

**Atmospheric Oxalic Acid and SOA Production from Glyoxal:  
Results of Aqueous Photooxidation Experiments**

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## **Abstract**

Aqueous-phase photooxidation of glyoxal, a ubiquitous water-soluble gas-phase oxidation product of many compounds, is a potentially important global and regional source of oxalic acid and secondary organic aerosol (SOA). Reaction kinetics and product analysis are needed to validate and refine current aqueous-phase mechanisms to facilitate prediction of in-cloud oxalic acid and SOA formation from glyoxal. In this work, aqueous-phase photochemical reactions of glyoxal and hydrogen peroxide were conducted at pH values typical of clouds and fogs (i.e., pH = 4–5). Experimental time series concentrations were compared to values obtained using a current kinetic model and reaction rate constants from the literature. Experimental results demonstrate the formation of low volatility organic acids, namely glyoxylic and oxalic acids, as predicted by current aqueous phase mechanisms. However, these mechanisms poorly predict glyoxylic and oxalic acid concentrations and do not include other observed products. Observed oxalic acid yields from glyoxal are much greater than predicted by the initial mechanism and results suggest that large multifunctional compounds also form. An expanded aqueous-phase oxidation mechanism for glyoxal that reasonably explains experimental observations is proposed. Model predictions substantially improved using the expanded mechanism; the coefficient of determination for oxalic acid prediction was improved from 0.0003 to > 0.8. This work suggests that glyoxal, and its precursor volatile organic compounds (VOCs), are more effective in-cloud SOA precursors than previously predicted.

## **1. Introduction**

The generally poor understanding of the sources and formation of secondary organic particulate matter (PM) is a major source of uncertainty in predictions of aerosol concentrations and properties that affect health, visibility and climate (EPA, 2004; IPCC, 2001; Kanakidou et

al., 2005). There is growing evidence suggesting that, like sulfate, secondary organic aerosol (SOA) is formed through aqueous phase reactions in clouds, fogs and aerosols (Blando and Turpin, 2000; Warneck, 2003; Ervens et al., 2004; Crahan et al., 2004; Gelencser and Varga, 2005; Lim et al., 2005; Carlton et al., 2006; Altieri et al., 2006). However, this formation pathway is poorly understood. As was the case for sulfate, model simulation is needed to evaluate the regional and global importance of SOA formed as a result of aqueous phase atmospheric chemistry. This effort is hampered by the lack of kinetic data for recognized pathways and because many products and pathways are unknown.

A large gap between measurements and model predictions of organic PM was recently observed in the free troposphere (Heald et al., 2005). This discrepancy might arise from atmospheric processes not yet parameterized in current models, such as in-cloud SOA formation. In-cloud SOA formation is likely to enhance organic PM concentrations in the free troposphere and organic aerosol concentrations in locations affected by regional pollutant transport. Predictions and experiments provide strong support for the following. Alkene and aromatic emissions are oxidized in the interstitial spaces of clouds; the water-soluble products partition into cloud droplets where they oxidize further forming low volatility compounds that remain at least in part in the particle phase after droplet evaporation, forming SOA (Blando and Turpin, 2000; Warneck, 2003; Ervens et al., 2004; Crahan et al., 2004; Gelencser and Varga, 2005; Lim et al., 2005; Carlton et al., 2006; Altieri et al., 2006). Recent kinetic modeling supports in-cloud oxalic acid and thus SOA formation from glyoxal and other gas-phase precursors (Warneck, 2003; Ervens et al., 2004; Lim et al., 2005). Measured atmospheric concentration dynamics suggests that glyoxal is an in-cloud precursor for carboxylic acids (Chebbi and Carlier, 1996) that likely contribute to SOA due to their low volatility (e.g., glyoxylic and oxalic acids). Batch

photochemical experiments support the in-cloud SOA hypothesis through product analysis that demonstrates low volatility product formation from glyoxal (e.g., glyoxylic acid, Buxton et al., 1997) and pyruvic acid (e.g., glyoxylic and oxalic acids, Carlton et al., 2006, and large oligomeric compounds, Altieri et al., 2006; Guzman et al., 2006) at pH values typical of clouds. Differences between aqueous and gas phase chemistry suggest that SOA formation from aldehydes is more favorable in the aqueous phase than in the gas phase. The aqueous medium enables formation of new structures (i.e., gem diols) whose functional groups are oxidized during reactions with  $\cdot\text{OH}$  and other oxidants, while the C-C bond structure is initially preserved. In contrast, in the gas phase C-C bonds are usually broken yielding smaller, more volatile compounds (e.g., glyoxal oxidizes to form volatile compounds,  $\text{HO}_2$ ,  $\text{CO}$ ,  $\text{HCHO}$ , in the gas phase; Atkinson et al., 2006).

Glyoxal is the gas-phase oxidation product of many compounds of anthropogenic (Kleindienst et al., 1999; Atkinson, 2000; Volkamer et al., 2001; Magneron et al., 2005; Volkamer et al., 2005), biogenic (Atkinson, 2000; Spaulding et al., 2003), and marine (Miller and Moran, 1997; Warneck, 2003) origin. It is found widely in the environment in the gas and aerosol phases and in cloud, fog and dew water (Sempere and Kawamura, 1994; Matsumoto et al., 2005). While glyoxal is present at lower concentrations than  $\text{SO}_2$  (5 – 280  $\mu\text{M}$  in cloud water; Munger et al., 1990), at cloud relevant pH the water solubility of glyoxal (effective Henry's law constant,  $H_{\text{eff}} > 3 \times 10^5 \text{ M atm}^{-1}$  at  $25^\circ\text{C}$ ; Betterton and Hoffmann, 1988) is 3 orders of magnitude greater than that of  $\text{SO}_2$ . (Cloud processing is an important pathway for particulate sulfate formation from  $\text{SO}_2$ ; Seinfeld and Pandis, 1998.) Also, glyoxal has fast uptake by droplets (Schweitzer et al., 1998), is observed in cloud water (e.g., 5 – 280  $\mu\text{M}$  observed in California; Munger et al., 1990), and is highly reactive in the aqueous phase (Buxton et al.,

1997). Therefore, since glyoxal is ubiquitous in the environment, can enter a cloud or fog droplet readily, and is predicted to form low volatility compounds through aqueous-phase photooxidation, SOA formation through cloud-processing of glyoxal is likely. It is important to note that low volatility products (e.g., glyoxylic and oxalic acids) are expected from aqueous phase glyoxal oxidation but gas phase oxidation produces high volatility compounds (e.g., HO<sub>2</sub>, CO, HCHO) not expected to contribute to SOA directly (Ervens et al., 2004). Other similar water-soluble organics are found in clouds (Kawamura et al., 1996) and are likely to contribute to in-cloud SOA formation as well (e.g., methylglyoxal and glycolaldehyde; Warneck, 2003; Ervens et al., 2004; Lim et al., 2005).

Dicarboxylic acids are similarly ubiquitous in the atmosphere and oxalic acid is the most abundant dicarboxylic acid (Kawamura et al., 1996). Primary sources of oxalic exist (e.g. fossil fuel combustion), however they are insufficient to support measured ambient concentrations (Yu et al., 2005). There is growing evidence from atmospheric observations that oxalic acid is a product of cloud processing (Kawamura and Gagosian, 1987; Kawamura and Usukura, 1993; Chebbi and Carlier, 1996; Kawamura et al., 1996; Crahan et al., 2004; Yu et al., 2005; Sorooshian et al., 2006; Heald et al., 2006). For example, Crahan et al., (2004) measured in-cloud and below-cloud oxalate in the coastal marine atmosphere and found that, as for sulfate with a known in-cloud production mechanism, the in-cloud concentration was approximately three times the below-cloud concentration and the size distributions of sulfate-containing and oxalate-containing particles were similar. Sorooshian et al. (2006) compared measured and modeled in-cloud oxalate concentrations from the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT) study and concluded that cloud processing was the major source of atmospheric oxalate. They observed that 1) the detection frequency and

particulate oxalate concentration in cloud-free air parcels were significantly lower than for samples collected in-cloud, 2) the highest oxalate concentrations (aerosol and droplet residuals) were observed in clouds influenced by anthropogenic plumes, and 3) sulfate and oxalate were correlated though they are not linked by production chemistry.

Current aqueous phase models that predict in-cloud oxalic acid formation from glyoxal assume glyoxal is oxidized to glyoxylic acid and subsequently to oxalic acid (shaded pathway, Figure 1). However, organic product analysis in previous glyoxal aqueous oxidation experiments was limited to glyoxylic acid (Buxton et al., 1997); oxalic acid formation was not confirmed, nor was the potential formation of other low volatility products investigated. The controlled laboratory experiments and product analysis presented below demonstrate the formation of oxalic acid and other low volatility products from aqueous photooxidation of glyoxal at pH values typical of clouds. Detailed product analysis was used to identify major mechanistic revisions that enabled accurate prediction of oxalic acid formation in the reaction vessel. The expanded reaction mechanism can be used to refine cloud chemistry models. The formation of low volatility species through aqueous photooxidation of glyoxal provides support to the hypothesis that SOA forms through cloud processing.

## **2. Methods**

### *2.1 Batch Reactions*

Batch photochemical aqueous reactions of glyoxal (GLY) and hydrogen peroxide were conducted as described previously in detail (Carlton et al., 2006). Experimental conditions are listed in Table 1. UV photolysis of H<sub>2</sub>O<sub>2</sub> provided a source of ·OH for glyoxal oxidation. The UV source was a low pressure monochromatic (254 nm) mercury lamp (Heraeus Noblelight, Inc.

Duluth, GA) in a quartz immersion well in the center of a 1 L borosilicate reaction vessel (ACE Glass Inc., Vineland, NJ). For each experiment (GLY + UV + H<sub>2</sub>O<sub>2</sub>), three types of control experiments were performed: 1) GLY + H<sub>2</sub>O<sub>2</sub> without UV, 2) GLY + UV without H<sub>2</sub>O<sub>2</sub>, and 3) H<sub>2</sub>O<sub>2</sub> + UV without GLY.

Reaction solutions were prepared in 1L volumetric flasks and then poured into the reaction vessel. Solutions were continuously mixed, maintained at constant temperature and ambient UV penetration was minimized. All experiments began with oxygen-saturated solutions. Samples for H<sub>2</sub>O<sub>2</sub> and organic analysis were taken as follows. The first sample was taken directly from the volumetric flask. The second sample was taken immediately after the solution transfer to the reaction vessel, with a third sample taken after 5 minutes. Samples were then taken at ~ 10 minute intervals for the 1 hour experiment (Experiment 1) and ~ 30 minute intervals, with an extra sample during the first hour, for the 5+ hour experiment (Experiment 2). Hydrogen peroxide in the experiment and control samples was destroyed through the addition of catalase (H<sub>2</sub>O<sub>2</sub> → H<sub>2</sub>O) (0.25 μL/1 mL of sample) immediately after sampling (Stefan et al., 1996). Samples were stored frozen until analysis.

