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Patron: Druschel, Greg

Journal Title: Aquatic geochemistry.

Volume: 9 Issue: 2

Month/Year: 2003

Pages: 145-eea

Article Author:

Article Title: Druschel, G. K., R. J. Hamers, G. W. Luther, III, and J. F. 'Kinetics and mechanism of trithionate and tetrathionate oxid'

Imprint: Dordrecht ; Boston ; Kluwer Academic Pub

ILL Number: 630812



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Kinetics and Mechanism of Trithionate and Tetrathionate Oxidation at Low pH by Hydroxyl Radicals

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(Received in final form: 24 November 2003)

Abstract. The oxidation kinetics of trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) with hydroxyl radicals (OH^*) have been investigated in systems analogous to acid mine drainage (AMD) environments. The discovery of hydroxyl radical (OH^*) formation on pyrite surfaces (Borda et al., 2003) suggests hydroxyl radicals may affect the oxidation kinetics of intermediate sulfur species such as tetrathionate. Cyclic voltammetry experiments in acidic solutions indicate that the reaction of $S_4O_6^{2-}$ with OH^* goes through an unknown intermediate, tentatively assigned as $S_3O_4^{n-}$. An outer-sphere electron transfer mechanism for the reaction of $S_4O_6^{2-}$ with OH^* to form $S_3O_4^{n-}$ is proposed based on experimental results. Oxidation rates for trithionate and tetrathionate in the presence of Fenton's reagent (which forms hydroxyl radicals) are too fast to be directly measured using UV-Vis spectrophotometry, electrochemical, or stop-flow spectrophotometry methods. Competitive reaction kinetics within the context of the Haber-Weiss mechanism suggests that the rate constant for the oxidation of trithionate and tetrathionate with OH^* is in excess of $10^8 M^{-1} sec^{-1}$.

1. Introduction

Polythionates, intermediate sulfur species of the general formula $S_xO_6^{2-}$, are important species in the redox transformations of sulfur compounds in many environments and in the metabolism of sulfur-oxidizing and reducing microorganisms (Xu et al., 2000; Schippers and Sand, 1999; Takano et al., 2000; Stuedel et al., 1987; Suzuki, 1999; Kelly, 1999; Chambers and Trudinger, 1978). Polythionates are not the predominant stable form of sulfur in oxygenated environments, and represent a potential intermediate along the oxidation and reduction pathways between more reduced sulfur species and sulfate. Polythionate chemistry in low pH solutions is of particular interest for determination of the role of intermediate sulfur species in the oxidation of metal sulfide minerals to sulfate (Schippers et

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al., 1999; Goldhaber, 1983; Moses et al., 1987) and in the chemistry of volcanic crater lakes (Takano et al., 2000). Trithionate ($S_3O_6^{2-}$) and tetrathionate ($S_4O_6^{2-}$) homogeneous oxidation (i.e., in the absence of surfaces) in low pH, ferric-iron rich solutions was investigated by Druschel et al. (2003). Results suggest that these species should be present in significant quantities if pyrite oxidation progresses through aqueous thiosulfate.

In environments where sulfide minerals are being oxidized, it is important to determine the reactivity of intermediate sulfur species with respect to potential catalysts, products of catalytic reactions, and photochemical reaction products.

Hydrogen peroxide (H_2O_2) and hydroxyl radicals (OH^*) are produced through photochemical reactions in many environments (Stumm and Morgan, 1996; Hoigné, 1990). Hydroxyl radicals have been shown to form in illuminated waters associated with AMD (Allen et al., 1996). Hydroxyl radicals are also known to be formed from photolysis reactions involving nitrate, nitrite, and aqueous iron complexes (Stumm and Morgan, 1996). Hydrogen peroxide decomposes to hydroxyl radical through a Haber-Weiss mechanism in soil environments (Pettigara et al., 2002; Watts et al., 1999). Recently, it was observed that pyrite and other disulfide minerals catalyze the formation of hydroxyl radicals and hydrogen peroxide in non-illuminated and photochemical conditions (Borda et al., 2001; Borda et al., 2003). Borda et al. (2001) also showed that one source of the OH^* is the reaction between wetted pyrite surfaces and water. In AMD solutions (i.e., solutions containing abundant Fe^{2+}), the OH^* also may be formed by the Fenton reaction. These reactions may yield sufficient concentrations of intermediate oxygen species to affect sulfur redox chemistry in some environments.

Microbial enzymes also catalyze redox reactions involving sulfur compounds. Many microbial species utilize polythionates and other intermediate sulfur species to make S-bearing biomolecules (e.g., amino acids such as cysteine) and for metabolic energy generation (Pronk et al., 1990; Hallberg et al., 1996; Friedrich et al., 2001). The ability of microorganisms to utilize redox-active species for metabolic energy generation requires that the kinetics of enzymatic reactions be faster than inorganic reactions. It may be hypothesized that bacteria not able to utilize intermediate sulfur species for metabolic energy may still affect sulfur speciation in their environment through enzymatic catalysis. Microbes generate oxygen radicals as metabolic byproducts and manufacture enzymes (e.g., superoxide dismutase) to eliminate radicals (Brock and Madigan, 1991). Thus, microbes may also affect sulfur chemistry through release/consumption of intermediate oxygen species.

An understanding of sulfur compounds in the environment requires a survey of the kinetics of oxidation of sulfur species by H_2O_2 and OH^* . Based on the results of inorganic experiments it was suggested that hydrogen peroxide and hydroxyl radicals increase the rate of pyrite oxidation (McKibben and Barnes, 1986). Moses et al. (1987) proposed that hydroxyl radicals are associated with hexaquo ferric iron reduction coupled to pyrite oxidation. Sulfite is well known to oxidize rapidly in the presence of hydrogen peroxide and hydroxyl radicals, with rate constants on

the order of $10^5 M^{-1} s^{-1}$ (Moses et al., 1997; Huie and Wood, 1994), illustrating that trithionate species in solution react with OH^* , characterized by rate constants of sec^{-1} (Schoenshoefer, 1994). Trithionate ($S_3O_6^{2-}$) reacts rapidly with other sulfur species, and hydroxyl radicals (OH^*) (Druschel et al., 2003).

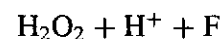
A series of experiments were conducted with both thiosulfate and tetrathionate (Allen et al., 1984; Das et al., 1999). The trithionate radical anion ($S_3O_6^{2-}$) reduction of $S_4O_6^{2-}$ by OH^* has a high potential for the coupled reaction.

Reactivity of trithionate and hydroxyl radicals generated through photochemical means is of great importance in sulfur transformation.

2. Methods

2.1. EXPERIMENTAL

The kinetic investigations were primarily carried out in a stirred reactor, chemical, and spectroscopic studies of polythionate reactions. Fenton's reagent in the presence of reactant(s) were added to a solution containing



Titration experiments were conducted by adding polythionate stock to tetrathionate and Fe^{2+} . The first set of titration experiments was carried out in a 0.01 M HCl in 1-cm quartz cells with a 100 W Xe lamp. These experiments were conducted with spectra collected in the 200-400 nm range. The experiments were performed

chemistry of volcanic tetrathionate ($S_4O_6^{2-}$) at low pH, ferric-iron rich waters suggest that these species undergo rapid oxidation progresses

and, it is important to consider the effect of pH on reaction products.

are produced through the reaction of hydrogen peroxide and iron(II) ions (Morgan, 1996; and Borden, 1996). In natural illuminated waters, iron(II) ions are also known to be oxidized to iron(III) in aqueous iron complexes composed of hydroxyl radicals (Pettigara et al., 1996) and other disulfide species (hydrogen peroxide in water) (Borden, 2001; Borda et al., 2001). The OH^* is the reactive species in the Fenton reaction. The reactive oxygen species

of sulfur compounds. Intermediate sulfur species (thiosulfate) and for metal ions (Friedrich et al., 1996; Friedrich et al., 1996). Species for metabolic reactions are faster than those of iron(II) ions. Iron(II) ions are able to utilize inter-sulfur speciation in the presence of oxygen radicals (hydrogen peroxide dismutase) and other oxygen species.

requires a survey of the reaction. Based on the results of the reaction of iron(II) ions and hydroxyl radicals (Friedrich et al., 1996; Moses et al., 1986). Moses et al. (1986) with hexaquo ferric iron(II) ions rapidly oxidize iron(II) ions with rate constants on

the order of $10^5 M^{-1} sec^{-1}$ and $5 \times 10^9 L mol^{-1} sec^{-1}$, respectively (Ermakov et al., 1997; Huie and Neta, 1987). The rapid oxidation of thiosulfate ($S_2O_3^{2-}$) with hydrogen peroxide is utilized in one method to synthesize trithionate (Kelly and Wood, 1994), illustrating both the rapid oxidation of thiosulfate and the stability of trithionate species in concentrated H_2O_2 solutions. Thiosulfate also reacts rapidly with OH^* , characterized by a second-order rate constant of $8.6 \times 10^9 L mol^{-1} sec^{-1}$ (Schoenshoefer, 1973). Hoffman (1977) showed that H_2S and polysulfides (S_n^{2-}) react rapidly with H_2O_2 in acidic solutions. In contrast to reactivity of many other sulfur species, elemental sulfur is resistant to reaction with both H_2O_2 and OH^* radicals (Druschel, 2002).

