Supporting Information

Effects of Precursor Concentration and Acidic Sulfate in Aqueous Glyoxal-Hydroxyl Radical Oxidation and Implications for Secondary Organic Aerosol

Yi Tan, Mark J. Perri, Sybil P. Seitzinger, Barbara J. Turpin

This supporting information section contains: 10 pages, 3 figures, and 2 tables.

Analytical Methods

Carboxylic acids were quantified by IC (ICS-3000, Dionex, Sunnyvale, CA) with a conductivity detector. A photodiode array detector provided additional product validation. The IC employed an IonPac AS11-HC column with AG11-HC guard column (Dionex, Synnyvale, CA). The column is specifically designed to separate a large number of inorganic anions and organic acid anions in gradient runs using hydroxide eluent systems. The system was operated in gradient mode (0.4 ml min^{-1}) programmed from 1 mM to 84 mM hydroxide in 35 min. The IC run time was about 40 min. The column temperature was maintained at 30˚C. An ASRS-ULTRA II (2-mm) anion self-regenerating suppressor after the column was used to remove potassium hydroxide and reduce background noise levels. The conductivity detector cell was maintained at 35˚C. Most organic acid anions are detected by both the conductivity detector and photodiode array (PDA) detector at 205 nm, while some inorganic anions, such as sulfate, are only detected in the conductivity detector. Monovalent anions such as glycolate (5.9 min), formate (6.8 min) and glyoxylate (9.7 min) are only weakly retained, bivalent ions such as succinate (20.4 min), malonate (21.5 min) and oxalate (24.6 min) elute after monovalent ions, and trivalent ions such as citrate are strongly retained and elute even later. Acetate and glycolate (5.9 min), succinate and malate (20.4 min), as well as malonate and tartrate (21.5 min) coelute. Glyoxal partially disproportionates in the alkaline mobile phase and is detected as glycolic acid. Disproportionation is suppressed by acids and therefore the glycolic acid signal cannot be used to quantify glyoxal. Unretained compounds elute at ~ 3.5 min. They are observed in the PDA detector, but not the conductivity detector, since they do not form ions. Chromeleon software (version 6.80 SP2, Dionex) is used to quantify products.

Electrospray ionization mass spectrometry (ESI-MS) is a soft ionization method that does not fragment ions. Carboxylic acids are detected in the negative ionization mode as molecular weight minus one ion because of the loss of an acidic proton. Aldehydes and alcohols are detected in the positive mode. Glyoxal is detected as m/z^+ 117 and 131 as previously reported. The ion m/z^+ 117 was used to qualitatively represent glyoxal in this work.

Fresh samples from batch experiments were analyzed by electrospray ionization mass spectrometry (ESI-MS) (HP-Agilent 1100) as described previously (Altieri et al, 2006). Mobile phase (40% of 0.05% formic acid in water and 60% of pure methanol) was delivered at 0.22 mL/min. Samples (20 μL) were analyzed in both negative and positive ionization mode over the mass range 50 – 1000 amu with a fragmenter voltage of 40 V and capillary voltage of 3000 V. Nitrogen was the drying gas (10 L/min, 350 °C). Unit mass resolution spectra were recorded in Chemstation (version A.07.01) and exported to EXCEL (Microsoft, Inc.) for interpretation.

A frozen sample (-20 °C) taken 30 minutes into the experiment (3000 μM glyoxal + ·OH; experiment #13 Table S1) was analyzed by Fourier transform ion cyclotron resonance (FT-ICR) ESI-MS (Thermo-Finnigan LTQ-XL, Woods Hole Oceanographic Institute Mass Spectrometer Facility) to determine the elemental formulas of products from 95 – 500 amu (mass resolution 100 k – 750 k) as described by Perri et al. (2009). The instrument was mass calibrated with an external calibrant (Thermo Scientific LTQ-

FT external calibration mix). Analyte was delivered to FT ICR ESI-MS at 5 µL/min, with a source voltage between 2.5-3.5 kV, capillary temperature of 250 ˚C, and no sheath gas flow.

Total organic carbon analysis was performed on selected samples using a Shimadzu TOC-5000A Total Carbon Analyzer (Sharp et al., 1993). HCl (8µL, 6M) was added to 3.5 mL of sample (diluted 1/4 for 300 µM experiment and 1/40 for 3000 µM experiment) and sparged with zero-air to eliminate inorganic carbon (CO, H_2CO_3). Organic carbon was then combusted to CO_2 and measured using infrared absorption. Hydrogen peroxide in organic control experiments (H_2O_2 ± H_2SO_4 + UV) was quantified using the triiodide method and UV-visible spectrometer (Allen et al., 1952). Quantification was based on 5-point calibration conducted just prior to sample analysis.

