.

3 Results

All solutions containing $(NH_4)_2SO_4$ exhibited a color change visible to the naked eye within ~1 h of preparation, with a final color of yellow to dark brown depending on the initial concentration of glyoxal in the mixture.

3.1 UV/Vis absorption

Using UV/Vis spectrophotometry we observed that products of the glyoxal-$(NH_4)_2SO_4$ interaction absorb light at UV and visible wavelengths (see Figs. 1 and 2). Figure 1a shows the time evolution of the UV spectrum of a solution initially containing 2.21 M glyoxal over a period of 4 days. Absorbance at 277 nm is observed to increase linearly

until the maximum absorbance measurable with this instrument is reached at ~6 h. A second peak at 355 nm develops and increases in magnitude between 6–12 h. At 24 h the spectrum consists of a single broad absorption band that shifts to include longer wavelengths as time increases. Figure 1b shows the absorbance of this solution at 277 nm, 355 nm, and 550 nm as a function of time. The error bars shown reflect an uncertainty of ± 0.2 AU in the measured absorbances based on variation observed in the baseline signal, perhaps due to fluctuations in the intensity of the lamp or the temperature in the instrument room.

Spectra shown in Fig. 2a were measured 24 h after each solution was prepared. Figure 2b shows absorbance at 277 nm and 355 nm at 24 h as a function of intial glyoxal concentration. The peaks at 277 and 355 nm increase in magnitude and broaden with increasing initial glyoxal concentration, until at 2.21 M the spectrum consists of a nearly featureless broad absorption band.

Control experiments were performed as follows: UV/Vis absorption spectra were obtained for 1) an aqueous glyoxal solution containing no salt 2) an aqueous ammonium sulfate solution containing no glyoxal (see Fig. 2), and 3) an aqueous solution of 2.21 M glyoxal and 5.1 M NaCl, and 4) an aqueous solution of 2.21 M glyoxal and 1.18 M Na_2SO_4. Full results of the control experiments can be found in the supplementary material (http://www.atmos-chem-phys-discuss.net/9/59/2009/acpd-9-59-2009-supplement.pdf). The control samples appeared clear to the naked eye and did not absorb significantly at wavelengths above 300 nm. Glyoxal in aqueous solution has a weak, broad absorbance peak at 275 nm at ambient temperatures (Malik and Joens, 2000).

3.2 MALDI-MS

MALDI-MS analysis of the products of glyoxal in mildly acidic aqueous $(NH_4)_2SO_4$ solution revealed the presence of high-molecular-weight organic material, consistent with an accretion reaction. Normalized MALDI mass spectra of the samples and the matrix (background) are shown in Fig. 3. Multiple peaks with signal $\geq 2\times$ the matrix

background were present at mass-to-charge ratios ranging from ~500–600 amu.

Control experiments were performed as follows: MALDI mass spectra were obtained for 1) an aqueous glyoxal solution containing no salt 2) an aqueous ammonium sulfate solution containing no glyoxal, and 3) an aqueous solution of 2.21 M glyoxal and 5.1 M NaCl. No peaks above the matrix background were present in the spectra for solutions 1) and 2). For solution 3) multiple signal peaks were observed at 500–600 amu. Some, but not all, of the peaks overlap with the glyoxal-ammonium sulfate sample spectrum. Full results of the control experiments can be found in the supplementary material (http://www.atmos-chem-phys-discuss.net/9/59/2009/acpd-9-59-2009-supplement.pdf).

3.3 Surface tension measurements

The glyoxal/sulfate products were not observed to be surface active (see Fig. 4). Surface tension did not decrease with increasing glyoxal concentration compared to the surface tension of the pure ammonium sulfate solution.

3.4 Irreversibility of product formation

As a first-order test of whether the formation of the light-absorbing products was reversible, a 5 mL sample of a solution initially containing 2.21 M glyoxal and 3.11 M $(NH_4)_2SO_4$ was dehydrated overnight in a petri dish inside a vacuum oven at ambient temperature. A thick brown residue remained in the petri dish after dehydration, suggesting that product formation is irreversible over this time scale.