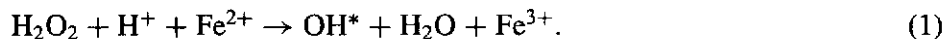
A series of experiments with pulse radiolysis techniques have been carried out with both thiosulfate and tetrathionate solutions (Schöneshöfer, 1973; Mehnert et al., 1984; Das et al., 1999). These experiments showed the formation of a tetrathionate radical anion, $S_4O_6^{3-}$, resulting from either oxidation of thiosulfate or reduction of $S_4O_6^{2-}$ by a hydrated electron. Das et al. (1999) report a reduction potential for the couple $S_4O_6^{3-}/2 S_2O_3^{2-}$ of $+1.07 \pm 0.03 V$.

Reactivity of trithionate and tetrathionate with hydrogen peroxide and hydroxyl radicals generated through the Fenton reaction may have considerable environmental importance. In this paper, we investigate these reactions and evaluate their importance in sulfur transformations at low pH.

2. Methods

2.1. EXPERIMENTAL METHODS

The kinetic investigation of tetrathionate oxidation by hydrogen peroxide was primarily carried out in batch reactions utilizing ion chromatographic, electrochemical, and spectroscopic determination of intermediate species. Investigation of polythionate reaction with hydroxyl radicals was accomplished by utilizing Fenton's reagent in batch and titration experiments (where limited amounts of reactant(s) were added to solutions then analyzed immediately). Fenton's reagent is a solution containing both H_2O_2 and Fe^{2+} that forms hydroxyl radicals via:



Titration experiments at pH 1, open to atmospheric O_2 , were carried out by: (1) adding polythionate solutions to Fenton reagent, (2) adding H_2O_2 to a solution of tetrathionate and Fe^{2+} , and (3) adding H_2O_2 into a solution of polythionates. The first set of titration experiments was performed by adding 400 μl of 1 mM $S_4O_6^{2-}$ stock to a 0.01 M HCl solution containing 2 mL of 1 mM H_2O_2 and 1 mM Fe^{2+} in 1-cm quartz cells while being scanned (using a 15 millisecond integration time). These experiments were analyzed on an Ocean Optics S2000 spectrophotometer, with spectra collected between 200 and 800 nm. The second set of titration experiments were performed by adding 1, 1.5, 2, 4, and 10 mM H_2O_2 to 10 mL 0.01 M

HCl solutions containing 2 mM tetrathionate and 5 mM Fe^{2+} . Analyses of sulfur species (HS^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, SO_3^{2-} , and SO_4^{2-}) were carried out by ion chromatography. In the third set of titration experiments, 10 mL of 500 μM tetrathionate in a 0.1 M HCl solution containing 5 mM ferrous iron was allowed to equilibrate to a solution of $\sim 25\%$ trithionate. 400, 800, 1000, 1200, and 1400 μmoles H_2O_2 were then titrated into identical solutions before analysis for trithionate and tetrathionate by ion-pairing chromatography. All experiments were carried out between pH 0.5 and 2.

Another set of titration experiments was conducted under high-purity argon purged conditions using an electrochemical system. 10 ml solutions of 0.01 N HCl and H_2SO_4 were purged for 4 minutes with high purity argon in the electrode stand cell before the addition of 200 μM tetrathionate and 1 mM H_2O_2 . 20 μl aliquots of a 10 mM ferrous iron solution were titrated into the reaction cell and each standard addition point was scanned in triplicate.

2.2. ANALYTICAL METHODS

Chromatographic analysis of collected aliquots for tetrathionate experiments was performed on a Dionex Series 500 ion chromatograph equipped with a conductivity detector and a UV-Vis detector. Spectra were collected at 230 nm. Sulfate, sulfite, thiosulfate, dithionate, and sulfide were detected by ion chromatography using an isocratic 5 mM $\text{NaHCO}_3/5$ mM Na_2CO_3 eluent at a 1.0 ml/min flow rate through an IonPac AS16 column. All peaks except sulfate were detectable with the UV-Vis detector. Polythionates were detected by ion-pairing chromatography using an isocratic 30% acetonitrile: H_2O eluent containing 2 mM tetrabutylammonium hydroxide, buffered with 3 mM $\text{NaHCO}_3/3$ mM Na_2CO_3 and run through an IonPac NS1 column. The method was modified following Steudel et al. (1987), Sturge and Lagu (1993), Wolkoff and Larouse, (1975), Rabin and Stansbury (1985), Steudel and Holt (1986), Zou et al. (1993), and O'Reilly et al. (2001). Tri-, tetra-, and penta-thionate were all detectable down to 5 μM concentrations using a 25 μl sample loop. Elemental sulfur was analyzed by high pressure liquid chromatography (HPLC) using a Shimadzu system UV-Vis at 254 nm, an Alltech C18 column, and an isocratic 95% methanol: H_2O eluent at 1.0 ml/min after the method detailed in McGuire and Hamers (2000) and Strauss and Steudel (1987). Fe^{2+} was analyzed using 1,10 phenanthroline, and total iron was analyzed using a Ferrozine method on a Hach model 2010 portable datalogging spectrophotometer.

Electrochemical measurements were performed using an AIS model DLK 100-A electrochemical analyzer and Princeton EG&G Model 303A Hanging Mercury Drop Electrode (HMDE) stand equipped with a Ag/AgCl reference electrode and a platinum counter electrode. Cyclic voltammetry (CV) scans were performed in triplicate at a scan rate of 500 mV/second from -0.02 to -1.4 V vs. the Ag/AgCl reference and back to -0.02 V. Standards of HS^- , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_3\text{O}_6^{2-}$, and HSO_3^- were prepared and compared to new signals in the CV wave-

form as a result of reagent. 5 ppm SO_2 in forms. Standards of 1 baseline to peak height

Potassium tetrathionate and sodium trithionate salts (1994). Solutions of were prepared from appropriate before use as chromatography prepared from NIST-standard solutions were prepared (grade) and stored in were 0.2 μm filter. 1 molar stock solutions were prepared by addition in the electrochemical cell concentrations. (FischerBrand certified) spiked with the appropriate

CALCULATIONS

Understanding of the reaction as a result of reactive Chem3D (Version 5) assemble polythionates. The z-matrix of the run using Gaussian 94 University of Wisconsin in a spherical container (25 $^\circ\text{C}$) employing B Local charge densities et al., 2001). Models (2000) with the Gaussian

3. Results

3.1. H_2O_2 AND FERROUS SPECTROPHOTOMETRY

Tetrathionate reactivity exceeded reactivity in not appreciably reacted

Analyses of sulfur
out by ion chromato-
1 μ M tetrathionate in
ed to equilibrate to a
1 μ moles H_2O_2 were
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out between pH 0.5

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tions of 0.01 N HCl
n the electrode stand
 O_2 . 20 μ l aliquots of
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matography using an
butylammonium hy-
m through an IonPac
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bury (1985), Steudel
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4 V vs. the Ag/AgCl
 $\text{S}_2\text{O}_6^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_4\text{O}_6^{2-}$,
als in the CV wave-

form as a result of reaction progress from the tetrathionate reaction with Fenton's reagent. 5 ppm SO_2 in N_2 was also bubbled through 0.01 M HCl to identify waveforms. Standards of H_2O_2 and $\text{S}_4\text{O}_6^{2-}$ were used for calibration by measuring the baseline to peak height.