Initial glyoxal concentrations in the experiments were greater than those typically found in cloud and fog droplets (Matsumoto et al., 2005), but concentrations this high have occasionally been observed in the ambient atmosphere (Munger et al., 1995). It is worth noting also that cloud droplet evaporation leaves aerosol particles with very concentrated aqueous solutions (i.e., exceeding concentrations used in these experiments). End products and reaction rate constants for glyoxal experiments are not expected to be concentration dependent below 1M (above 1M, glyoxal polymerizes) ( Whipple, 1970; Kunen et al., 1983; Hastings et al., 2005).

Reaction solutions were prepared with excess oxidant in order to have pseudo-first order kinetics with regard to glyoxal. However, initial oxidant levels were limited by the need to keep quenching times (i.e., time to completely destroy H<sub>2</sub>O<sub>2</sub> in the samples) short and maintain laboratory safety (e.g., by using H<sub>2</sub>O<sub>2</sub> concentrations and H<sub>2</sub>O<sub>2</sub>-to-catalase ratios that have been previously employed; Stefan et al., 1996). The quenching time was less than 2 minutes for the first sample and sharply decreased with time as the H<sub>2</sub>O<sub>2</sub> concentration in the reaction solutions decreased. Initial modeling using state-of-the-art aqueous phase mechanisms for glyoxal (Ervens et al., 2004; Lim et al., 2005) suggested that the initial conditions of Table 1 would yield intermediate and end product concentrations that would be sufficiently above detection limits on the time scale of the experiments.

## *2.2 Analytical Procedures*

### *2.2.1 HPLC-UV/vis analysis of Organic Acids*

Organic acid analysis is described in detail in the supporting information of Carlton et al. (2006). Briefly, all standards and samples were analyzed in triplicate for carboxylic acids by high performance liquid chromatography (HPLC) with UV absorbance detection at 205 nm (Beckman Coulter, System Gold, Fullerton, CA). The HPLC employed an Alltech, organic acid ion exclusion column (OA 2000) with the corresponding guard column. The stationary phase was sulfonated polystyrene divinylbenzene and is specifically designed to retain only compounds with organic acid and/or alcohol functional groups ([www.alltechweb.com](http://www.alltechweb.com)). Compounds containing multiple functional groups are expected to interact with the column multiple times and generate broad peaks. Compounds without these functionalities, should they be present, are not retained by the column and elute immediately. In the chromatogram unretained products are

contained within the void volume, the initial peak associated with sample injection. The mobile phase was H<sub>2</sub>SO<sub>4</sub> (pH = 2.3); the flow rate was 0.7 ml min<sup>-1</sup> and the column temperature was maintained at 45 °C. The mean absorbance ( $\pm$  1 standard deviation of triplicate analyses) was used for quantitation. Multivariate HPLC calibration was performed by partial least squares (PLS) regression (Martens and Naes, 1989) with Statistical Analysis System software (SAS; V8.2, Cary, NC) using 25 mixture standards with an orthogonal design (Brereton, 1997) spanning the range of sample concentrations. Formic and acetic acids were calibrated with single component standards, also at five concentration values spanning the range of sample concentrations. Glyoxal and catalase were analyzed alone and added to 12% of the calibration standards. Neither was detected in the chromatograms, and chromatograms of standards with and without glyoxal and catalase were indistinguishable. (Glyoxal was detected by electrospray ionization-mass spectrometry, ESI-MS see below) Ten percent of the mixture standards were re-analyzed and independent single component standards were analyzed to assess analytical accuracy. Recoveries for individual acids were calculated by placing standards in the reaction vessel and sampling the solution as for experimental samples. Ten percent of experiment samples were collected in duplicate to determine method precision.

### 2.2.2 Hydrogen Peroxide

Hydrogen peroxide in the time series samples was quantified by the triiodide method (Klassen et al., 1994) within 1 hour of sampling. Solutions were prepared according to Allen et al. (1952) and were not stored longer than one month. Calibration was performed with 5 H<sub>2</sub>O<sub>2</sub> concentration values and a blank of milli-Q water (18 M $\Omega$ ). All samples were analyzed in triplicate, one calibration standard was re-analyzed after sample analysis and one independent

standard was analyzed during calibration. Method detection limits were determined from analysis of 8 independent blank solutions, 8 times.

### 2.2.3 Photon Flux

The lamp intensity was measured before and after the glyoxal experiments using iodide-iodate actinometry (Rahn et al., 2003). Briefly, a 1 L actinometer solution of 0.6M KI, 0.1M KIO<sub>3</sub> and 0.01M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (borax) at pH 9.25 is prepared immediately prior to the photon flux measurement. The reactor is filled with actinometer solution and exposed to the mercury lamp. Samples are collected as quickly as possible (~ every 40 sec.). The absorbance of the solution is measured immediately with a spectrometer at 476 nm. An absorbance blank of milli-Q water was subtracted from the sample absorbances for photon flux calculations, described below. The intensity of the irradiation source received by solutions in the reaction vessel was calculated using the method described by Murov (1973).

### 2.2.4 ESI-MS

Selected samples were analyzed by electrospray ionization mass spectrometry (ESI/MS; HP-Agilent 1100) as described previously (Seitzinger et al., 2005; Altieri et al., 2006). Qualitative ESI results are presented here. An autosampler injected sample solutions (20 µL) from individual vials into an LC system which introduces the sample into the ESI source region. All samples were analyzed with no LC column attached. The mobile phase was 60:40 v/v 100% methanol and 0.05% formic acid in deionized water with a flow rate of 0.220 mL min<sup>-1</sup>. Samples were analyzed in the negative and positive mode over the mass range 50-1000 amu with a fragmentor voltage of 40 V and a capillary voltage of 3000 V. Nitrogen was the drying gas (350°C, 24 psig, 10 L min<sup>-1</sup>). The unit mass resolution spectra were recorded on Agilent

software (Chemstation version A.07.01) and exported to Access and Excel (Microsoft, Inc.) for statistical analysis and interpretation.

The ESI-MS uses a soft ionization process that does not fragment compounds at the low voltages used and provides molecular weight information with unit mass resolution. The positive ionization mode protonates compounds with basic functional groups (e.g. methyl, carbonyl) while the negative ionization mode deprotonates compounds with acidic functional groups (e.g. carboxylic acids). Single and mixed standards of glyoxal, glyoxylic acid and oxalic acid (plus H<sub>2</sub>O<sub>2</sub> at a 1:2 ratio and catalase (0.5%)) were analyzed using the same instrument conditions as the experimental samples (see Supporting Information, Figure S-1). Oxalic acid (*m/z* 89) and glyoxylic acid (*m/z* 73) were detected as monomers in the negative mode as would be expected for carboxylic acids (Figure S-1). Glyoxal was detected in the positive mode as a dimer (*m/z* 117; 2MW+ 1). Aldehyde dimerization is common during ESI analysis, in particular for glyoxal (Hastings et al., 2005; Loeffler et al., 2006). In addition to the glyoxal dimer ion, a second qualifying ion (*m/z* 131) was detected for glyoxal. The composition of this ion is unknown, but it appears in concert with the main glyoxal ion, and linearly increases in ion abundance when glyoxal concentration increases. The qualifier ion was used for identification purposes only.

#### 2.2.5 Dissolved Organic Carbon, pH, Dissolved Oxygen and Temperature

Samples were analyzed for bulk dissolved organic carbon (DOC) using a Shimadzu 5000A high temperature combustion analyzer (Sharp et al., 1993). The initial and final pH (Oakton Instruments Vernon Hills, IL) and dissolved oxygen (DO; YSI Inc., Yellow Springs, OH) concentrations were also measured. The pH meter was calibrated at pH = 4, 7, and 10; verification standards (pH = 2, H<sub>2</sub>SO<sub>4</sub>; pH = 3, HClO<sub>4</sub>) were analyzed each day of use. DO

readings were verified daily using O<sub>2</sub>-saturated solutions with known saturation values.

Temperature was measured throughout the experiment with an alcohol thermometer that was verified  $\pm 2$  °C at two temperatures.

### *2.3 Modeling*

Carboxylic acid concentration time profiles were predicted using a commercially-available differential equation solver (FACSIMILE; AEA Technology, Oxfordshire, UK). Initial kinetic modeling was based on the aqueous-phase mechanism of Ervens et al. (2004) which is summarized in Figure 1 (shaded pathway) and reactions 1-16 in Table 2. The corollary anion reactions and the acid/base equilibria are not depicted in Figure 1 though they occur (Stefan et al., 1996; Ervens et al., 2003) and were included in the model. The concentration of ·OH was not explicitly measured; the ·OH concentration time series was predicted (Table 2, reactions 1-4; Liao and Gurol, 1995) and the accuracy of these predictions was verified with H<sub>2</sub>O<sub>2</sub> measurements as shown below. After examination of the concentration dynamics of products, an expanded reaction mechanism was proposed (all pathways, Figure 1; all reactions, Table 2). The expanded mechanism, measured concentrations and the differential equation solver were used to fit unknown reaction rate constants and predict the formation of newly identified products.

## **3. Quality Control Results**

### *3.1 Organic Measurements*

The HPLC analysis was used for identification and quantification of compounds while the ESI-MS analysis was used only for identification of compounds. The PLS and single acid calibrations described more than 96% of the variance in concentration of each carboxylic acid in

the complex mixture standards analyzed by the HPLC. Quality control measures for organic acids are given in Table 3. Recoveries were high, and the lowest recovery (80%) was obtained for the most volatile compound (formic acid) as expected. (Formic acid concentrations were corrected for recoveries.) Method detection limits were determined from analysis of eight “organic control” (i.e., H<sub>2</sub>O<sub>2</sub> and UV) samples (Greenberg et al., 1991). Method precision is the pooled coefficient of variation of concentrations measured in duplicate samples. Accuracy was calculated as the percent difference between the actual and measured concentrations of independent standards of individual compounds not used in the calibration models. In the ESI-MS, glyoxal ( $m/z$  117, 131) was detected in the positive mode while glyoxylic acid ( $m/z$  73) and oxalic acid ( $m/z$  89) were detected in the negative mode. Note that formic acid has a molecular weight below the ESI-MS instrument detection limit ( $m/z$  50). The ESI-MS and HPLC control experiment results are provided in Supporting Information.

### *3.2 Photon Flux*

The calculated mean intensities from photon fluence measurements conducted before and after the glyoxal experiments agreed within one standard deviation. Hence, these experiments demonstrated that the received lamp intensity was constant during the experiments and the H<sub>2</sub>O<sub>2</sub> photolysis reaction rates (reaction 1 in Table 2) were constant across the experiments. The photolysis reaction rate constant ( $k_1$  in Table 2) was determined as described below.