4 Discussion

Our observation of broad absorption at 300–600 nm as shown in Figs. 2 and 3 is similar to observations for HULIS or bulk WSOC isolated from atmospheric aerosols (Graber and Rudich, 2006; Hoffer et al., 2006). Ester oligomer products (Liggio et al., 2005a, b; Loeffler et al., 2006; Tong et al., 2006; Kua et al., 2008) and organosulfate products

(Liggio et al., 2005b; Surratt et al., 2007) have been reported previously for glyoxal reacting in aqueous inorganic aerosols. The results of our ab initio simulations of the excited states of the products reported in the literature are summarized in Table 1. Both the CIS and DFT simulations of the organosulfate molecules (a) (b) and (c) and the es-
5 ter products labeled (d) (e) and (f) suggest that none of these species, if present in the solution, would absorb at wavelengths >200 nm. Molecules (g) and (h) were investigated as possible aldol condensation products for glyoxal in the presence of ammonium sulfate. Products of this type were observed by Noziere and coworkers to result from the acid-catalyzed reactions of aldehydes in solution (Noziere et al., 2007; Noziere
10 and Esteve, 2007). These relatively small molecules (n=3 glyoxal monomers) were chosen in order to reduce the computational time required for the simulations. Both molecules are predicted to absorb strongly at >200 nm. In linear polyenes, the energy of the $\pi \rightarrow \pi^*$ transition will decrease with increasing chain length, resulting in higher absorption wavelengths for higher molecular weight species (Hudson and Kohler, 1974).
15 Therefore, it is possible that conjugated oligomeric molecules of this type could be responsible for the absorption at >400 nm observed at long times in this system. The excitation energies calculated using CIS are typically biased high by ~1 eV compared to experimental values (Dorogan, 2008). Therefore the absorption wavelengths we calculate may be biased low by as much as 80 nm, and correcting for this bias would
20 improve agreement between the CIS and DFT results.

MALDI-MS causes significant fragmentation (as evidenced by the matrix-only spectrum in Fig. 3), which makes it challenging to uniquely identify organic compounds using this technique. Nevertheless, it is clear that the observed peaks at ~500–600 amu correspond to parent molecules of a much greater molecular weight than the expected
25 *m/z* of products shown in Table 1 or their clusters with ammonium, sulfate, glyoxal, or water. This suggests that an accretion reaction is responsible for the observed peaks. To our knowledge this is the first direct observation of high-molecular-weight material formed by glyoxal reacting in aqueous inorganic aerosol mimics, although abundant indirect evidence for such a process exists in the literature (Kalberer et al., 2004; Hast-

ings et al., 2005; Loeffler et al., 2006; Gao et al., 2006; Gomez-Gonzalez et al., 2008; Muller et al., 2008).

The UV/Vis, MALDI, and ab initio simulation results taken together are consistent with an aldol condensation-type accretion reaction taking place in the ammonium sulfate solutions, resulting in the formation of unsaturated, pi-conjugated products. The evolution of the UV spectra with increasing time and initial glyoxal concentration suggests that the chemical identity, not just the quantity, of the light-absorbing products changed with these variables. Our observation that the high-molecular-weight products in the glyoxal-NaCl solution were not strongly light absorbing suggests that an alternate pathway for oligomerization dominates for the NaCl solutions, perhaps resulting in the formation of an ester-type oligomer product. If sulfate addition to the hydrated glyoxal monomer to form molecule (b) or (c) is an early reaction step when ammonium sulfate is present, this would likely inhibit the propagation of the ester polymerization reaction to form products such as (e), but the organosulfate monomer species still could participate in the aldol condensation mechanism, resulting in pi-conjugated organosulfate species such as molecule (h).