Quality Assurance / Quality Control (QA/QC)

Data quality for organic acids is presented in Table S2. Organic acids were quantified by quadratic regression of 5 points in IC with coefficients of determination, r^2, better than 99% for all acids. Mixed standards containing organic acids (oxalic, formic, glyoxylic, glycolic, malonic and succinic acids, all at 100 µM) were sampled from the reaction vessel to determine recoveries. Recoveries are around 100% except for glyoxylic acid (86.5%). With the addition of 15 mM H_2O_2 and 20 µL of a 1% catalase solution into 10 mL mixed standard, recoveries were unchanged for glycolic acid, malonic acid, succinic acid and oxalic acid. However, glyoxylic acid disappeared and the formic acid concentration increased. Method detection limits are from Perri et al. (2009) using the same analytical protocol. Method precision (4.1%) is the pooled standard deviation of replicate analysis of samples on the IC divided by the mean concentration for organic acids excluding glyoxylic acid and formic acid; replicates were analyzed at the beginning and end of each run. Analytical precision (1.5%) was calculated as the pooled standard deviation divided by the mean of duplicate samples analyzed sequentially.

Supporting Information References

Allen, A. O.; Hochanadel, C. J.; Ghormley, J. A.; Davis, T. W., Decomposition of Water and Aqueous Solutions under Mixed Fast Neutron and γ-Radiation. *J. Phys. Chem.* **1952,** *56*, (5), 575-586.

Altieri, K. E.; Carlton, A. G.; Lim, H.-J.; Turpin, B. J.; Seitzinger, S. P., Evidence for Oligomer Formation in Clouds: Reactions of Isoprene Oxidation Products. *Environ. Sci. Technol.* **2006,** *40*, (16), 4956-4960.

Perri, M. J.; Seitzinger, S.; Turpin, B. J., Secondary organic aerosol production from aqueous photooxidation of glycolaldehyde: Laboratory experiments. *Atmos. Environ.* **2009,** *43*, (8), 1487-1497.

Sharp, J. H.; Benner, R.; Bennett, L.; Carlson, C. A.; Dow, R.; Fitzwater, S. E., Re-evaluation of High Temperature Combustion and Chemical Oxidation Measurements of Dissolved Organic Carbon in Seawater. *Limnol. Oceanogr.* **1993,** *38*, (8), 1774-1782.

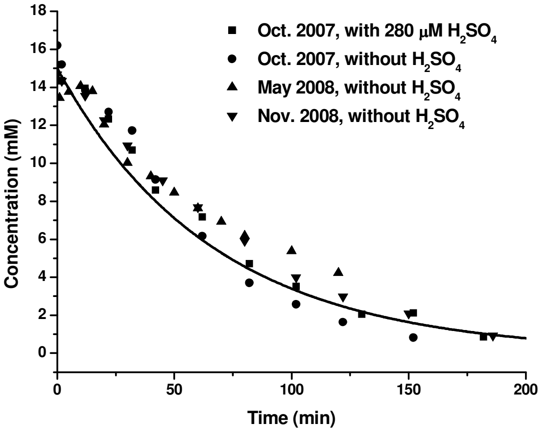

Figure S1. H_2O_2 concentration (mM) and time (min) in H_2O_2 + UV ± H_2SO_4 control experiments. Line is the model fit (Table 3, reactions 1 – 5), where the H_2O_2 photolysis rate (Table 3, k_1 = 1.1E-4 s^{-1}) is a fitted value.

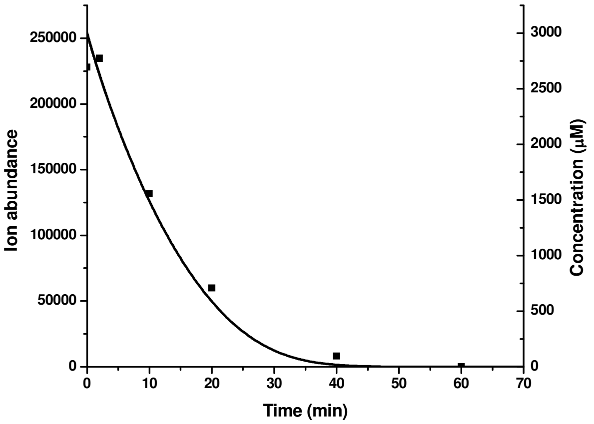

Figure S2. Decay of m/z$^+$ 117 (glyoxal) in ESI-MS positive mode analysis of 3000 μM experiment samples (squares) and kinetic model prediction on glyoxal (solid line).