### *3.3 Hydrogen Peroxide*

The photolytic decomposition of H<sub>2</sub>O<sub>2</sub> to ·OH in pure water is well understood (Liao and Gurol, 1995; Stefan et al., 1996) and is described in the first 4 reactions of Table 2. Hydrogen peroxide concentrations from H<sub>2</sub>O<sub>2</sub> + UV control experiments (N=2) and model predictions agree well (Figure 2) providing confidence that concentrations of ·OH are described well in the

experiments. (Note that reaction rate constants  $k_2$ - $k_4$  are known and the photolysis rate ( $k_1$ ) depends on photon fluence from the lamp and was a fitted parameter.) While experimental and control solutions were prepared with 10 mM  $H_2O_2$ , an  $H_2O_2$  concentration of 8 mM was used to initialize the model simulation because  $H_2O_2$  concentrations in the GLY +  $H_2O_2$  control experiments were stable at  $\sim 8$  mM (see Supporting Information, Figure S-2). This is reasonable because  $H_2O_2$  photolyzes to  $\cdot OH$  at wavelengths ( $\lambda$ ) present in ambient light and the solution was exposed to ambient light for the  $\sim 3$ -4 minutes required for solution preparation and transfer into the shielded reaction vessel. Hydrogen peroxide was not detected in the GLY + UV control samples.  $H_2O_2$  photodecomposition experiments ( $H_2O_2$  +UV) have also been performed at an initial  $H_2O_2$  concentration of 20 mM (i.e., as part of the pyruvic acid experiments; Carlton et al., 2006). The model also successfully reproduced these measurements. These experiments provided a photolysis reaction rate constant of  $1.0(\pm 0.2) \times 10^{-4} \text{ sec}^{-1}$ , which was used in model simulations (Table 2, reaction 1) and is similar to values obtained by others conducting similar experiments (Herrmann et al., 1995).

## 4. Experimental Results

### 4.1 Concentration Dynamics

Glyoxal ( $m/z$  117, 131) was present in the 0 minute sample and was completely absent by 9 minutes as demonstrated in the ESI-mass spectra (Figure 3). This decrease in glyoxal coincided with the very rapid formation of formic acid (Figure 4; HPLC retention time (RT) 3.3 min). The formic acid concentration reached a maximum within the first two minutes of the experiment (Figure 4); it was not a predicted product. Glyoxylic acid, an expected product (Figure 1), has a maximum HPLC absorbance at 9 minutes, however observations never

exceeded detection limits (Figures 4-5). Total dissolved organic carbon decreased by approximately a factor of ten within the first hour.

In addition to the compounds predicted in the initial reaction scheme (shaded pathway, Figure 1), the formation of large molecular weight compounds was evident in both the HPLC chromatograms and the ESI-mass spectra. By ~9 minutes the positive mode ESI-MS spectra showed numerous peaks clustered between  $m/z$  80-200 (Figure 3). At ~30 minutes there were still higher molecular weight peaks in the positive mode spectra and, in addition, there were higher molecular weight peaks in the negative mode spectra. After ~30 minutes the complexity in the spectra of both positive and negative modes dissipated. (Note: the simple mass spectra of controls and mixture standards containing all expected products, shown and discussed in Supporting Information, provides strong evidence that the ESI-MS “complexity” is not an instrumental artifact.) A feature with the same temporal evolution was found in the HPLC chromatograms (Figure 4). The HPLC chromatograms exhibited a broad peak with a long retention time whose area reached a maximum at ~30 minutes (Figure 4). The broad peak suggests the formation of larger, multifunctional products, and the long retention time suggests relatively high  $pK_a$  values (typical of alcohols). After 30 minutes, the retention time of this peak increased (shifted from 6.4 to 8 minutes) and the peak area decreased. Column characteristics indicate that the shift to a longer retention time is most likely associated with an increase in compound  $pK_a$ , or size. The decrease in area strongly suggests a decrease in concentration, however this is not explicitly known since the analytical sensitivity could change with the changing product mix. A dramatic increase in the oxalic acid concentration occurred after 30 minutes (Figure 3-5), as the ESI-MS “complexity” dissipated and the broad peak of unresolved carbon in HPLC chromatograms decreased. Glyoxylic acid concentrations are insufficient to

account for this increase in oxalic acid. Concentration dynamics suggest that the degradation of larger multifunctional compounds is somehow responsible. The oxalic acid concentration reached a plateau at 50 - 150 minutes (HPLC, RT=1.5 min; ESI-MS,  $m/z$  89 negative mode) (Figures 3-5). After 150 minutes, oxalic acid was the only peak present in the chromatograms and dominated the ESI mass spectra as its concentration gradually decreased.

#### 4.2 Modeling Organic Acid Formation

These experiments demonstrate that while oxalic acid does form from aqueous phase photooxidation of glyoxal, as expected, the mechanism is more complex than previously thought. Large multi-functional compounds and rapid formic acid formation and degradation were not predicted by the original mechanism, and the current experiments suggest that glyoxylic acid oxidation is not the predominant oxalic acid formation pathway. Current atmospheric aqueous-phase models predict oxalic acid production from glyoxal *via* glyoxylic acid (pathway *b*; Figure 1). While glyoxylic acid oxidation could explain the initial formation of oxalic acid, glyoxylic acid concentrations are insufficient to account for the substantial oxalic acid growth after 30 minutes. Oxalic acid forms rapidly as the broad HPLC peak suggestive of larger multifunctional compounds decreases and as the ESI-mass spectral complexity decreases, suggesting that oxalic acid forms primarily through the degradation of a class of larger multifunctional compounds (pathway *a*; Figure 1).

The model using the initial mechanism (Table 2, reactions 1 - 16) failed to reproduce the concentrations of species as well as their temporal dynamics in the experiments (Figure 6). Glyoxylic acid concentrations predicted using the initial mechanism were substantially greater than observed values. Predicted oxalic acid concentrations were substantially less than measured

in the experiments, and the model failed to reproduce the concentration dynamics. Lower than predicted glyoxylic acid concentrations using the original mechanism (shaded pathway, Figure 1) were also observed in previous glyoxal photooxidation experiments (Buxton et al., 1997).

Based on the experimental results, the original mechanism (shaded pathway, Figure 1) was expanded to include the formation and degradation of formic acid and large molecular weight compounds (all pathways, Figure 1). Table 2 presents the reactions and fitted rate constants used in the expanded mechanism model. Reactions were added for formic acid formation, dissociation and oxidation (reactions 17-20, 24-26). The rapid formation of formic acid very early in the time series suggests it is a direct glyoxal oxidation product; its concentration dynamics could not be reproduced until the reactions  $\text{GLY} + 2\cdot\text{OH} \rightarrow 2\text{HCOOH}$  and  $\text{GLY} + \text{H}_2\text{O}_2 \rightarrow 2\text{HCOOH}$  (reactions 17 and 24) were added to the expanded mechanism. The first reaction is reasonable because  $\alpha$ -dicarbonyl compounds are highly reactive, and the proximity of the two carbonyl double bonds enhances their reactivity toward nucleophilic (e.g.,  $\cdot\text{OH}$ ) attack (Vollhardt and Schore, 1994). The second reaction route is supported by substantial experimental evidence (Gavagan et al., 1995; Rao and Rao, 2005; Seip et al., 1993), although, to the best of our knowledge, a rate constant for this reaction is not provided in the literature. The expanded mechanism therefore includes direct formic acid production from glyoxal through reactions with  $\cdot\text{OH}$  and  $\text{H}_2\text{O}_2$  (pathway *c*, Figure 1). Reactions were added (reactions 21-23) to parameterize the formation and degradation of a class of larger multifunctional intermediates (i.e., the unresolved carbon) that appear to be responsible for most of the oxalic acid formation. These simplified reactions do not explicitly characterize the products, as they are unknown and appear to change with time. The rate constants ( $k_{21}$ - $k_{23}$ ) were adjusted so that model predictions fit the observed concentrations of quantified species (e.g., formic and oxalic acids). Fitting was

not directly possible for the “higher molecular weight compounds” because they are unidentified and therefore calibration relationships cannot be calculated. However, the model fit for quantifiable species was excellent and these calculated rate constants are consistent with other investigators who note that aqueous phase reaction rate constants involving the hydroxyl radical occur at or near diffusion limits (i.e.,  $\sim 10^{10}$ ) (Haag and Yao, 1992; Zhu and Nicovich, 2003). For both the original mechanism and the expanded mechanism, initial concentrations of  $\text{H}_2\text{O}_2$  and  $\cdot\text{OH}$  were optimized at 9 mM and 0.15 mM, respectively, reflecting the fact that some  $\text{H}_2\text{O}_2$  photolyzes to  $\cdot\text{OH}$  during solution preparation (see Supporting Information). Additionally, organic reactions with  $\text{H}_2\text{O}_2$  were added to the model (reactions 25-28). Including these reactions is reasonable because pyruvic (Stefan and Bolton, 1999; Carlton et al., 2006) and glyoxylic acids (Seip et al., 1993; Gavagan et al., 1995; Rao and Rao, 2005) have been shown to react with  $\text{H}_2\text{O}_2$ . Their inclusion improved model performance for the experiments and controls.

Using the expanded mechanism (Figure 1) and reactions 1-28 (Table 2) with certain rate constants as fitting parameters ( $k_{17}$ ,  $k_{21}$ - $k_{28}$ ), predicted and measured concentration profiles are in reasonable agreement, and the predictions reproduce the measured concentration dynamics (Figure 7). The expanded mechanism describes 81% of the variance in oxalic acid observations. Formic acid predictions account for 64% of the variance in observations. This modest agreement for formic acid might be explained by the lower recovery for formic acid or the fact that formic acid appears very rapidly and degrades early in the experiment, when uncertainty in the independent variable (i.e., time) is still a relatively large fraction of the measurement. The predicted glyoxylic acid concentrations using the expanded mechanism are below detection limits, as observed. The expanded model suggests that less than 1% of oxalic acid in the reaction vessel is formed through the glyoxylic acid pathway (pathway *b*, Figure 1).

### 4.3 Model Limitations

Reactions 21-23 are surrogates for poorly understood processes that enhance reactant disappearance. For example, glyoxal could also react with unidentified products (e.g., radicals or large multifunctional compounds observed in the HPLC and ESI mass spectra). The large multifunctional products appear to change during the experiment, as exhibited by the shifts in the HPLC retention time and distribution of mass species in the ESI-MS. Further experimental work to identify products and their formation mechanisms is required for further model improvement and for accurate prediction of the properties and concentration dynamics of the larger molecular weight products. Prediction of SOA formation through aqueous-phase photochemistry is hampered by the lack of understanding of the thermodynamic properties, atmospheric stability and concentrations of these unknown products.

## 5. Yields

In these batch reactor experiments a fixed quantity of glyoxal was reacted with  $\cdot\text{OH}$  generated by  $\text{H}_2\text{O}_2$  photolysis leading to the formation, evolution and eventual destruction of low volatility products. Because the chemical composition in the reaction vessel continues to evolve after all glyoxal has reacted (9 min), the mass of product per mass of glyoxal reacted (frequently called the yield) is not a constant, but a function of the reaction time. After 10 minutes of aqueous phase processing the reaction vessel contained 0.01 g oxalic acid per g glyoxal reacted (1%). (Note: 10 minutes is a typical cloud droplet lifetime and an air parcel might be processed through tens of cloud cycles during regional transport; Ervens et al, 2004.) At the oxalic acid concentration maximum ( $\sim 90$  min), the reaction vessel contained 0.02 g oxalic acid per g

glyoxal reacted (2%). After ~ 150 min the mass of oxalic acid in the reaction vessel decreased, until all oxalic acid was oxidized to CO<sub>2</sub> (> 300 min). Atmospheric yields of oxalic acid (and SOA) from cloud processing of glyoxal will depend not only on the aqueous-phase chemistry investigated in this research, but also on the rate at which oxidants and glyoxal are (continuously) supplied by gas phase chemistry, on photolysis rates, and on cloud dynamics (e.g., aqueous reaction time).