A simplified kinetics model of the polymerization reactions of glyoxal and an organosulfate monomer was developed in order to further aid in the interpretation of the UV/Vis data. The model results suggest that the immediate evolution of the product species absorbing at 277 nm (see Fig. 1b), along with its dependence on the initial glyoxal concentration (see Fig. 2b), is consistent with this product resulting from the direct reaction of glyoxal with itself or ammonium sulfate. The product or products absorbing at 355 nm appear after a delay of roughly 3 h and exhibit a power-law dependence on initial glyoxal concentration (exponent=1.65 ± 0.06), consistent with a second generation product (i.e., glyoxal reacting with the organosulfate monomer, or a higher order polymer of glyoxal). The species absorbing at $\lambda>500$ nm appear after a delay of ~12 h, suggesting a still higher-order product. Full details of the model used can be found in the supplementary material (http://www.atmos-chem-phys-discuss.net/9/59/2009/acpd-9-59-2009-supplement.pdf).

Based on the data shown in Fig. 1 for solutions initially containing 2.21 M glyoxal and 3.11 M $(NH_4)_2SO_4$ after 4 days, and estimating based on the MALDI-MS data that the species absorbing at $\lambda > 500$ nm are macromolecules formed by 9 glyoxal monomer units, a lower-bound estimate of the molar absorptivity of the 9-mer at 550 nm is

5    $\varepsilon \geq 3\,L\,mol^{-1}\,cm^{-1}$.

Surface tension measurements provide an indirect method for detecting film formation at the interface, since the presence of an organic surface film will reduce the surface tension of an aqueous solution. Our observation that the glyoxal/sulfate products in this system are not surface active distinguishes them from HULIS, which has been

10   found by many groups to be surface-active (Kiss et al., 2005; Salma et al., 2006; Badger et al., 2006). One limitation of the pendant drop technique is the large sample volume required (~100 µl) relative to a typical aerosol particle volume. The high surface area-to-volume ratio of a submicron aerosol particle means that a greater fraction of the surfactant molecules will partition to the interface, raising the number of molecules

15   that can be present before the critical micelle concentration is reached in the aerosol bulk (McNeill et al., 2006). Additionally, the small size of aerosol particles leads to supersaturated salt concentrations which are not accessible in this experiment (Tang et al., 1997; Tang, 1997; Tang and Munkelwitz, 1994). Increased salt concentration could lead to a "salting-out" effect and further surface partitioning of the organic material

20   (Setschenow, 1889).

5   Conclusions

We have observed the formation of light-absorbing and high-molecular-weight secondary organic products from the reaction of glyoxal in aqueous ammonium sulfate solutions at pH=4. The experimental results along with ab initio predictions of the UV/Vis

25   absorption of potential products suggest an aldol condensation mechanism. If similar products are formed in atmospheric aerosol particles, they could change the optical properties of the seed aerosol over its lifetime. Aqueous oligomerization reactions of

this type may enhance the gas-particle partitioning of glyoxal to aqueous aerosols.

Supplementary material available

Details of the pendant drop apparatus and technique, UV/Vis and MALDI-MS spectra of the control solutions, and details of the ploymerization kinetics model are available online in the supplementary material (http://www.atmos-chem-phys-discuss.net/9/59/2009/acpd-9-59-2009-supplement.acpd-2008-0590-sp1.pdf).

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Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄ ►►

◄ ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Light-absorbing SOA from glyoxal

E. L. Shapiro et al.

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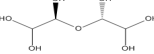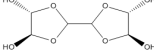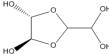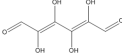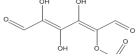
Light-absorbing SOA from glyoxal

E. L. Shapiro et al.

Table 1. Results of ab initio predictions for UV/Vis absorption of potential products. Results are shown from CIS/cc-pvtz(-f) and DFT B3LYP/cc-pvtz(-f) simulations (see text for details). The energy and corresponding wavelength of transitions with oscillator strength $f > 0.1$ are shown for the CIS simulations, and the energy of the HOMO-LUMO transition is shown for the DFT calculations. Only aldol condensation product molecules g) and h) are predicted to absorb strongly at UV/Vis wavelengths. References are indicated by: 1) Liggio et al. (2005b); 2) Surratt et al. (2007); 3) Jang and Kamens (2001); 4) Liggio et al. (2005a); 5) Loeffler et al. (2006); 6) Tong et al. (2006); 7) Hastings et al. (2005).