Potassium tetrathionate salts were obtained from Sigma (>99.9% purity). Sodium trithionate salts were prepared according to the method of Kelly and Wood (1994). Solutions of sulfide, thiosulfate, disulfate, metabisulfite, and sulfite were prepared from appropriate salts under a nitrogen or argon atmosphere immediately before use as chromatographic standards. Sulfate chromatographic standards were prepared from NIST-certified stock solution (VWR Scientific). Fe^{2+} and Fe^{3+} stock solutions were prepared from chloride salts obtained from Sigma (ACS reagent grade) and stored in 0.5 M HCl to minimize Fe^{2+} oxidation. All stock solutions were 0.2 μ m filter sterilized. Hydrogen peroxide additions were made from a 1 molar stock solution (3% FisherBrand certified), and Fenton reagent solutions were prepared by adding H_2O_2 to Fe^{2+} solutions. Hydrogen peroxide stocks used in the electrochemical experiments were iodometrically titrated to determine precise concentrations. Experimental solutions were prepared from normalized HCl (FischerBrand certified 1 N HCl solution), diluted with 18 M Ω nanopure H_2O , and spiked with the appropriate standard solutions to the reaction vessel.

CALCULATIONS

Understanding of the geometry, electronic structure, and electron density shifts as a result of reaction was accomplished with several computational techniques. Chem3D (Version 5.0, CambridgeSoft Scientific Computing, Inc.) was used to assemble polythionates, polysulfane monosulfonic acids, and sulfite, and the geometry was initially minimized using the molecular mechanics algorithm MM2. The z-matrix of the resulting molecule was output into a Gaussian input file and run using Gaussian98 (Frisch et al., 2001) on the computational cluster at the University of Wisconsin Department of Chemistry. All species were calculated in a spherical continuum with a dielectric constant of 80 (equivalent to water at 25 °C) employing B3LYP density functional theory and the LANL2DZ basis set. Local charge densities were calculated using Natural Bond Orbital 5.0 (Glendening et al., 2001). Models were visualized using Molden3.7 (Schaftenaar and Noordik, 2000) with the Gaussian98 output for each molecule.

3. Results

3.1. H_2O_2 AND FENTON CHEMISTRY: CHROMATOGRAPHIC AND SPECTROPHOTOMETRIC EXPERIMENTS

Tetrathionate reactivity with H_2O_2 in pH 0.5–2 solutions with excess H_2O_2 did not exceed reactivity in control solutions without H_2O_2 . Because tetrathionate does not appreciably react with either Fe^{2+} ($r = 10^{-6.61 \pm 0.3} [\text{S}_4\text{O}_6^{2-}]^{0.3 \pm 0.08} [\text{Fe}^{3+}]^{0.15 \pm 0.09}$

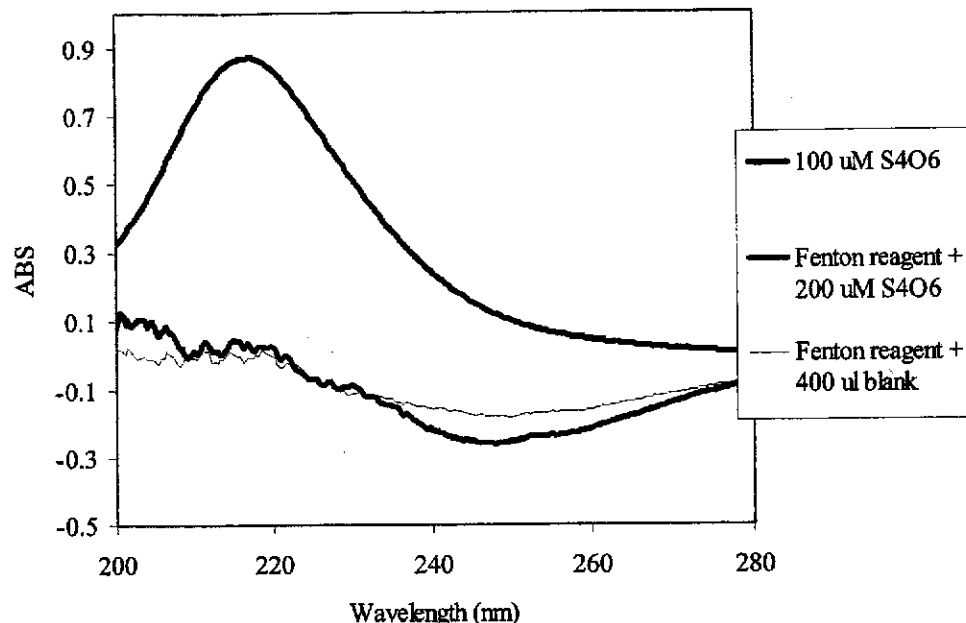


Figure 1. UV spectra of an experiment where a $S_4O_6^{2-}$ solution was titrated into Fenton's reagent. Spectra were collected within seconds of additions. The blank was the same volume of 0.01 M HCl matrix in which the $S_4O_6^{2-}$ solution was prepared.

from Druschel, 2002) or H_2O_2 (blanks run for experiments in this work show no decline in polythionates) over comparable times, it was possible to test for the effect of OH^* on tetrathionate oxidation using Fenton's reaction (see Equation (1)) which generated the radical species OH^* . For experiments in a UV-Vis cell (Figure 1), the disappearance of the tetrathionate signal is faster than the mechanical mixing of the reactants (observations with standard additions indicate this is less than 3 seconds, data not shown). Analysis of the resulting solutions by chromatographic methods within 2–3 minutes only detected sulfate. No significant concentrations of intermediate sulfur species were detected via either in situ UV-Vis or chromatography.

Experimental results of the titration of H_2O_2 added to a 0.01 M HCl solution containing 2 mM tetrathionate and 5 mM Fe^{3+} are presented in Table I. A plot of these results (Figure 2) illustrates the overall molar relationship between H_2O_2 (equivalent to OH^* generated by Equation (1)) additions and sulfate generation, yielding a slope of approximately 1.6. As before, the rate of the reaction was too fast to measure using these methods.

Experiments comparing the rates of reaction of trithionate and OH^* with tetrathionate and OH^* in 0.1 M HCl solutions are illustrated in Figure 3 (where H_2O_2 is equivalent to OH^* generated by Equation (1)). This experiment does not expressly measure the rate of each, but utilizes a limited amount of oxidant (OH^*

Table I. Results from a 0.01 M HCl solution. Recall H_2O_2 added (1))

2000 μM $S_4O_6^{2-}$
H_2O_2 added (μM)
1000
1500
2000
4000
10000

12000
10000
8000
6000
4000
2000
0

Figure 2. Plot of H_2O_2 added (μM) versus sulfate generated in a 0.01 M HCl solution containing 2 mM $S_4O_6^{2-}$ and 5 mM Fe^{2+} yields OH^*

Table I. Results of experiment where 1 M H_2O_2 was titrated into a 0.01 M HCl solution containing 2 mM $\text{S}_4\text{O}_6^{2-}$ and 5 mM Fe^{2+} . Recall H_2O_2 added in excess Fe^{2+} yields equivalent OH^* (Equation (1))

2000 μM $\text{S}_4\text{O}_6^{2-}$, 0.01 M HCl, 5 mM Fe^{2+}			
H_2O_2 added (μM)	SO_4^{2-} measured (μM)	% $\text{S}_4\text{O}_6^{2-}$ oxidized	H_2O_2 added/ SO_4^{2-} measured
1000	752	9%	1.33
1500	1117	14%	1.34
2000	1855	23%	1.08
4000	3029	38%	1.32
10000	5890	74%	1.70

— 100 μM S_4O_6
 — Fenton reagent + 200 μM S_4O_6
 — Fenton reagent + 400 μM blank

280

was titrated into Fenton's
 ank was the same volume

in this work show no
 ssible to test for the
 action (see Equation
 nts in a UV-Vis cell
 aster than the mech-
 dditions indicate this
 esulting solutions by
 sulfate. No signific-
 ted via either in situ