We expect that the larger multifunctional products formed from aqueous glyoxal photooxidation will also contribute to SOA. Experimental observations suggest that the maximum higher molecular weight compound concentration occurs at ~30 minutes, when the median molecular weight in the ESI-mass spectra was ~ 175 g/mole (Figure 3). Using this as the estimated molecular weight, a maximum of 0.3 g higher molecular weight compounds / g reacted glyoxal (30%) was estimated for the reaction vessel (~30 min). Note there is substantial uncertainty in this estimate as compounds are unknown and there is uncertainty in the calculated reaction rate constants. Plus, while we expect higher molecular weight material to remain largely in the particle phase upon droplet evaporation (Loeffler et al., 2006), its gas-particle partitioning is not well characterized. However, this value indicates that model investigations of cloud-produced SOA that neglect higher molecular weight compounds (e.g. rely on carboxylic acid production solely) could substantially under-predict SOA formation.

## **6. Discussion**

This work supports the hypothesis that aqueous phase photooxidation of glyoxal leads to SOA formation. Oxalic acid formation is confirmed, and an expanded formation mechanism is proposed. The coupled atmospheric concentration dynamics of glyoxal and oxalic acid (Chebbi

and Carlier, 1996), results from recent field campaigns (Crahan et al., 2004; Sorooshian et al., 2006) and this work support the hypothesis that aqueous phase chemistry is the predominant formation mechanism for oxalic acid. Good agreement is found between measured and modeled oxalic acid concentrations using the expanded mechanism developed herein. This work suggests that large multifunctional compounds are also products of aqueous phase glyoxal photooxidation. Both oxalic acid and large multi-functional compounds will contribute SOA upon droplet evaporation.

The larger multifunctional products are likely to be covalently bonded oligomers or compounds with relatively high  $pK_a$  values and carboxylic acid or alcohol functional groups. The evidence supporting this is as follows; the HPLC column retains only carboxylic acids and alcohols, high  $pK_a$  compounds have longer elution times in this column, and multifunctional compounds have broad chromatographic peaks. Also, the complexity in the ESI-mass spectra occurs in both the positive (e.g., alcohols) and negative (e.g. carboxylic acids) modes. The formation of larger multi-functional compounds has been reported previously in similar photooxidation experiments of carboxylic acids (e.g., pyruvic acid; Altieri et al., 2006). These compound classes (i.e., alcohols, covalently-bonded oligomers and large carboxylic acids) are consistent with proposed cloud water HULIS (humic-like substances) components (Cappiello et al., 2003). Oligomers and HULIS have been found in atmospheric aerosols (Gao et al., 2006; Kalberer et al., 2004; Kalberer et al., 2006) and in clouds ( Fuzzi et al., 2002; Cappiello et al., 2003). It has been suggested that these large compounds form in a concentrated liquid phase (i.e., acidic particles; Tolocka et al., 2004; Kroll et al., 2006), but we provide evidence that larger multi-functional compounds can also form in dilute solutions (i.e., cloud droplets) as suggested by Blando and Turpin (2000) and Gelencser and Varga (2005). Still, further work is

needed to better characterize these unidentified products, their formation chemistry and relevant atmospheric properties.

The work presented here demonstrates one of the many complex pathways leading to the formation of SOA through cloud processing. SOA yields from glyoxal could be substantially higher than oxalic acid yields because oxalic acid is only one of many potential low volatility products. For example, in addition to oxalic acid and large multifunctional compounds, organosulfur compounds (e.g., glyoxal-sulfur adducts; Munger et al., 1984; Munger et al., 1995; Liggio et al., 2005) could form and contribute to SOA. Also, while glyoxal is a gas phase oxidation product of many VOCs, it is only one of many potential aqueous phase SOA precursors. Thus, the inclusion of in-cloud SOA formation pathways in chemical transport models is likely to reduce the gap between measured and modeled organic PM in the free troposphere (Heald et al., 2006).

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Table 1. Glyoxal experimental design

Note: GLY = glyoxal

Initial Glyoxal conc.	2 mM
Initial H <sub>2</sub> O <sub>2</sub> conc.	10 mM
Number of experiments	2
pH	4.1 - 4.8
Temperature	25 ± 1 °C
Experiment	GLY + UV + H <sub>2</sub> O <sub>2</sub>
UV Control	GLY + H <sub>2</sub> O <sub>2</sub>
H <sub>2</sub> O <sub>2</sub> Control	GLY + UV
Organic Control	UV + H <sub>2</sub> O <sub>2</sub>

**Table 2. Glyoxal Oxidation Mechanism (initial: reactions 1-16; expanded: reactions 1-28)**

Reaction	Rate ( $M^{-1} s^{-1}$ )	Ref.	Estimated, Measured or Fitted
1 $H_2O_2 + h\nu \rightarrow 2 OH$	$1.0E-4 (s^{-1})$	1	m*
2 $OH + H_2O_2 \rightarrow HO_2 + H_2O$	$2.8E+10$	1	m
3 $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$	3.7	1	m
4 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	$8.3E+05$	1	m
5 $GLY + OH \rightarrow GLYAC + HO_2$	$1.1E+09 / 1.0E+08$	2	m, f
6 $GLYAC + OH \rightarrow OXLAC + HO_2 + H_2O$	$3.6E+08$	3	m
7 $GLYAC^- + OH \rightarrow OXLAC^- + HO_2 + H_2O$	$2.2E+09$	3	m
8 $OXLAC + 2 OH \rightarrow 2 CO_2 + 2 H_2O$	$1.4E+06$	3	m
9 $OXLAC^- + OH \rightarrow CO_2 + CO_2^- + 2 H_2O$	$1.9E+08 / 2.2E+08$	3	m <sup>1</sup>
10 $OXLAC^{2-} + OH \rightarrow CO_2 + CO_2^- + OH^-$	$1.6E+08$	3	m
11 $CO_2^- + O_2 \rightarrow O_2^- + CO_2$	$2.4E+09$	4, 5	m
12 $H_2O = H^+ + OH^-$	$K_{eq} = 1.0E-14$ $k_a = 1.4E11$	7, 8	m
13 $HO_2 = Hp1 + O_2^-$	$K_{eq} = 1.6E-5$ $k_a = 5.0E10$	7, 6	m, e
14 $GLYAC = H^+ + GLYAC^-$	$K_{eq} = 3.47E-4$ $k_a = 2.0E10$	5, 6	m, e
15 $OXLAC = H^+ + OXLAC^-$	$K_{eq} = 5.67E-2$ $k_a = 5.0E10$	5, 6	m, e
16 $OXLAC^- = H^+ + OXLAC^{2-}$	$K_{eq} = 5.42E-5$ $k_a = 5.0E10$	5, 6	m, e
17 $GLY + 2 OH \rightarrow HCO_2H + HCO_2H$	$5.0E+03$	n/a	f
18 $HCO_2H + OH \rightarrow CO_2 + HO_2 + H_2O$	$1.3E+08$	3	m
19 $HCO_2^- + OH \rightarrow CO_2^- + H_2O$	$3.2E+09$	3	m
20 $HCO_2H = HCO_2^- + H^+$	$K_{eq} = 1.77E-4$ $k_a = 5.0E10$	3	m,e
21 $GLY + OH \rightarrow Products$	$3.E+10$	n/a	f <sup>2</sup>
22 $Products + OH \rightarrow OXLAC$	$3.E+10$	n/a	f <sup>2</sup>

23	Products + OH → GLYAC	1.E+09	n/a	f <sup>2</sup>
24	GLY + H <sub>2</sub> O <sub>2</sub> → HCO <sub>2</sub> H + HCO <sub>2</sub> H	1	n/a	f
25	GLYAC + H <sub>2</sub> O <sub>2</sub> → HCO <sub>2</sub> H	0.9	n/a	f <sup>3</sup>
26	HCO <sub>2</sub> H + H <sub>2</sub> O <sub>2</sub> → CO <sub>2</sub> + H <sub>2</sub> O	0.2	n/a	f <sup>3</sup>
27	OXLAC + H <sub>2</sub> O <sub>2</sub> → 2 CO <sub>2</sub>	0.11	n/a	f <sup>3</sup>
28	OXLAC <sup>-</sup> + H <sub>2</sub> O <sub>2</sub> → 2 CO <sub>2</sub>	1.5E-04	n/a	f <sup>3</sup>

**Notes:** Reactions 1-16 (shaded portion), used in initial mechanism, Reactions 17-28 added for expanded mechanism

GLY = glyoxal, GLYAC = glyoxylic acid, OXLAC = oxalic acid; m = measured, e = estimated, f=fitted

Dissociation rate constants ( $k_d$ ) are calculated from the equilibrium constant ( $K_{eq}$ ; i.e.,  $k_d = K_{eq} * k_a$ ).

\* $k_1$  is a fitted parameter with observations fit to the Liao et al. (1995) parameterization.

<sup>1</sup>This reaction rate constant is within the uncertainty of the measured value present by Ervens et al. 2003 ( $k=1.9(\pm 0.6)E+08$ ).

<sup>2</sup> These simplified reactions are surrogates for unknown formation processes.

<sup>3</sup>These fitted reaction rate constants for H<sub>2</sub>O<sub>2</sub> reaction with carboxylic acids are reasonable and close in value to the measured reaction rate constant for pyruvic acid + H<sub>2</sub>O<sub>2</sub> ( $0.11 \text{ M s}^{-1}$ ; Stefan and Bolton, 1999).