| Molecule	Ref.	CIS			DFT (HOMO-LUMO)	
		energy (eV)	λ (nm)	oscillator strength	energy (eV)	λ (nm)
a)	1	12.42 12.61	99.8 98.3	0.1362 0.2317	8.785	141.1
b)	2	10.41	119.1	0.2577	6.219	199.4
c)	1	11.23	110.5	0.1818	8.173	151.7
d)	3–6	11.26	110.1	0.1303	8.286	149.6
e)	4, 6	10.43 11.98	118.9 103.5	0.1076 0.2265	7.800	159.0
f)	4,5,7	none	N/A	N/A	7.647	162.1
g)	This work	4.840	**256.2**	0.8856	2.834	**437.6**
h)	This work	4.926 5.000	**251.7** **248.0**	0.5172 0.2654	3.547	**349.6**
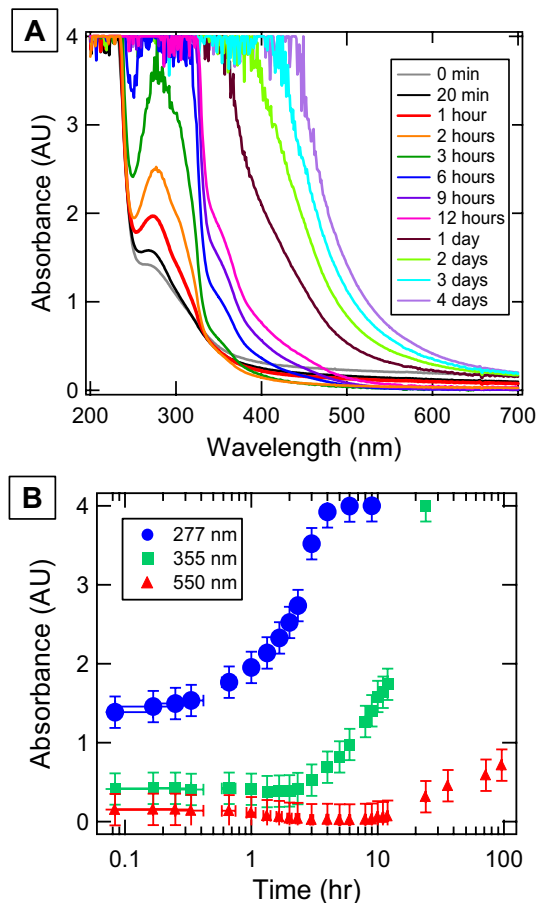
Fig. 1. Kinetics of product formation in an aqueous mixture containing 2.21 M glyoxal and 3.1 M $(NH_4)_2SO_4$ (pH=4). **(A)** Time series of UV/Vis spectra. **(B)** Time dependence of absorption at 277 nm, 355 nm, and 550 nm.
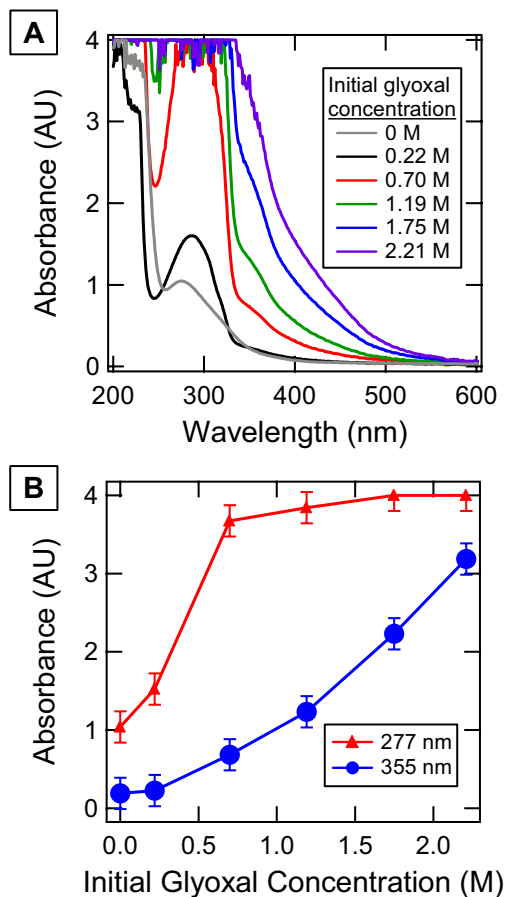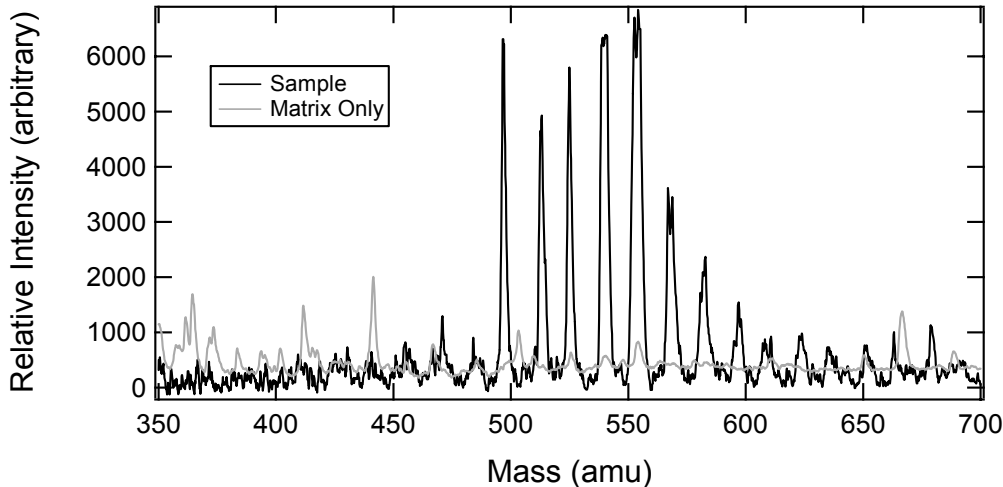