0.01 M HCl solution
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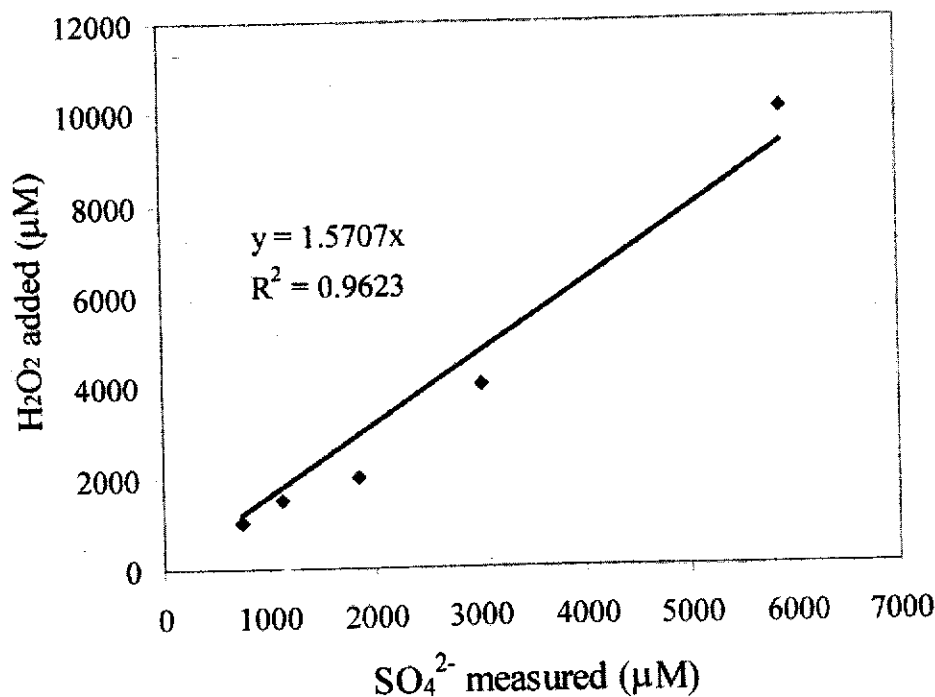


Figure 2. Plot of experimental results from Table II where 1 M H_2O_2 was titrated into a 0.01 M HCl solution containing 2 mM $\text{S}_4\text{O}_6^{2-}$ and 5 mM Fe^{2+} (recall that H_2O_2 added to excess Fe^{2+} yields OH^* after Equation (1)).

Table II. Tabulated results of electrochemical experiments. 20 μ l aliquots of a 10 mM FeCl_2 solution were sequentially added to a 10 ml solution of 200 μM $\text{S}_4\text{O}_6^{2-}$ and 1000 μM H_2O_2 and scanned in triplicate in an HMDE cell. Peak at -0.34 V concentration (μM) was inferred by assuming an equimolar relationship with $\text{S}_4\text{O}_6^{2-}$

Fe^{2+} (μM)	$\text{S}_4\text{O}_6^{2-}$ (μM)	Peak at -0.34 V	H_2O_2 (μM)
0	200	0	1000
20	170	50	794
40	152	75	745
60	132	96	684
80	112	117	625
100	86	144	535
120	76	171	441
140	49	191	375
160	37	200	314
180	26	198	259
200	12	173	221
220	6	156	192
240	0	121	152
260	0	119	139
280	0	96	111
300	0	77	86

generated from Equation (1)) to compare the amounts of reactants left after each step. A significant difference in reactivity would lead to depletion of one species over than the other in the course of the reaction (observed in steps by limiting the amount of reactant). The experiment illustrates trithionate reacts at a rate similar to tetrathionate with hydroxyl radicals (within experimental error).

3.2. FENTON CHEMISTRY – ELECTROCHEMICAL EXPERIMENTS

Electrochemical measurements of the reaction of tetrathionate and OH^* support the extremely fast reaction kinetics observed above. Tetrathionate reacted completely with each addition of OH^* before the reaction cell was scanned, in a time frame of a few seconds. This in situ analysis and much faster sampling times did indicate the formation of a sulfur intermediate as a result of the oxidation

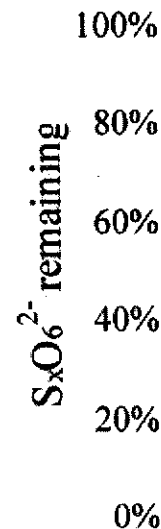


Figure 3. Comp
 H_2O_2 (recall tha

of tetrathionate by potential of approx of H_2S $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_3^{2-}$ of SO_2 gas through this reaction were whether Fe^{2+} was Spikes of H_2S , $\text{S}_2\text{O}_3^{2-}$ bubbling of SO_2 g illustrates that the of these ions. Resi approximately a 1 with addition of Fe this 1:1 ratio for S are generally with consumed at each of intermediates v The intermediate presence of excess than $\text{S}_4\text{O}_6^{2-}$ does, the $\text{S}_4\text{O}_6^{2-}$ is cons UV-Vis spectroph

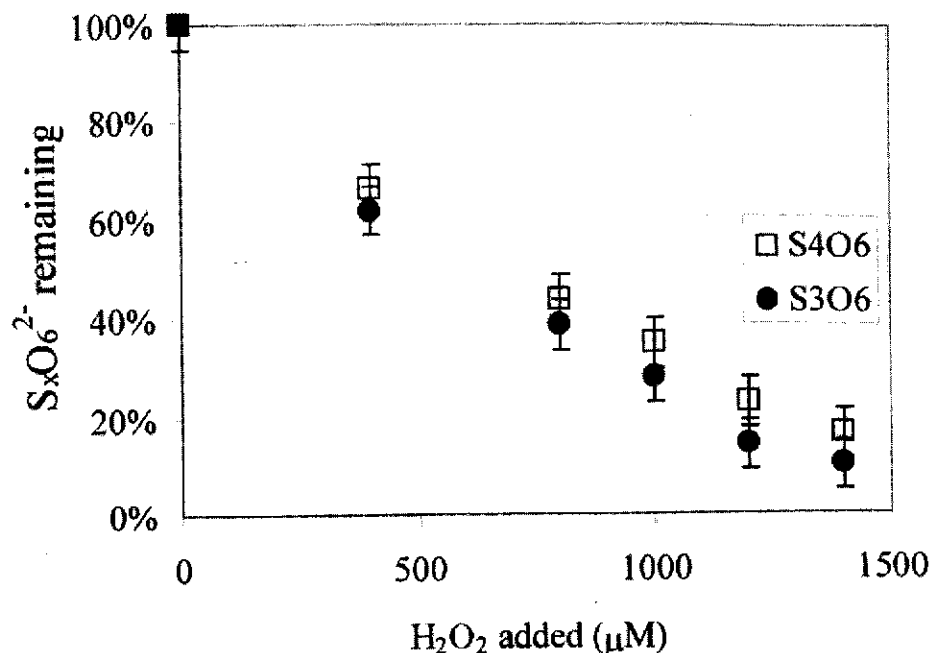


Figure 3. Comparison of trithionate and tetrathionate measured after sequential additions of H_2O_2 (recall that H_2O_2 added to excess Fe^{2+} yields OH^* after Equation (1)).

of tetrathionate by OH^* . $\text{S}_4\text{O}_6^{2-}$ was oxidized to a species exhibiting a peak at a potential of approximately -0.34 V (Figure 4), that is not a signal due to formation of H_2S , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_3\text{O}_6^{2-}$, HSO_3^{2-} , or products from bubbling of SO_2 gas through acidic media (Figure 5). The products generated as a result of this reaction were consistent in different matrices (0.01 N HCl and H_2SO_4) and whether Fe^{2+} was titrated into excess H_2O_2 or H_2O_2 was titrated into excess Fe^{2+} . Spikes of H_2S , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_2\text{O}_5^{2-}$, $\text{S}_4\text{O}_6^{2-}$, $\text{S}_3\text{O}_6^{2-}$, HSO_3^{2-} and products from bubbling of SO_2 gas into a solution containing this species (data not shown) also illustrates that the peak at -0.34 V is not from a Fe^{2+} or Fe^{3+} complex of any of these ions. Results show that the oxidation of $\text{S}_4\text{O}_6^{2-}$ to this species occurs at approximately a 1:1 relationship with the addition of OH^* (which is related 1:1 with addition of Fe^{2+} to excess H_2O_2 via Equation (1)) (Figure 6). Deviations from this 1:1 ratio for $\text{S}_4\text{O}_6^{2-}$ and Fe^{2+} in the course of the experimental data (Table II) are generally within experimental error, while deviations of the amount of H_2O_2 consumed at each step are outside experimental error and indicate some reaction of intermediates with H_2O_2 in this experiment (which lacks molecular oxygen). The intermediate species at -0.34 V species did not measurably oxidize in the presence of excess H_2O_2 over several hours. The species reacts with OH^* slower than $\text{S}_4\text{O}_6^{2-}$ does, and thus does not show oxidation by that reaction until most of the $\text{S}_4\text{O}_6^{2-}$ is consumed (Figure 6). That the species was not directly detected by UV-Vis spectrophotometry indicates that the species may not have an absorption

reactants left after each depletion of one species in steps by limiting the reacts at a rate similar to error).