**References:** <sup>1</sup>(Liao and Gurol, 1995); <sup>2</sup>(Buxton et al., 1997); <sup>3</sup>(Ervens et al., 2003); <sup>4</sup>(Buxton et al., 1988); <sup>5</sup>(Warneck, 2003); <sup>6</sup>(Ervens et al., 2003); <sup>7</sup>(Warneck, 1999); <sup>8</sup>(Lelieveld and Crutzen, 1991)

Table 3. Carboxylic acid quality control measures

	Formic Acid	Glyoxylic Acid	Oxalic Acid
Recovery	80% (N=2)	90% (N=2)	100% (N=2)
Method Detection Limit	0.07 mM (N=8)	0.12 mM (N=8)	0.06 mM (N=8)
Method Precision	Pooled C.V. = 17%, N= 5		
Accuracy	15% (N=2)	10% (N=3)	5% (N=3)

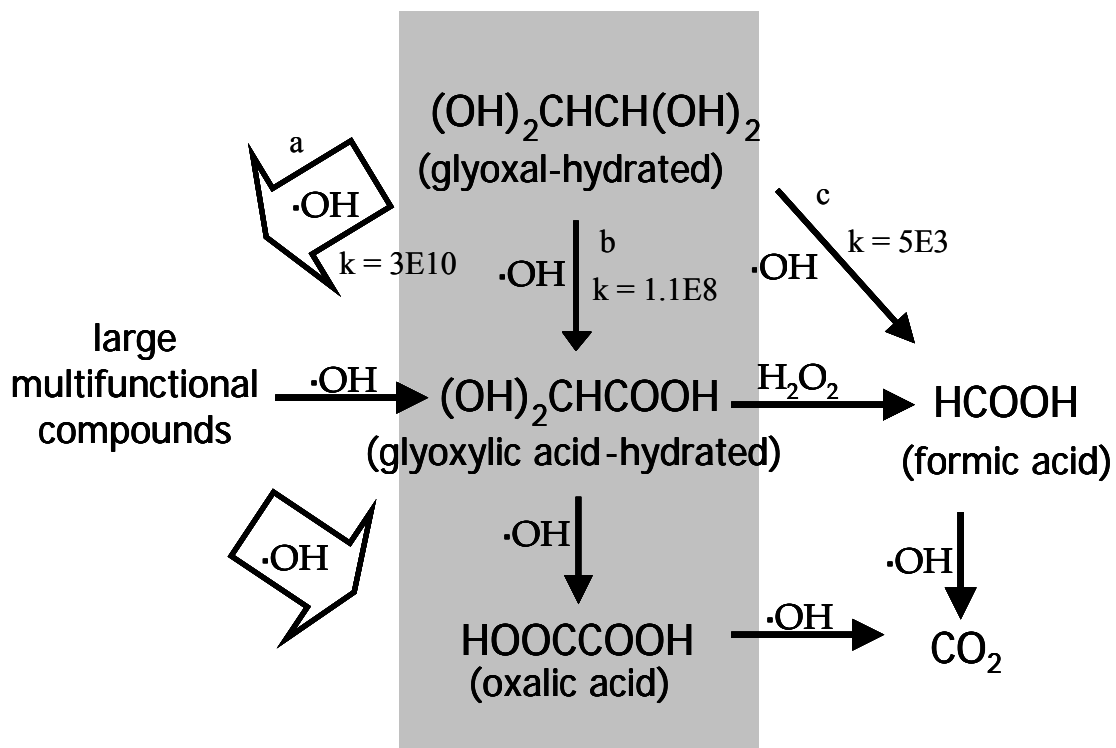


Figure 1. Aqueous phase glyoxal oxidation pathways. Glyoxal, glyoxylic acid and glyoxylate are predominantly hydrated in solution (Ervens et al., 2003). The initial mechanism (pathway “b”, shaded) is adapted from Ervens et al. (2004). Pathways “a” and “c” are supported by experimental evidence contained herein.

\*\*AM : Should arrow from MF to glyoxylic acid be « Cartoon arrow » also ??

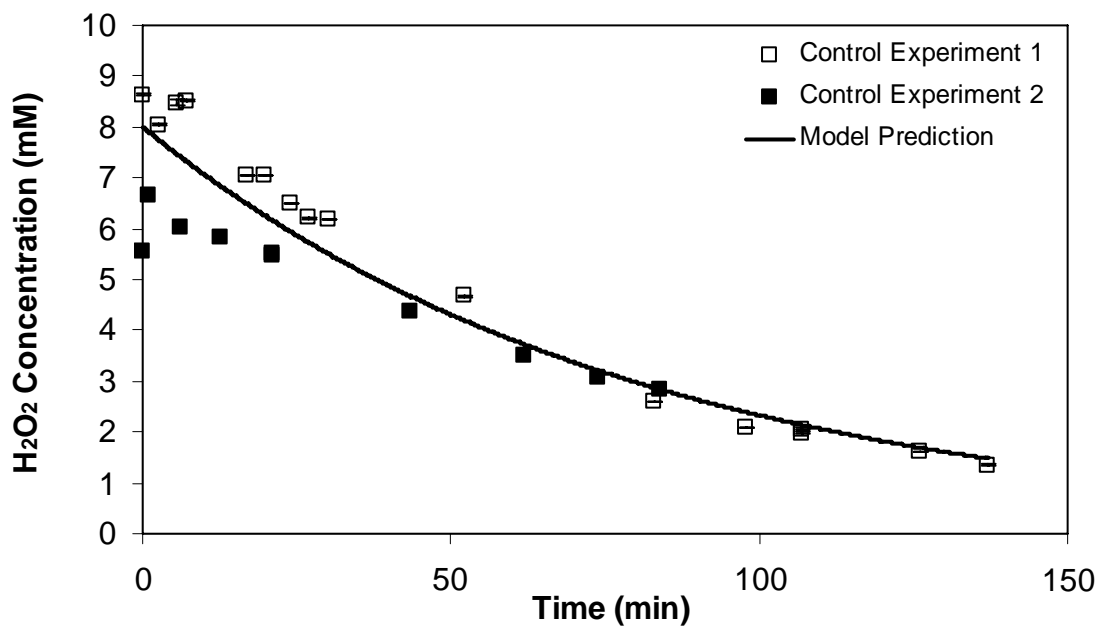


Figure 2. Hydrogen peroxide measurements and model predictions. The photolysis rate constant for  $\text{H}_2\text{O}_2 \rightarrow 2 \cdot\text{OH}$ , ( $1.0\text{E-}04 \text{ s}^{-1}$ ), was a fitted parameter (see Table 2, Reaction 1). Note that the  $\text{H}_2\text{O}_2$  model concentration at  $t=0$  was considered to be equal to the  $\text{H}_2\text{O}_2$  concentration observed throughout the GLY +  $\text{H}_2\text{O}_2$  control experiment (Figure S-2). This accounts for  $\text{H}_2\text{O}_2$  photolysis due to ambient UV during solution preparation.

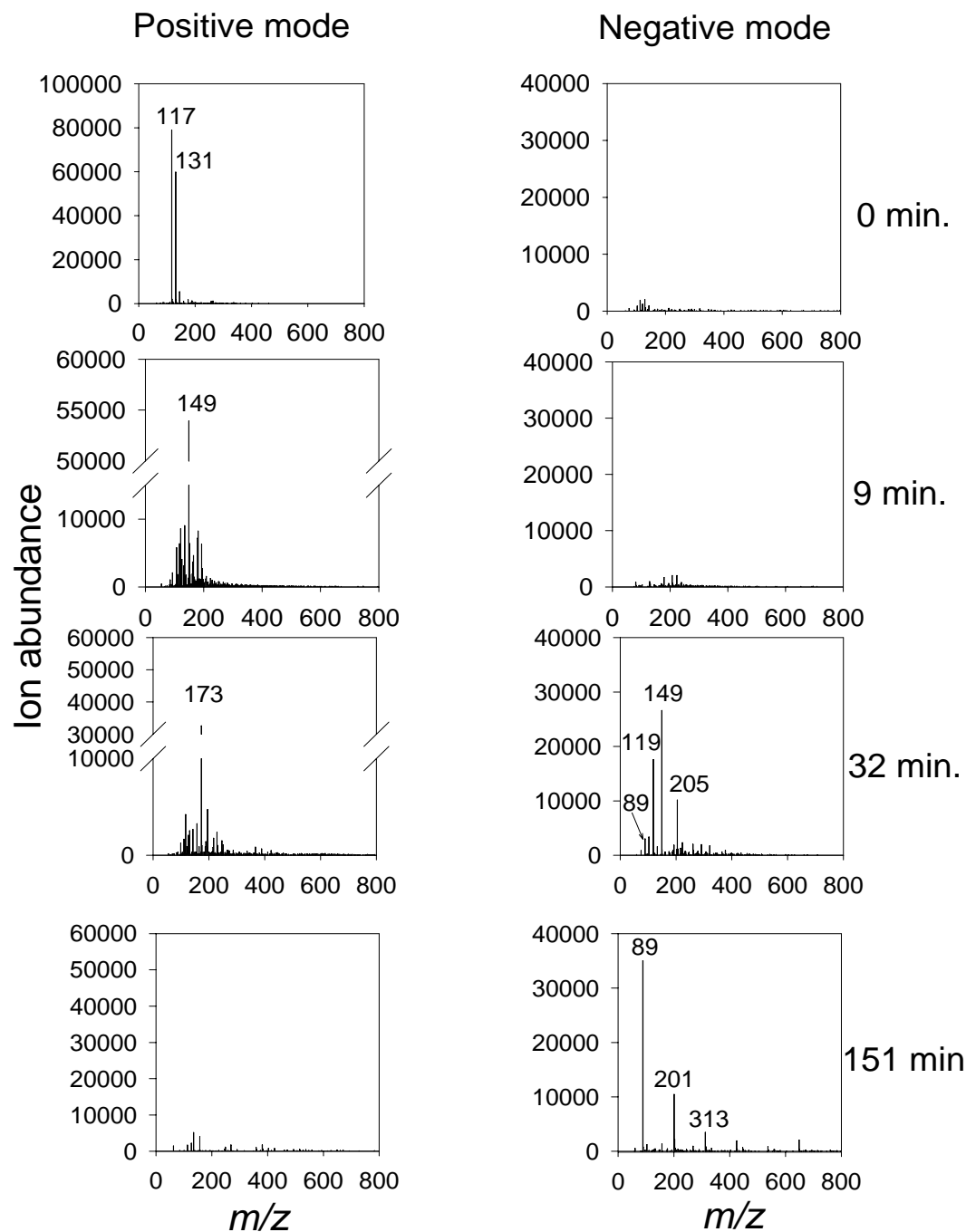


Figure 3. ESI-mass spectra of selected samples from experiment 2 with increasing reaction time. Note change in y-axis scale for the first positive mode spectrum. Glyoxal ( $m/z$  117, 131) is clearly present in the 0 min. sample. Oxalic acid ( $m/z$  89) is clearly present in the 151 min. spectrum. Molecular level identification of other products will require higher resolution ESI-MS or other complementary analytical techniques.