Fig. 2. Dependence of product formation on initial glyoxal concentration in an aqueous mixture containing 3.1 M $(NH_4)_2SO_4$ (pH=4). **(A)** UV/Vis spectra 24 h after mixing. **(B)** Initial glyoxal concentration dependence of absorption at 277 nm and 355 nm at 24 h.
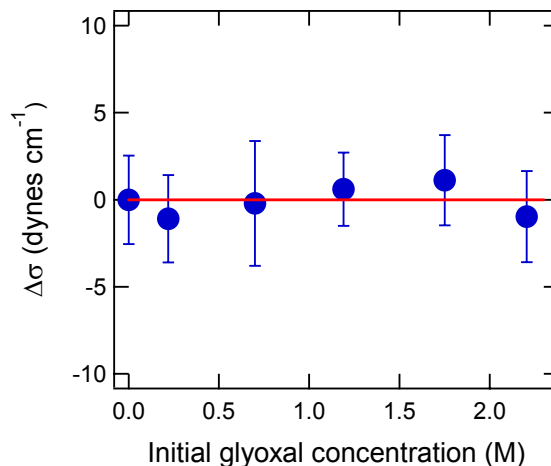
Fig. 3. MALDI-MS spectrum of the products of 2.21 M glyoxal reacting in a mildly acidic (pH=4) aqueous mixture containing 3.1 M $(NH_4)_2SO_4$. The measurement was made several days after mixing. Spectrum is also shown for the matrix only.

Fig. 4. The results of pendant drop tensiometry measurements of aqueous mixtures containing 3.1 M $(NH_4)_2SO_4$ (pH=4) as a function of initial glyoxal concentration, expressed as deviation in surface tension from that of the 0 M glyoxal solution. The measurements were made 24 h after mixing. Each point reflects the weighted average of three measurements, and the error bars represent the standard deviation in the raw data. The line at $\Delta\sigma=0$ is provided as a guide to the eye.