IMENTS

onate and OH^* support trithionate reacted com- was scanned, in a time faster sampling times result of the oxidation

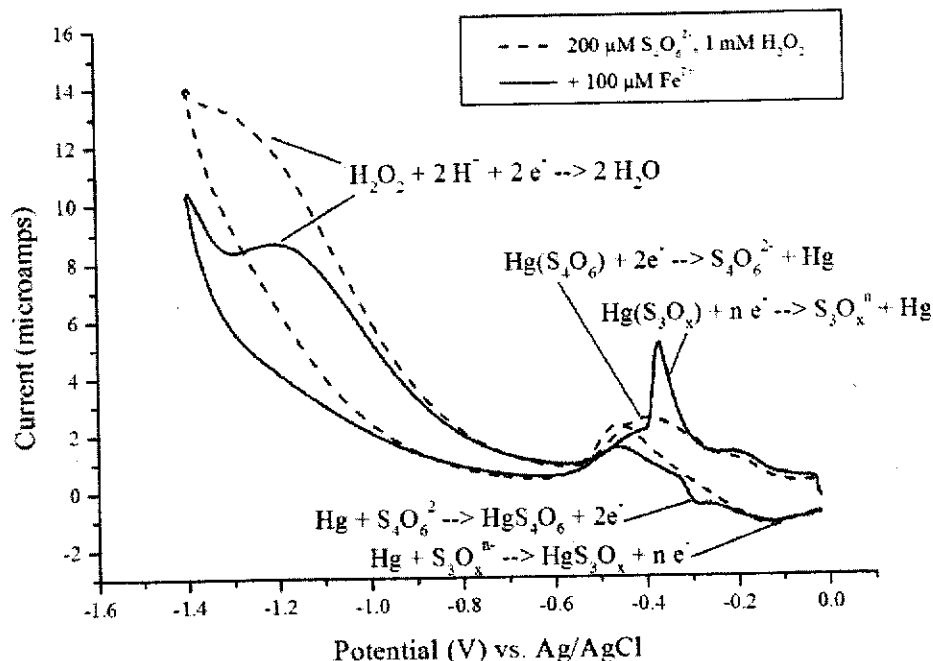


Figure 4. Selected cyclic voltammograms illustrating the reaction of $S_4O_6^{2-}$ with Fenton's reagent, with appropriate peaks labeled. Voltammetric scans begin after a potential of -0.1 V is held for 3 seconds, which electrochemically oxidizes Hg to form a complex of the form $Hg(S_xO_y^n)$. The amalgam is reduced (observed as increased current) as the scan goes to -1.4 V, and oxidation to re-form the $Hg(S_xO_y^n)$ occurs as the scan returns from -1.4 V to 0.05 V. The peak at -0.34 V is tentatively assigned as $S_3O_x^{n-}$.

signal in those ranges or it is identical to the tetrathionate signal. It is possible that this species oxidized before or during the chromatographic analyses and no mass balance problem was detected for this reason.

4. Discussion

4.1. OH^* AND H_2O_2 REACTIVITY

Tetrathionate and trithionate solutions spiked with H_2O_2 showed no increase in reactivity compared to a blank. However, solutions exposed to OH^* generated through the Fenton reaction (Equation (1)) oxidized at a rate faster than analytically resolvable by these methods (Figure 1). There is no statistically significant difference between trithionate and tetrathionate oxidation rates by OH^* (Figure 3), probably because the OH^* cleaves similar SO_3^- groups from these molecules.

The full oxidation of tetrathionate to sulfate may be represented by the half reaction:

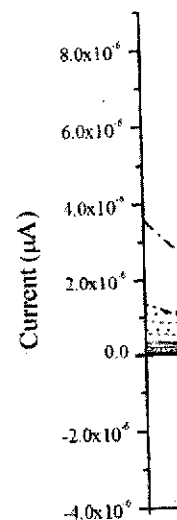
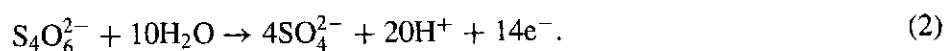
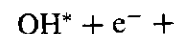


Figure 5. Cyclic voltammogram from reaction of potentials listed. $150 \mu M H_2SO_3$, $500 \mu M$ and has is the result of b The peak tentativ 5) is labeled with

OH^* reduction may

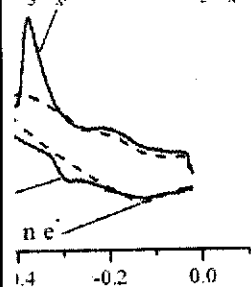
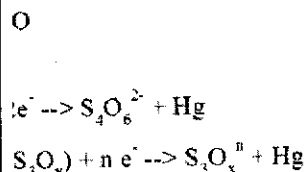


If all H_2O_2 added to 1), and OH^* is the oxidation of 1 mol average observed I 14. This indicates one electron oxidation OH^* , but are most

A previously observed in voltammetry consistent with a $S_2O_6^{2-}$, $S_2O_5^{2-}$, $S_2O_3^{2-}$ through acidic me

GORY K. DRUSCHEL ET AL.

$S_2O_8^{2-}$, 1 mM H_2O_2
 $\sqrt{Fe^{2+}}$



ion of $S_4O_6^{2-}$ with Fenton's reagent after a potential of -0.1 V form a complex of the form $(S_4O_6^{2-})_n$ as the scan goes to -1.4 V turns from -1.4 V to 0.05 V.

signal. It is possible that cyclic analyses and no mass

showed no increase in current used to OH^* generated at a rate faster than analytical rates by OH^* (Figure 3), in these molecules. The reaction is represented by the half

(2)