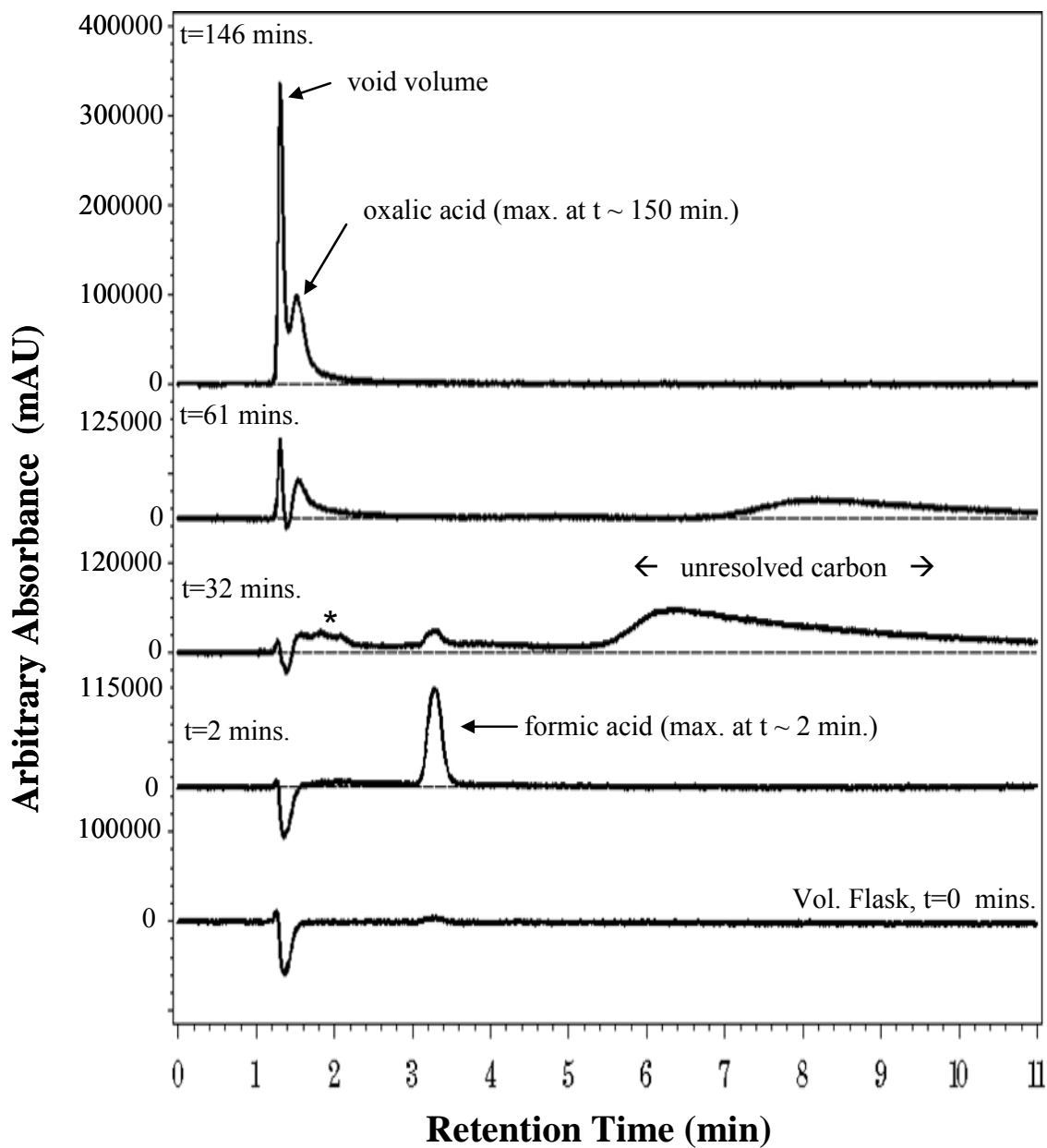


Figure 4. HPLC chromatograms of selected samples from experiment 2. Oxalic acid plateaus at ~ 50 - 150 mins. and is the only product observed in the chromatograms after the 146 min. sample. Formic acid appears quickly and is no longer present after the 32 min. sample. The unresolved carbon maximum occurs at ~ 30 minutes. Note: mAU = milli-absorbance units; \*indicates the small glyoxylic acid presence in the 32 minute sample. Note that the y-axis units are arbitrary absorbance units. Note that unretained species are included in the void volume peak.

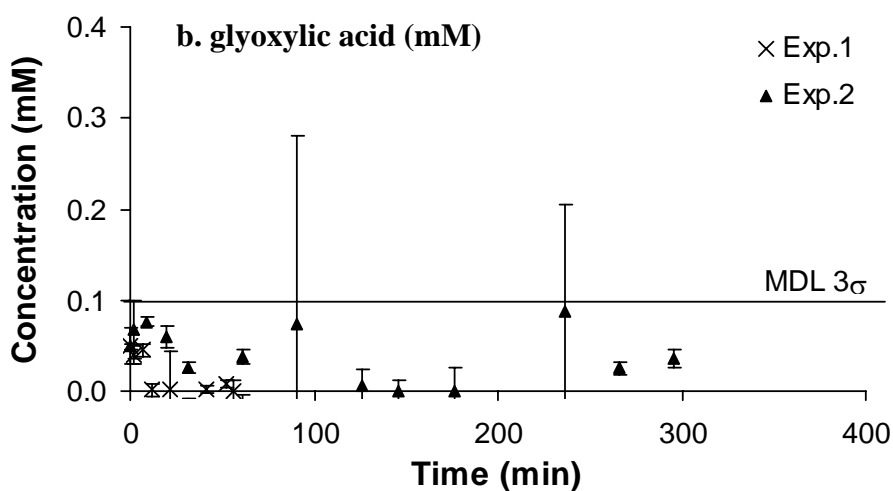
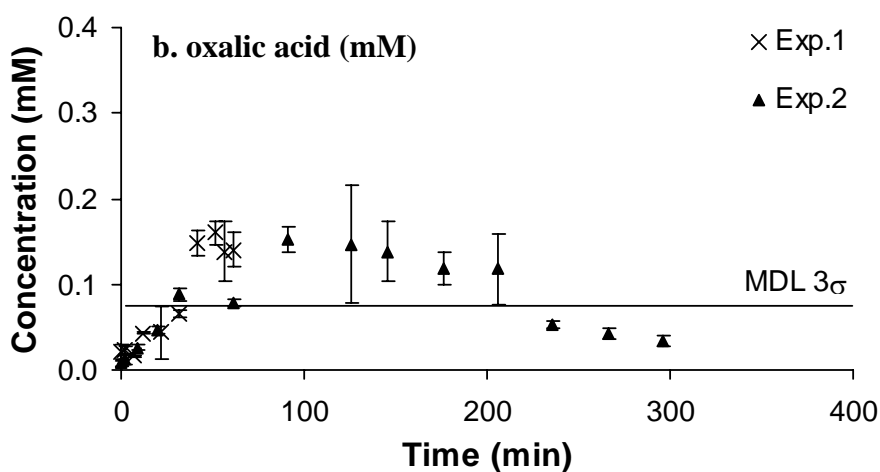
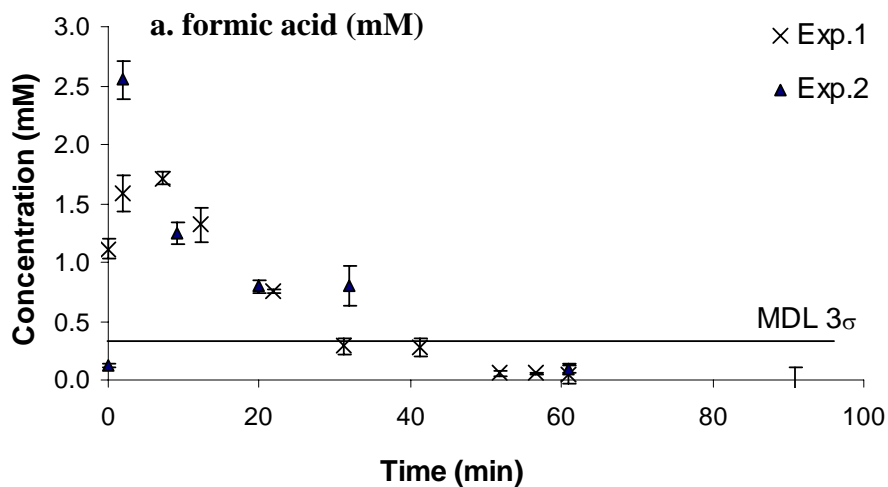


Figure 5. Formic acid (a), oxalic acid (b), and glyoxylic acid (c) production in glyoxal experiments. The experiments had good repeatability; carboxylic acid concentrations across experiments were within measurement uncertainties. MDL is method detection limit.

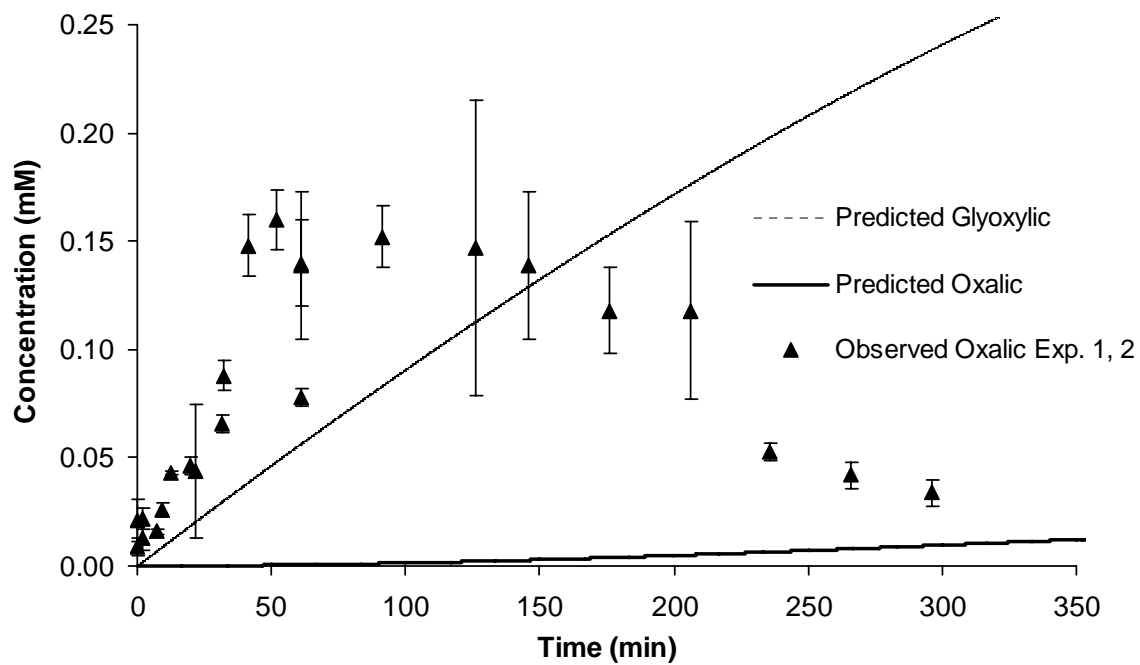


Figure 6. Measured and predicted concentrations of oxalic acid using initial mechanism (shaded pathway, Figure 1; Table 2, reactions 1-16). Note that observed glyoxylic acid concentrations are all below detection limits.

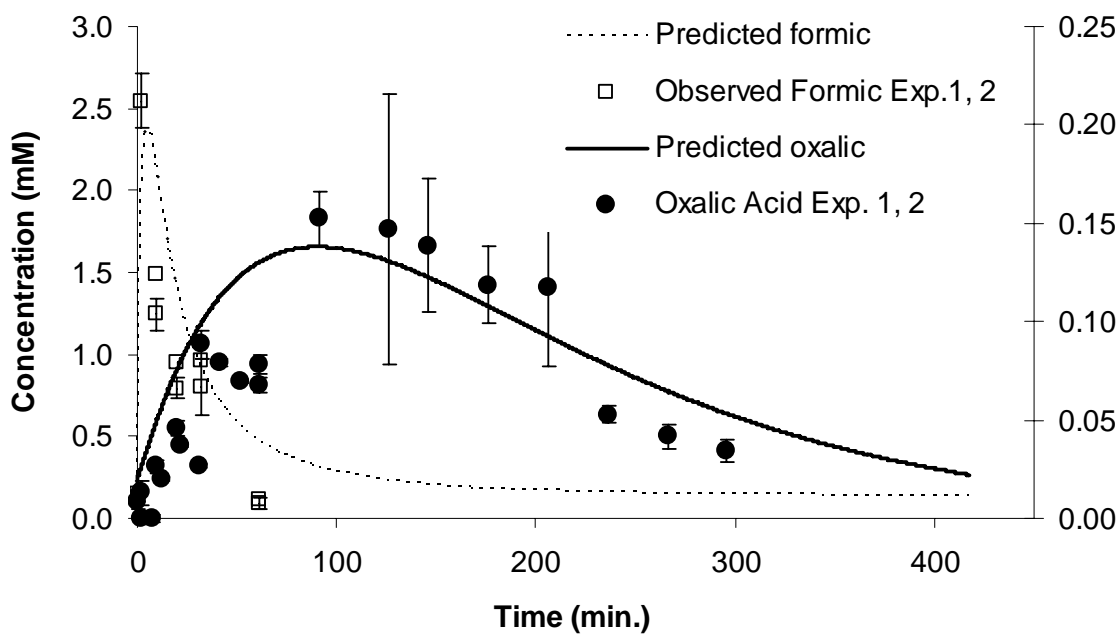


Figure 7. Measured and predicted concentrations of formic and oxalic acids using expanded mechanism (all pathways, Figure 1; Table 2, reactions 1-28). Glyoxylic acid concentrations are too small ( $< 0.02$  mM) to see at this scale. Glyoxal is below detection limits by the 9 minute sample.