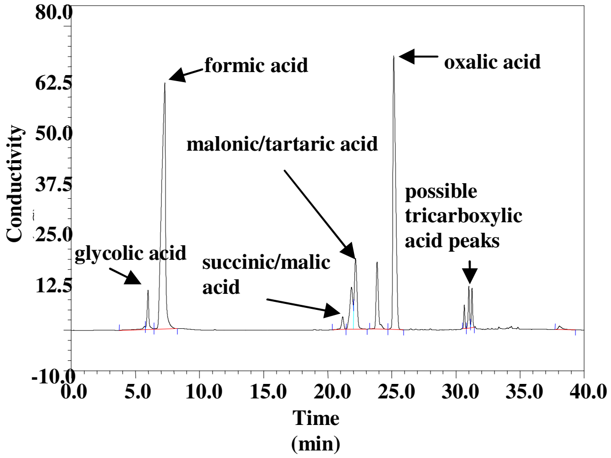

Figure S3. IC chromatogram of a sample from 3000 micromolar experiment 13, t = 20 minutes, analyzed on conductivity detector.

Table S1. Glyoxal ± H_2SO_4 + OH radical aqueous batch reaction experiments.

Exp. #	**Glyoxal (μM)**	**H_2O_2 (mM)**	**H_2SO_4 (μM)**	**Estimated ·OH (10^{-12} M)**	**Oxalic acid molar yield**	**Oxalic acid mass yield (%)**
1	30	0.15	0	3.5	0.866	133%
2	30	0.15	0	3.5	0.959	149%
3	30	0.15	280	3.5	0.850	132%
4	30	0.15	280	3.5	0.888	138%
5	30	0.15	840	3.5	0.834	129%
6	30	0.15	840	3.5	0.864	134%
7	300	1.5	0	4.7	0.646	100%
8	300	1.5	0	4.7	0.590	92%
9	300	1.5	280	4.7	0.619	96%
10	300	1.5	280	4.7	0.613	95%
11	300	1.5	840	4.7	0.533	83%
12	300	1.5	840	4.7	0.718	111%
13	3000	15	0	5.8	0.261	41%
14	3000	15	0	5.8	0.263	41%
15	3000	15	280	5.8	0.242	38%
16	3000	15	280	5.8	0.239	37%
17	3000	15	840	5.8	0.241	37%
18	3000	15	840	5.8	0.232	36%

OH radical concentrations are modeled using the reactions in Table 1. Oxalic acid yield is defined as maximum oxalic acid mass (or moles) divided by mass (moles) of glyoxal reacted. Atmospheric yields will differ from experimental yields in part due to lower atmospheric concentrations of H_2O_2. Atmospheric yields can be determined using the kinetic model for glyoxal < 300 μM.

Table S2. Quality control measures for organic acids in IC analysis.

	Glycolic acid	**Formic acid**	**Glyoxylic acid**	**Succinic acid**	**Malonic acid**	**Oxalic acid**
Retention time (min)	5.9	6.8	9.7	20.4	21.5	24.6
Coefficient of determination	99.95%	99.53%	99.70%	99.87%	99.98%	99.90%
Recovery in mixed standard recovery	106.4%	103.0%	86.5%	104.6%	99.7%	102.7%
Recovery in mixed standard with H_2O_2 and catalase	101.8%	158.0%	<5%	102.3%	98.6%	102.5%
Method Detection Limit (μM)	0.6	0.7	0.2	4.3	0.03	0.1
Method Precision	pooled standard deviation for all replicate analyses = 4.1% (n=28)					
Analytical Precision	pooled standard deviation for all duplicate samples = 1.5% (n=36)					

Retention time in IC, Coefficient of determination (r^2) of 5-point calibration; recovery of standards containing glycolic, formic, glyoxylic, succinic, malonic, and oxalic acids sampled from the reaction vessel and analyzed as samples; pooled standard deviation divided by mean for samples analyzed twice (replicates) and samples taken at the same time and analyzed as independent samples (duplicates). Method detection limits were determined by Perri et al. (23).