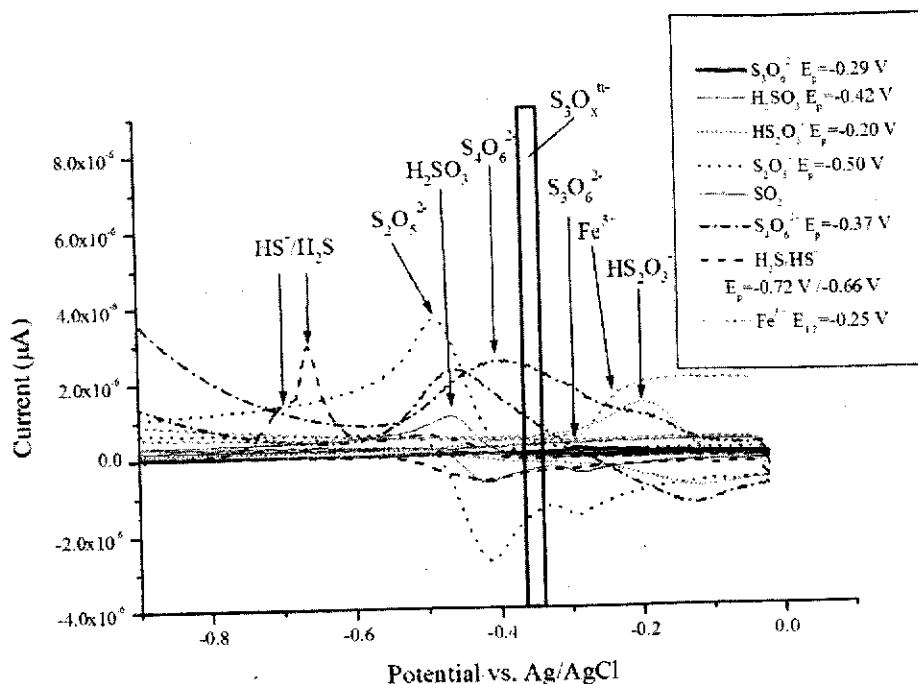


Figure 5. Cyclic voltammograms showing several sulfur intermediates potentially formed from reaction of tetrathionate and OH^* with corresponding peak (E_p) and half-wave ($E_{1/2}$) potentials listed. Concentrations range from $20 \mu M$ for sulfide at pH 6 (90% H_2S 10% HS^-), $150 \mu M H_2SO_3$, $200 \mu M HS_2O_3^-$, $200 \mu M S_4O_6^{2-}$, and $500 \mu M S_2O_5^{2-}$. $S_3O_6^{2-}$ was run at $500 \mu M$ and has a very weak signal relative to the other sulfoxyanions. The signal marked SO_2 is the result of bubbling SO_2 gas through an acidic solution (no significant peaks observed). The peak tentatively assigned $S_3O_x^{n-}$ observed from reaction of tetrathionate and OH^* (Figure 5) is labeled with a box in this diagram for comparison.

OH^* reduction may be represented via the half reaction:



If all H_2O_2 added to solutions containing excess Fe^{2+} is converted to OH^* (reaction 1), and OH^* is the sole oxidant of tetrathionate and all intermediate species, then oxidation of 1 mole of tetrathionate requires 14 moles of OH^* (equal to H_2O_2). The average observed H_2O_2/SO_4^{2-} ratio of 1.3 ± 0.22 (Table I) is significantly less than 14. This indicates that most OH^* is consumed rapidly by reaction with $S_4O_6^{2-}$ in a one electron oxidation. Products of this oxidation then may be partly consumed by OH^* , but are mostly oxidized to sulfate by reaction with H_2O_2 , O_2 , or Fe^{3+} .

A previously unobserved intermediate in the oxidation of polythionates was observed in voltammetry experiments (peak at -0.34 V Figure 4). This peak is not consistent with a signal for any of the sulfur intermediates tested (H_2S , $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_5^{2-}$, $S_4O_6^{2-}$, $S_3O_6^{2-}$, HSO_3^{2-} , or products from bubbling of SO_2 gas through acidic media; Figure 5). This intermediate was the reaction product of

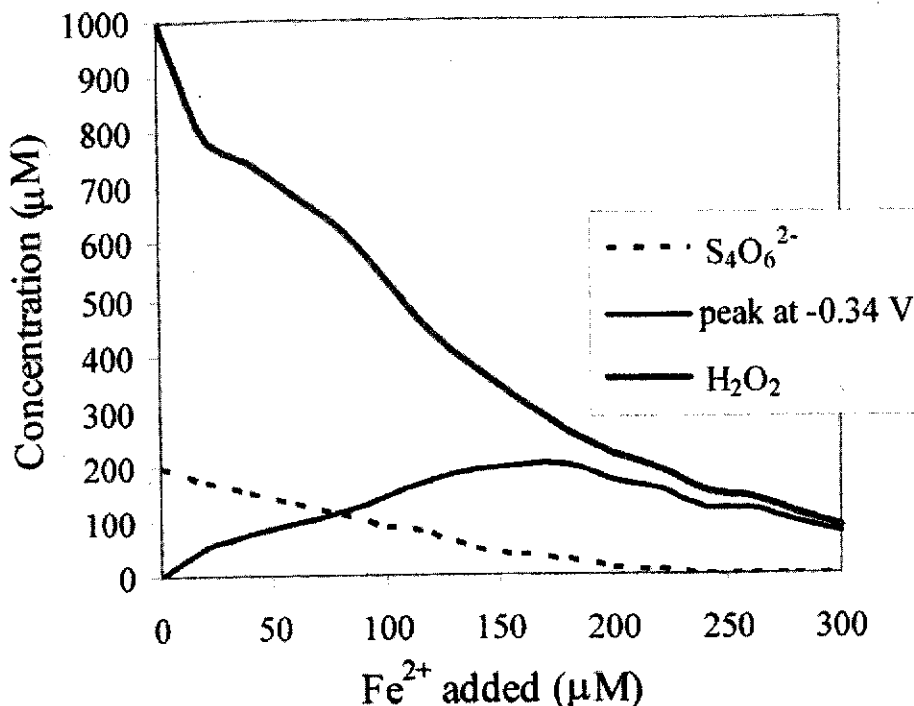


Figure 6. Reaction progress results from voltammetry of 200 mM $S_4O_6^{2-}$ in 1 mM H_2O_2 solution at 0.01 M HCl with additions of ferrous iron stock (yielding OH^* from reaction (1)).

tetrathionate with OH^* (equivalent to H_2O_2 via reaction 1), was resistant to oxidation by H_2O_2 , and was oxidized by OH^* at a rate slower than $S_4O_6^{2-}$ is oxidized by OH^* (Figure 6).

Chromatographic/spectrophotometric experiments (Table I; Figures 1, 2, and 3) and voltammetric experiments (Table II, Figures 4, 5, and 6) are different in that the former are exposed to atmospheric oxygen while the latter are not. This suggests that the intermediate observed in voltammetry experiments at -0.34 V (Figure 4) oxidizes quickly in the presence of molecular oxygen.

No other intermediates were observed in any of these experiments, though due to the number of electrons transferred and bonds broken as a result of the oxidation of $S_4O_6^{2-}$ to SO_4^{2-} , a number of steps and potential intermediates must be involved. Because elemental sulfur is resistant to reaction with all possible reactants, including OH^* (Druschel, 2002), and because S_8 would be observed by both the chromatographic and electrochemical techniques (Rozan et al., 2000) used, S_8 is not a significant product in the reaction pathway between $S_4O_6^{2-}$ and SO_4^{2-} involving OH^* . Other unknown intermediates must oxidize with excess O_2 , H_2O_2 , or Fe^{3+} faster than it was possible to observe them through the techniques employed in this study.

$H_2O_2 + Fe^{2+} \rightarrow$

4.3 x

Figure 7. Diagram of the presence of e

4.2. COMPETITIVE

The rates of reaction of H_2O_2 , OH^* , superoxide, and other species listed in Table III. In these experiments, some of the H_2O_2 was oxidized into a solution of OH^* (Reaction 1). The results are shown in Table I and Figure 4. The OH^* generated via these pathways shown in

If the rate constant for the reaction of OH^* with H_2O_2 is significantly slower ($k \approx 10^4 M^{-1} sec^{-1}$), then the rate constant for the reaction of OH^* with Fe^{2+} is significantly enhanced. The rate constant for the reaction of OH^* with Fe^{2+} is larger than that for the reaction with H_2O_2 (Buxton et al., 1988). The rate constant for the reaction of OH^* with Fe^{2+} is $2.3 \times 10^7 M^{-1} sec^{-1}$.

A rate constant for the reaction of OH^* with tetrathionate is not available, making it impossible to compare the rate constants for the reaction of OH^* with tetrathionate and

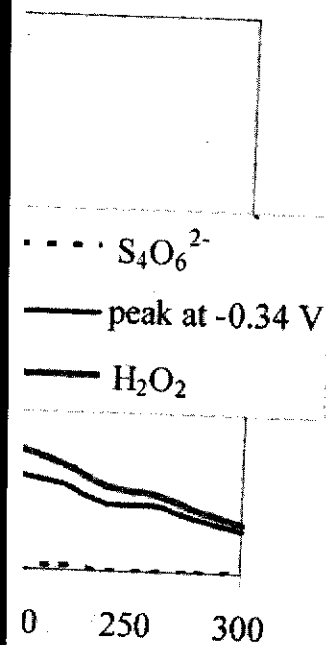


Figure 7. Diagram of selected parts of the pathway for tetrathionate and H_2O_2 oxidation in the presence of excess ferrous iron.