## Supporting Information: Control Experiments

ESI-mass spectra of mixed standards are shown in Figure S-1. If the initial atmospheric chemistry mechanism were complete, ESI-mass spectra of samples would resemble the simple spectra observed in the mixture standards, which included all expected carboxylic acid products and the precursor aldehyde.

Figure S-2 shows the concentration of  $\text{H}_2\text{O}_2$  in GLY +  $\text{H}_2\text{O}_2$  control samples, which was stable at 8 mM.

The HPLC chromatograms and ESI-mass spectra from control experiments are shown in Figures S-3 through S-6. Even after one hour of UV exposure, HPLC chromatograms (Figure S-3) and ESI-mass spectra (Figure S-4) of GLY + UV control samples provide no quantifiable evidence of product formation, consistent with the expectation that glyoxal is not photoreactive in the aqueous phase. A small amount of formic acid is present in the GLY +  $\text{H}_2\text{O}_2$  control samples (Figure S-5). Because the quantity of formic acid changes little with time, it is most likely a product of glyoxal oxidation with a trace amount of  $\cdot\text{OH}$  present in the system at  $t = 0$ , not by  $\text{H}_2\text{O}_2$  oxidation. (Recall that a small amount of the initial  $\text{H}_2\text{O}_2$  photo degrades during solution preparation.) Modeling of the GLY +  $\text{H}_2\text{O}_2$  control experiment, using reactions 17-19 and an initial  $\cdot\text{OH}$  concentration of 0.002 mM, produced results consistent with observations. The ESI-mass spectra for the  $t=66$  minute GLY +  $\text{H}_2\text{O}_2$  control sample (Figure S-6) shows a diminished ion abundance of glyoxal ( $m/z$  117, 131) and the presence of a few new peaks (small) though there is no product formation as in the experimental samples.

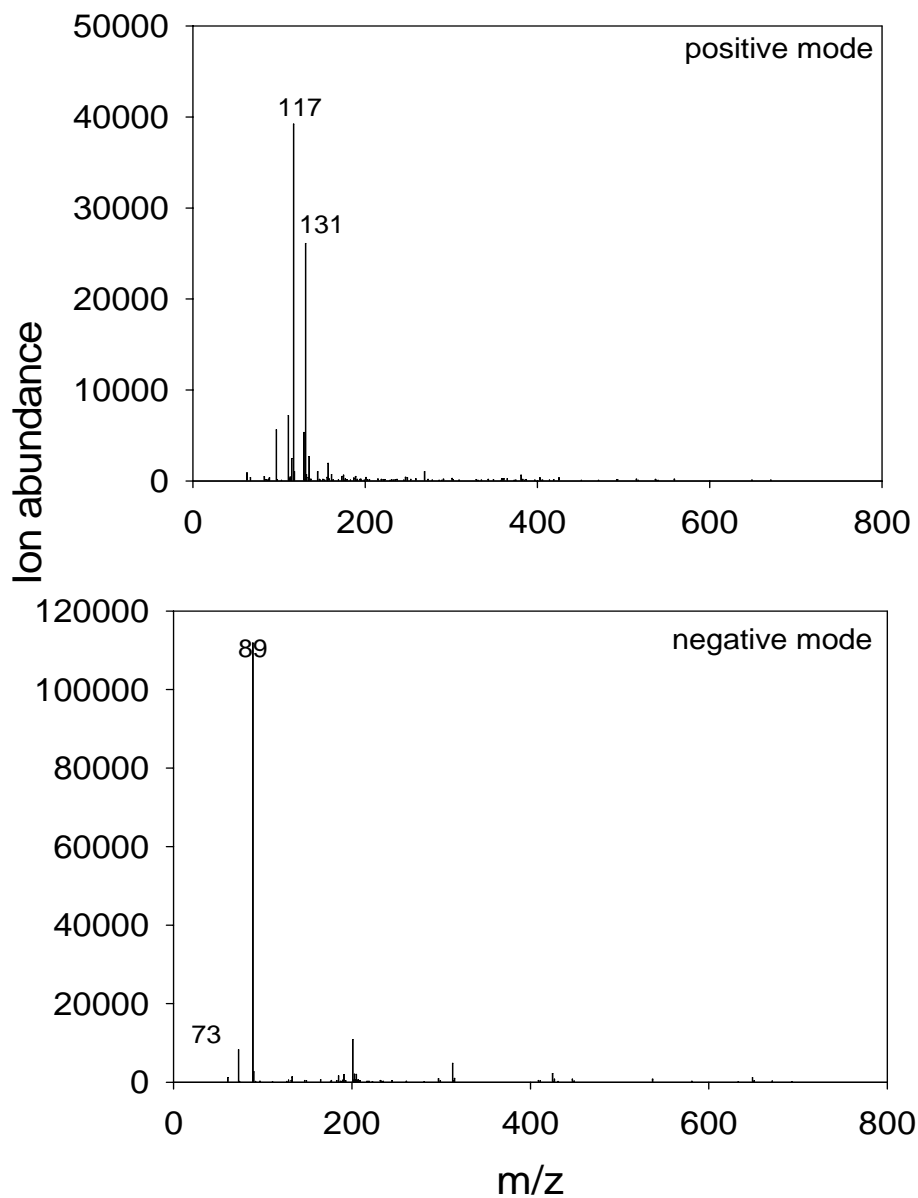


Figure S-1. ESI-MS positive and negative mode spectra of a 0.75 mM per compound mixed standard composed of glyoxal (m/z 117, 131), glyoxylic acid (m/z 73) and oxalic acid (m/z 89) plus hydrogen peroxide, and catalase (0.5%).

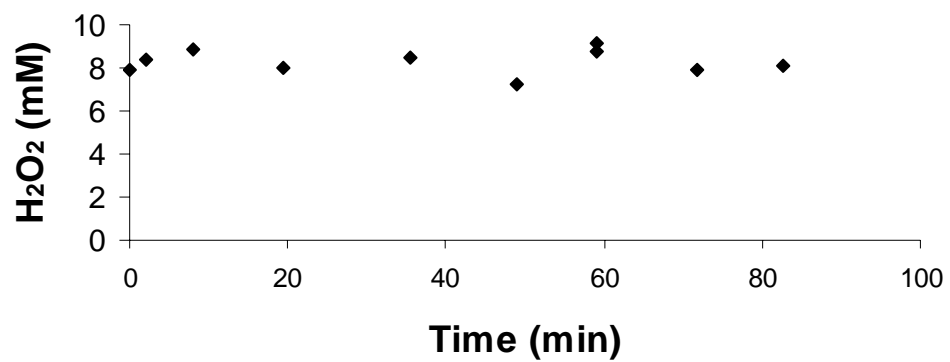


Figure S-2. H<sub>2</sub>O<sub>2</sub> concentration in GLY + H<sub>2</sub>O<sub>2</sub> control experiment.

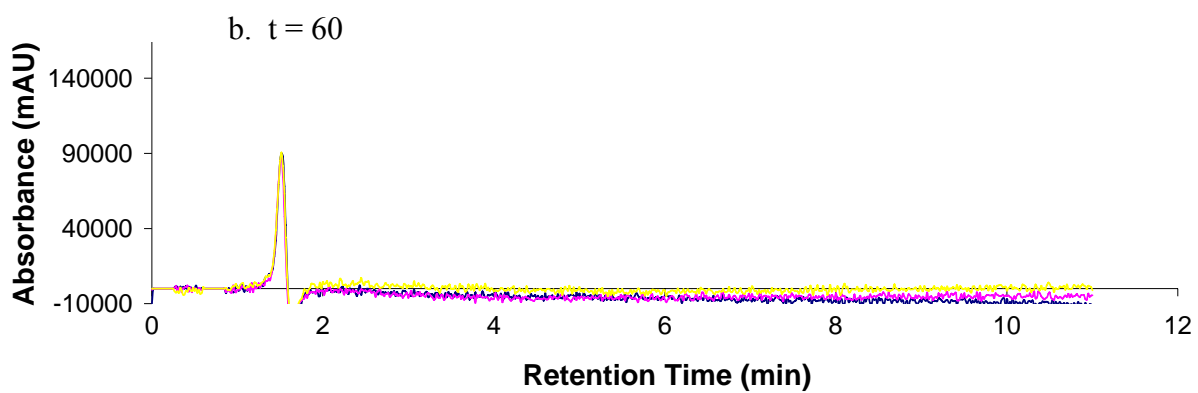
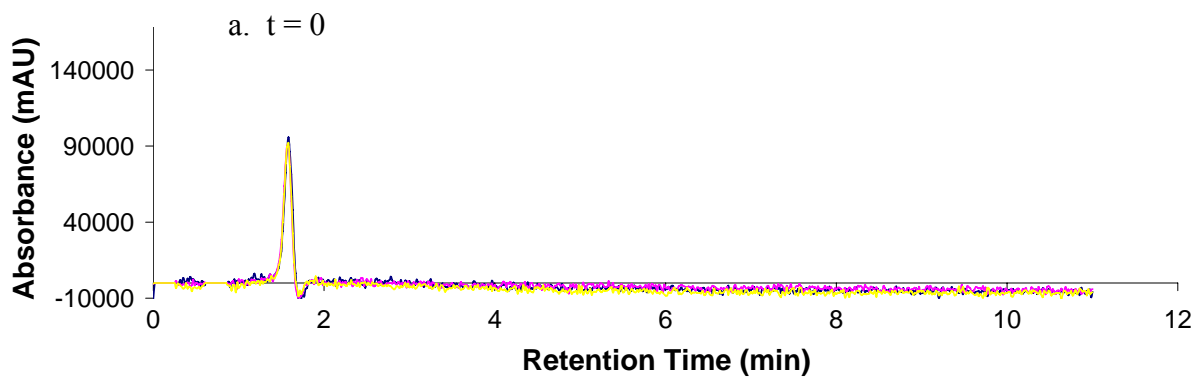


Figure S-3. HPLC Chromatograms of GLY + UV Control Samples at  $t = 0$  (a) and  $t=60$  (b). Note: each color represents a different replicate analysis. GLY=Glyoxal.