4.2. COMPETITIVE KINETICS

The rates of reactions involving iron and intermediate oxygen species, including H_2O_2 , OH^* , superoxide radical ($\text{O}_2^{\cdot-}$), and hydrogen superoxide radical (HO_2^*), are listed in Table III. Although the rate of tetrathionate oxidation was not directly measured, some constraints can be applied using rate data in Table III. Titration of H_2O_2 into a solution containing both $\text{S}_4\text{O}_6^{2-}$ and Fe^{2+} will initially react to form OH^* (Reaction 1). OH^* generation upon H_2O_2 addition for experiments described in Table I and Figure 2 occurs on the order of hundreds of microseconds. The OH^* generated may react either with tetrathionate or Fe^{2+} in the solution via the pathways shown in Figure 7.

If the rate constant for reaction of OH^* with tetrathionate (Figure 7, #2; k_+) is significantly slower than that for reaction with Fe^{2+} (Figure 7, #1; $k = 2.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$), then the OH^* will react with excess Fe^{2+} in the solution. Because significantly enhanced tetrathionate reactivity is observed (Figures 1 and 4), the rate constant for reaction of OH^* with tetrathionate must be comparable to, or larger than that for reaction with Fe^{2+} (the second-order rate constants for OH^* reaction with Fe^{2+} are $4.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at pH 3 and $2.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at pH 1, Buxton et al., 1988). The same argument for reactivity of the intermediate observed in HMDE experiments (at -0.34 V) may be made, with the further constraint that the rate constant is between that of tetrathionate and the rate of reaction for OH^* with Fe^{2+} ($2.3 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at pH 1).

A rate constant in excess of $10^8 \text{ M}^{-1} \text{ sec}^{-1}$ coupled with the methods of measuring tetrathionate concentrations amidst other sulfoxyanion reaction products make it impossible to directly quantify. The detection limits of UV-Vis spectrophotometry and electrochemical techniques for tetrathionate are on the order of

mM $\text{S}_4\text{O}_6^{2-}$ in 1 mM H_2O_2 during OH^* from reaction (1).

, was resistant to oxidation. $\text{S}_4\text{O}_6^{2-}$ is oxidized by

le I; Figures 1, 2, and 3) are different in that the are not. This suggests at -0.34 V (Figure 4)

periments, though due to result of the oxidation rates must be involved. possible reactants, in- observed by both the al., 2000) used, S_8 is $\text{S}_4\text{O}_6^{2-}$ and SO_4^{2-} in- with excess O_2 , H_2O_2 , or techniques employed

Table III. Reactions among oxygen intermediates and in contact with iron (the Haber–Weiss reactions) and the second-order reaction rate constants governing each (Data from Chen and Pignatello, 1997). Recall that the oxidation state order is: $O_2 > O_2^{\cdot-} > H_2O_2 > OH^* > H_2O$

Reaction	k ($M^{-1} \text{ sec}^{-1}$)
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^-$	76
$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^* + H^+$	0.01
$OH^* + H_2O_2 \rightarrow HO_2^* + H_2O$	2.7×10^7
$OH^* + Fe^{2+} \rightarrow Fe^{3+} + OH^-$	4.3×10^8
$Fe^{3+} + HO_2^* \rightarrow Fe^{2+} + O_2 + H^+$	1.0×10^4
$Fe^{2+} + HO_2^* + H^+ \rightarrow Fe^{3+} + H_2O_2$	1.2×10^6
$HO_2^* + HO_2^* \rightarrow H_2O_2 + O_2$	8.5×10^5
$HO_2^* \leftrightarrow O_2^{\cdot-} + H^+$	Forward = 3×10^{15}
Reverse = 5×10^{10} $pK_a = 4.8$	
$Fe^{3+} + O_2^{\cdot-} \rightarrow Fe^{2+} + O_2$	1.5×10^8
$Fe^{2+} + O_2^{\cdot-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2$	1.0×10^7
$HO_2^* + O_2^{\cdot-} + H^+ \rightarrow H_2O_2 + O_2$	9.7×10^7

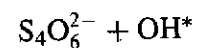
micromolar concentrations in these matrices (data not shown). Considering the limiting rate law as an elementary 2nd order redox reaction, the rate law may be defined:

$$\frac{d[S_4O_6^{2-}]}{dt} = -k_+[S_4O_6^{2-}][OH^+]. \quad (4)$$

Using $10^8 M^{-1} \text{ sec}^{-1}$ as the lower limit to the rate and $50 \mu M$ as the minimum change in concentration that needs to be detected in a solution containing $500 \mu M$ $S_4O_6^{2-}$ and OH^* , one point would have to be collected every 0.002 milliseconds. This is several orders of magnitude faster than most rapid kinetics systems can measure, and to increase the time interval to more measurable time periods (if the rate is around the lower limit of 10^8), the concentrations of the reactants must be pushed very close to or beyond the detection limit. Therefore, it is not feasible at present to provide quantitative rate data for this reaction beyond constraining the rate with previously determined and competitive reactions without first developing a much more sensitive detection method capable of making measurements at sub-millisecond intervals. Such an endeavor is certainly of great value but beyond the scope of the current project.

4.3. PROPOSED MECHANISMS

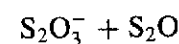
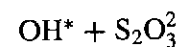
It is proposed that the reaction is an outer-sphere electro-



The highest occupied molecular orbital (HOMO) of the $S_4O_6^{2-}$ could facilitate fast electron transfer experiments definitive of any bridging ligand and electron density and could be $HS_3O_4^{2-}$ or $S_3O_4^{2-}$ distribution as a result (Das et al., 2003; Christensen et al., 2003; Christensen et al., 2003). It is proposed that the reaction is an outer-sphere electro- (at $E_p = -0.34$ V) product, $S_3O_4^{2-}$ (with unknown).

The assigned S_3 about its reactivity HOMO of the $HS_3O_4^{2-}$ +3 eV. This indicates LUMO of -0.44 eV and spectroscopic 1.3, indicating that OH^* in those experiments.

The $S_4O_6^{3-}$ radiolysis products in these experiments are $S_2O_3^-$ (Schönberger et al., 1999) could not form in the reaction. A significant source of hypothesis and subsequent intermediate via

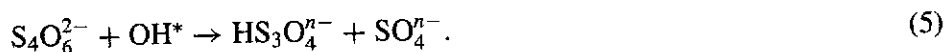


Das et al. (1999), results.

An $S_3O_6^{2-}$ product is the predominant product.

4.3. PROPOSED MECHANISM

It is proposed that the initial reaction of the $S_4O_6^{2-}$ ion with OH^* proceeds via an outer-sphere electron transfer:



The highest occupied molecular orbital (HOMO) of $S_4O_6^{2-}$ and the lowest unoccupied molecular orbital (LUMO) of OH^* are both π -type orbitals, which would facilitate fast electron transfer (Wulfsberg, 2000). No information from these experiments definitively supports a discreet associative complex or a dependence on any bridging ligands. OH^* acceptance of an electron would then result in a shift in electron density and weakening of S-S bonds in $S_4O_6^{2-}$, yielding products which could be $HS_3O_4^{2-}$ and SO_3^* or $HS_3O_4^*$ and SO_3^{2-} , depending on the details of electron distribution as a result of this reaction (Figure 8). It has been established (Druschel et al., 2003; Christidis et al., 1989) that the terminal S-S bonds of $S_4O_6^{2-}$ are weaker and more likely to break, a condition which should be consistent with this reaction. It is proposed that the intermediate observed in voltammetry experiments (at $E_p = -0.34$ V in Figures 4 and 5) is a derivative of this 3-sulfur oxyanion product, $S_3O_4^{n-}$ (whether or not this species is protonated under these conditions is unknown).

The assigned $S_3O_4^{n-}$ molecule has never been characterized, and little is known about its reactivity. However, density functional theory calculations show the HOMO of the $HS_3O_4^{2-}$ molecule to be π -type with an energy of approximately +3 eV. This indicates the molecule should be readily reactive with O_2 (π -type LUMO of -0.44 eV). In experiments containing saturated O_2 (chromatographic and spectrophotometric experiments), the ratio of OH^* to sulfate generated was 1.3, indicating that only a fraction of any intermediate was oxidized further by OH^* in those experiments (with the rest oxidized by O_2 or Fe^{3+}).

The $S_4O_6^{3-}$ radical anion observed in radiolytic experiments could only form in these experiments from reacting with a hydrated electron or a thiosulfate radical anion, $S_2O_3^-$ (Schöneshöfer, 1973; Mehnert et al., 1982). The $S_4O_6^{3-}$ radical anion could not form in these experiments as an initial product because there is no significant source of hydrated electrons. The formation of thiosulfate along the reaction path and subsequent reaction of that thiosulfate with OH^* to form $S_4O_6^{3-}$ as an intermediate via



Das et al. (1999), would consume more OH^* , which is not supported by these results.

An $S_3O_6^{n-}$ product was not observed by any technique employed, indicating the predominant pathway of the oxidation reaction to sulfate does not include this

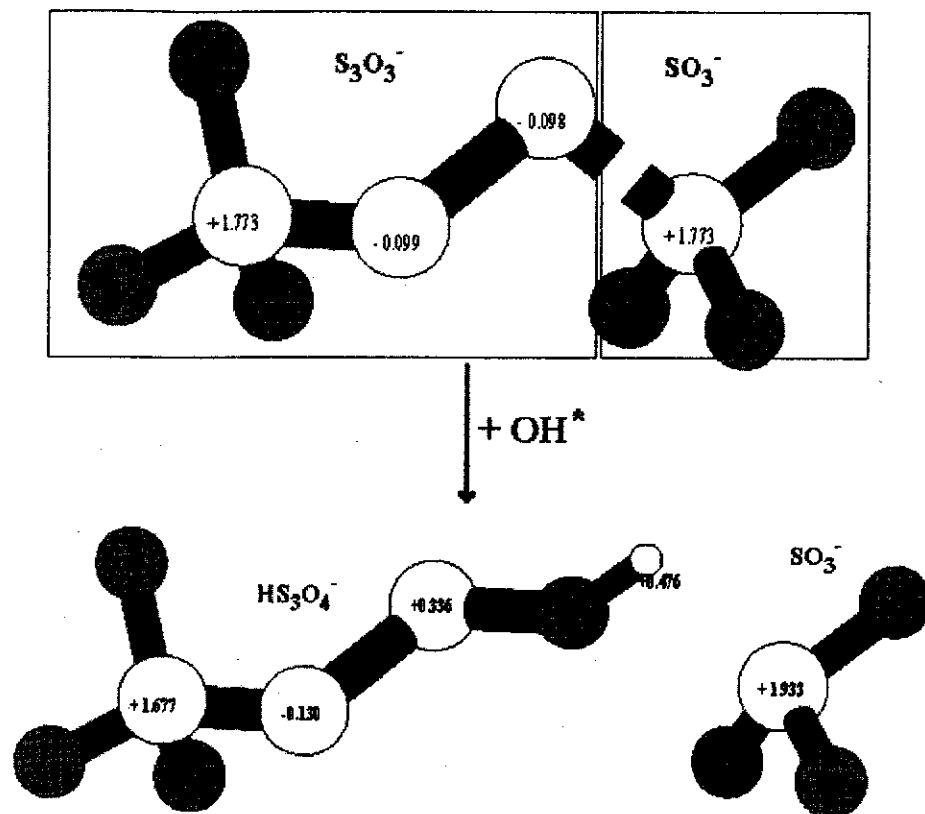
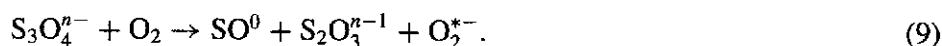
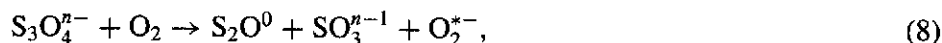


Figure 8. Schematic diagram of $S_4O_6^{2-}$ reaction with OH^* and subsequent reaction products. Natural charges on each atom were calculated with Gaussian98.

intermediate. The $S_3O_4^{n-}$ intermediate then must have reacted with molecular O_2 in those experiments to break another S-S bond via:

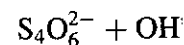


Sulfur monoxide and disulfur monoxide are well known in volcanic and atmospheric literature, and would be expected to oxidize very quickly to sulfate in the presence of light or oxygen (Moses et al., 2002). Protonation of S_2O does not qualitatively change the potential energy surface of any S_2O isomers (Davy and Skoumbourdis, 1998), and it is assumed that protonated forms would not be markedly more stable than unprotonated forms. The conversion of the $S_3O_4^{n-}$ product from reaction of $S_4O_6^{2-}$ and OH^* to SO_4^{2-} would therefore be expected to be very fast in solution, which is consistent with these experimental results.

The 1:1 relationship between Fe^{2+} added and $S_4O_6^{2-}$ degradation coupled with the appearance of the $S_3O_4^{n-}$ ion and the lack of any other observed intermediates suggest the process shown in Figure 8 is rate-determining.

5. Conclusions

Trithionate and tetrathionate are potential products of many potential reactions (Druschel, 2002). Kinetic studies of these species show that the reaction of trithionate with O_2 through a possible reactive intermediate is faster than with O_2 through a possible reactive intermediate.



(where n is the charge on the sulfur atom, determining and modifying the order rate constant). The rate constants have been defined as k_1 and k_2 is at minimum on the order rate constant. The rate constant was not theoretically determined. The best stopped-flow experiment was strained by the absence of trithionate and tetrathionate faster than with Fe^{2+} only known inorganic sulfate at low pH.

Acknowledgements

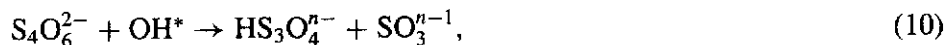
The authors thank helpful discussion with 2 anonymous reviewers. This research was supported by National Science Foundation Science Foundation.

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- Bielski B. H., Cabelli aqueous solution.
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5. Conclusions

Trithionate and tetrathionate are reasonably stable at low pH and in the presence of many potential catalysts found in AMD environments (Druschel et al., 2003, Druschel, 2002). However, greatly accelerated trithionate and tetrathionate oxidation kinetics result from reaction with OH^* . Experimental results also indicate that the reaction of tetrathionate with OH^* generated by Fenton's reagent proceeds through a possible $\text{S}_3\text{O}_4^{n-}$ intermediate, which is less reactive with OH^* but more reactive with O_2 than $\text{S}_4\text{O}_6^{2-}$. This one electron oxidation step,



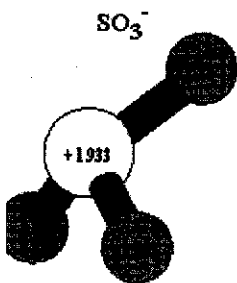
(where n is the charge dependent on the degree of electron redistribution) is rate-determining and may be assumed to be an elementary redox reaction with a 2nd order rate constant. Based on comparison with other reactions and their rates which have been defined (Chen and Pignatello, 1997), the rate constant for this reaction is at minimum on the order of $10^8 \text{ M}^{-1} \text{ sec}^{-1}$. Direct measurement of this reaction rate was not theoretically possible with current detection methods and even the best stopped-flow apparatus available; these rates therefore must remain only constrained by the above arguments. However, they do illustrate that the oxidation of trithionate and tetrathionate with OH^* at low pH is at least 14 orders of magnitude faster than with Fe^{3+} or O_2 (Druschel et al., 2003). OH^* oxidation provides the only known inorganic pathway by which polythionate may be rapidly converted to sulfate at low pH.

Acknowledgements

The authors thank Dr. Michael Borda, Dr. Martin Schoonen, and Dr. Bo Hu for helpful discussions. We also thank Dr. Frank Millero for editorial handling and 2 anonymous reviewers for helpful insights and suggestions on the manuscript. This research was supported by grant #CHE 9521731, #CHE 9807598 from the National Science Foundation (JFB) and grant #OLE 0096365 from the National Science Foundation (GWL).

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quent reaction products.

with molecular O_2

(8)

(9)

volcanic and atmospheric sulfur dioxide (SO₂) is oxidized to sulfate in the atmosphere. The oxidation of S₂O does not occur. The oxidation of S₂O isomers (Davy and others) would not be expected to occur. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur.

ation coupled with the formation of sulfuric acid. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur. The oxidation of the S₃O₄ⁿ⁻ would be expected to occur.

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