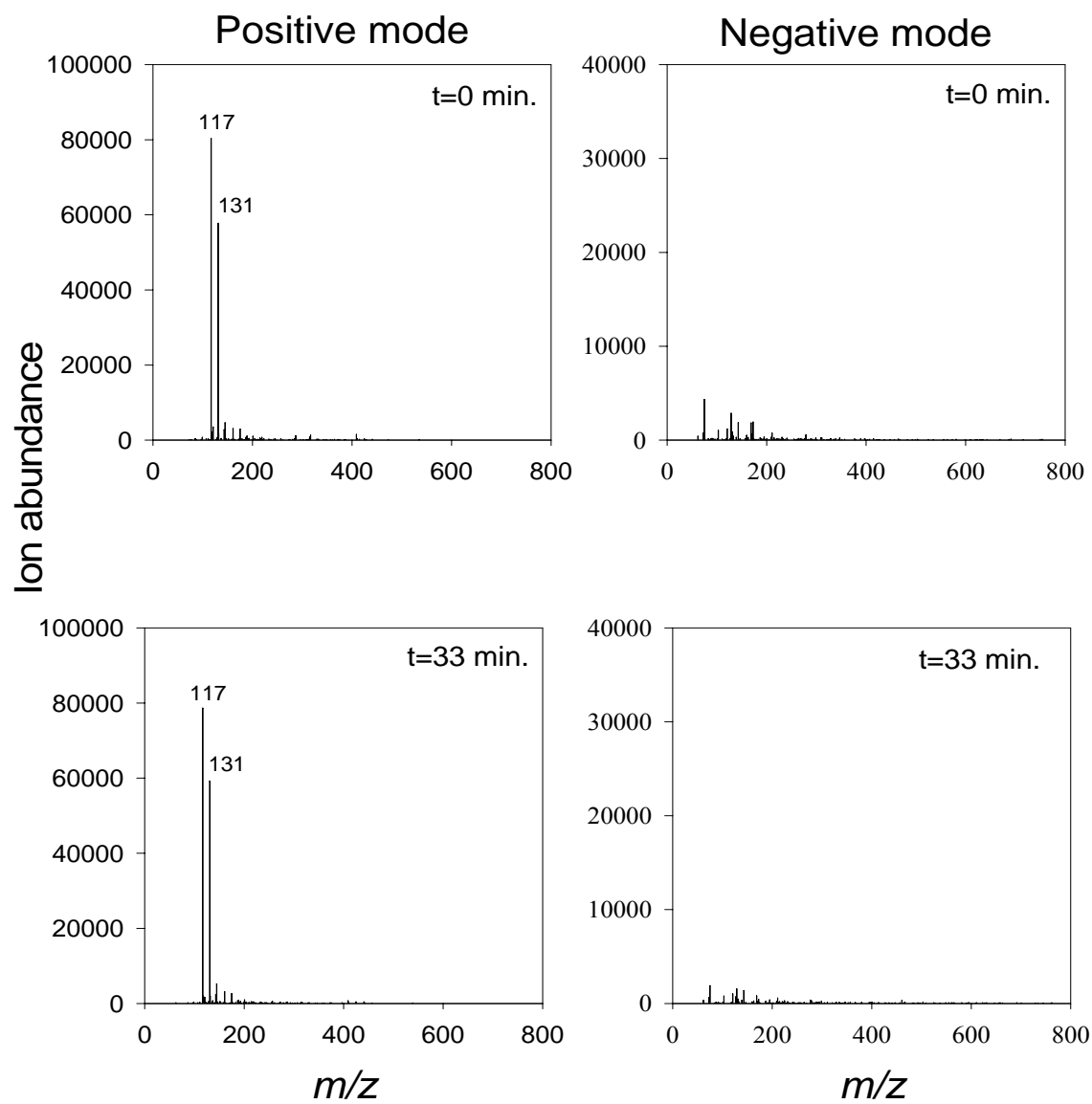


Figure S-4. ESI-MS positive and negative mode spectra of GLY + UV control sample (No H<sub>2</sub>O<sub>2</sub>) at t=0 and t=33 min.

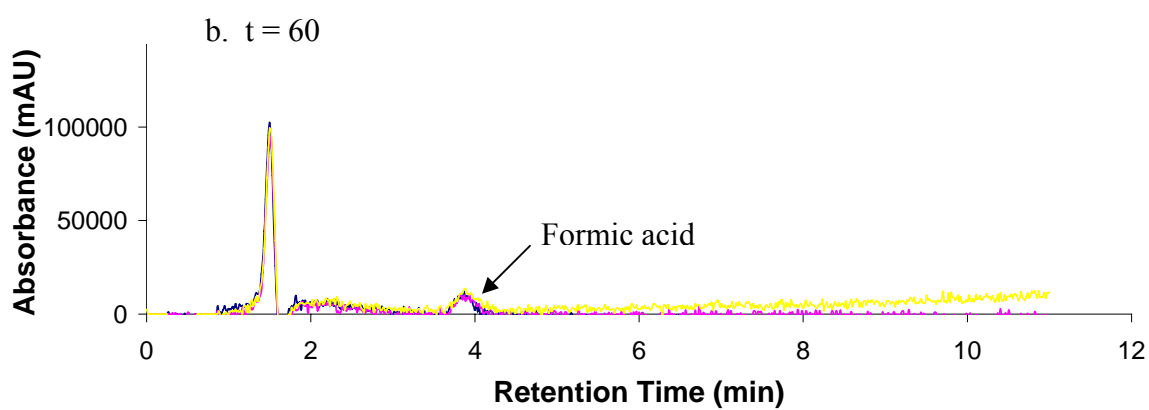
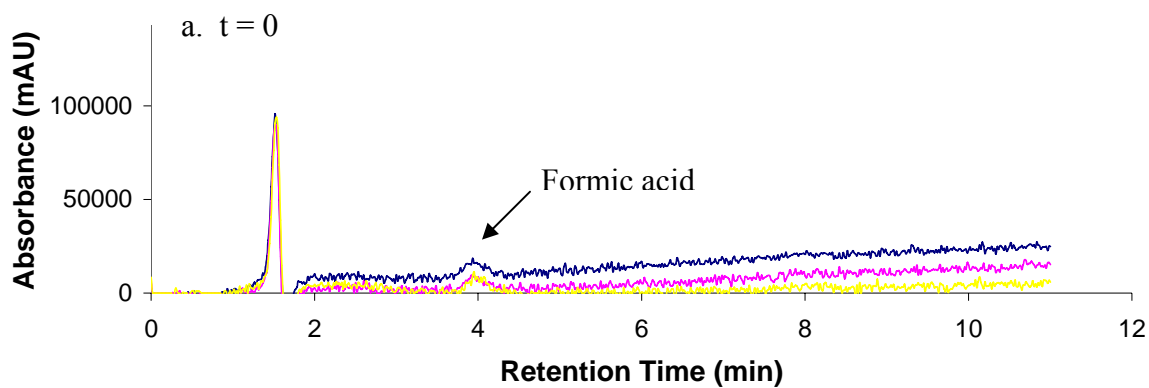


Figure S-5. HPLC Chromatograms of GLY + H<sub>2</sub>O<sub>2</sub> Control Samples at  $t=0$  (a) and  $t = 60$  (b). Note: each color represents a different replicate analysis. GLY=Glyoxal

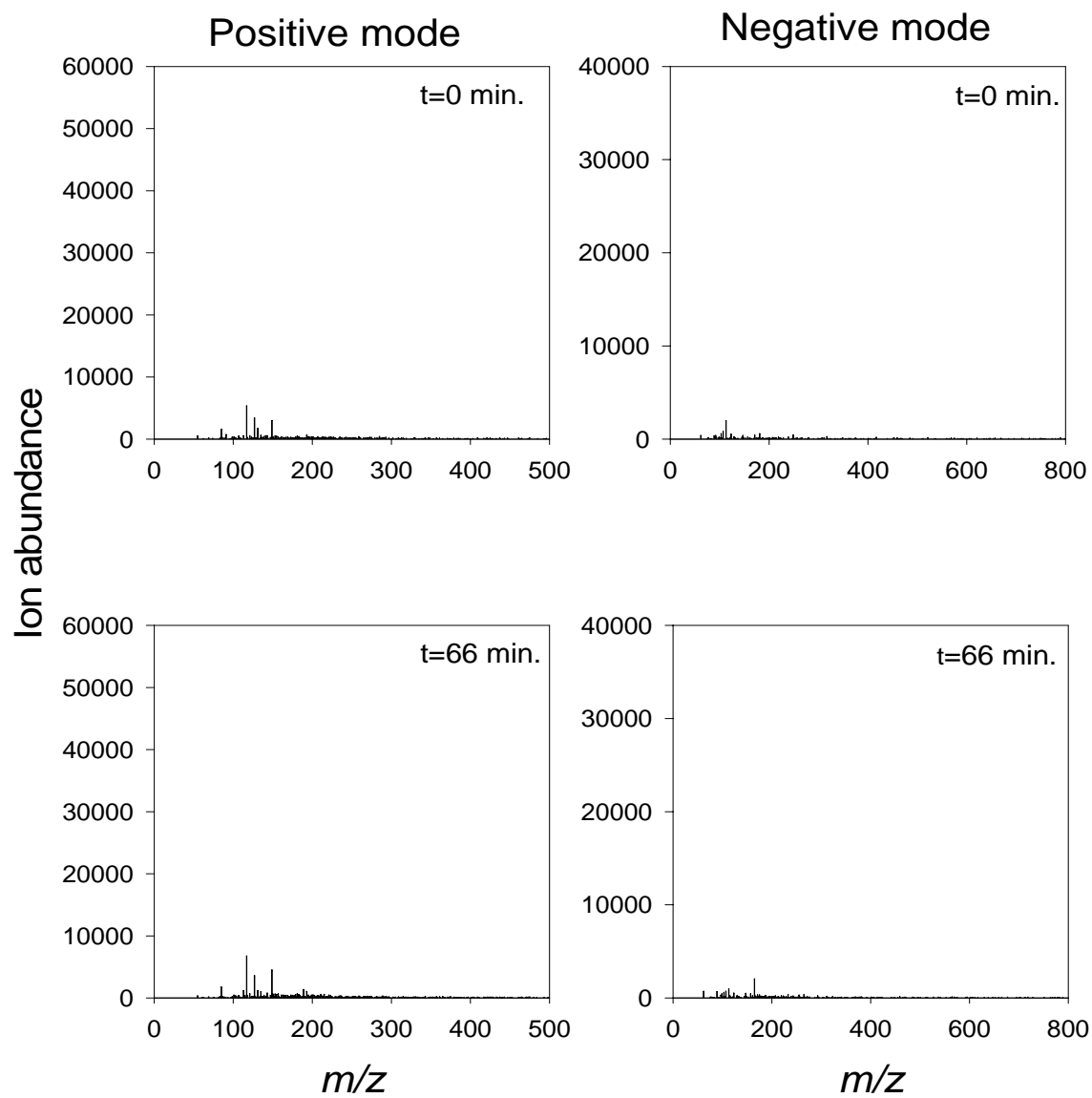


Figure S-6. ESI-MS positive and negative mode spectra of GLY + H<sub>2</sub>O<sub>2</sub> control sample at t=0 and t=66 min.

