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Photochemical Oxidation of As(III) in Ferrioxalate Solutions

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Photochemical reactions involving aqueous Fe(III) complexes are known to generate free radical species such as $OH^{\bullet}$ that are capable of oxidizing numerous inorganic and organic compounds. Recent work has shown that As(III) can be oxidized to As(V) via photochemical reactions in ferric-citrate solutions; however, the mechanisms of As(III) oxidation and the potential importance of photochemical oxidation in natural waters are poorly understood. Consequently, the objectives of this study were to evaluate oxidation rates of As(III) in irradiated ferrioxalate solutions as a function of pH, identify mechanisms of photochemical As(III) oxidation, and evaluate the oxidation of As(III) in a representative natural water containing dissolved organic C (DOC). The oxidation of As(III) was studied in irradiated ferrioxalate solutions as a function of pH (3−7), As(III), Fe(III), and 2-propanol concentration. Rates of As(III) oxidation (0.5−254 μM h^{-1}) were first-order in As(III) and Fe(III) concentration and increased with decreasing pH. Experiments conducted at pH 5.0 using 2-propanol as an $OH^{\bullet}$ scavenger in light and dark reactions suggested that $OH^{\bullet}$ is the important free radical responsible for As(III) oxidation. Significant rates of As(III) oxidation (4−6 μM h^{-1}) were also observed in a natural water sample containing DOC, indicating that photochemical oxidation of As(III) may contribute to arsenic (As) cycling in natural waters.

Introduction

The speciation of arsenic (As) in soils and natural waters is an important factor controlling the environmental fate and subsequent toxicology of this metalloid. The two common inorganic forms of As present in surface waters are arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$) and arsenite ($H_3AsO_3^0$), and transformation rates between these two valence states may be mediated by both microbiological and chemical processes (*1*). Chemical oxidation of arsenite (As(III)) in natural water systems may occur via reaction with $MnO_{2(s)}$ (*2*, *3*), Fe(III) (*4*), and H_2O_2, although significant rates of oxidation via H_2O_2 require pH values greater than the pK_a for $H_3AsO_3^0$ (e.g. pH > 9.3), and high concentrations of H_2O_2 relative to As(III) (*5*,*6*). However, H_2O_2 is an important reactant involved in the production of free radical species (e.g. $OH^{\bullet}$, $O_2^{\bullet-}$), which have been reported to oxidize As(III) (*7*, *8*). Specifically, the oxidation of As(III) has been reported in low pH (<2.5) irradiated ferric perchlorate solutions (*7*) and attributed to the production of free radical species, $OH^{\bullet}$ and $Cl_2^{\bullet-}$. In Fe(III)-citrate solutions, high-valence iron (i.e. Fe(IV)) was hypothesized to be the important reactive species responsible for the photochemical oxidation of As(III) (*8*). Although different mechanisms of As(III) oxidation were suggested in these studies, it is clear that high-valence iron and or free radical species generated from photochemical reaction products, such as H_2O_2, are responsible for As(III) oxidation in these systems.

The photochemical formation of H_2O_2 in natural waters is thought to occur as a result of disproportionation of hydroperoxyl ($HO_2^{\bullet}$; pK_a = 4.8) and superoxide ($O_2^{\bullet-}$) radicals formed from the capture of light energy by dissolved organic carbon (DOC) and subsequent reduction of $O_{2(g)}$ (*9*, *10*):

$$DOC + h\nu + O_2 \rightarrow DOC^{\bullet+} + O_2^{\bullet-} \quad (1)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (2)$$

The absorption of light by appropriate chromophore(s) of DOC results in an excited-state intermediate DOC*, which transfers electrons to O_2 to form the superoxide radical $O_2^{\bullet-}$ followed by disproportionation of $HO_2^{\bullet}$ to form H_2O_2 (*11*). Alternatively, H_2O_2 may be produced via the reaction of superoxide with reduced metals such as Fe(II):

$$O_2^{\bullet-}\ (HO_2^{\bullet}) + 2H^+ + Fe(II) \rightarrow H_2O_2 + Fe(III) \quad (3)$$

Once H_2O_2 is formed, it can react further with Fe(II) (Fenton's Reaction) in the dark to yield the hydroxyl radical ($OH^{\bullet}$), a strong oxidant capable of oxidizing many organic compounds and other environmentally relevant species (*12*, *13*):

$$H_2O_2 + Fe(II) \rightarrow Fe(III) + OH^{\bullet} + OH^- \quad (4)$$

The formation of H_2O_2 and $OH^{\bullet}$ has also been studied extensively in irradiated ferrioxalate solutions (*14*, *15*). The ferrioxalate system is a classic model for the study of photochemical formation of H_2O_2 and $OH^{\bullet}$, and oxalate is a common natural and anthropogenic compound found in nearly all natural waters including soil pore waters, surface waters, and atmospheric water (*14*, *16*). Oxalate has a high affinity for ferric iron, and even at molar oxalate:Fe ratios as low as 1:1, the Fe(III)−oxalato complexes are the dominant solution species of Fe(III) at pH 4 (*14*). It is thought that photolysis of the trioxalato ferrioxalate species yields the free radical $CO_2^{\bullet-}$ via the spontaneous decarboxylation of the oxalyl radical anion, $C_2O_4^{\bullet-}$ (*17*):

$$Fe^{III}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4^{2-} + C_2O_4^{\bullet-} \quad (5)$$

$$C_2O_4^{\bullet-} \rightarrow CO_2^{\bullet-} + CO_2 \quad (6)$$

The oxalyl radical has a short lifetime before decarboxylation to form $CO_2^{\bullet-}$, thus preventing its participation in other reactions (*17*). Under aerobic conditions, $CO_2^{\bullet-}$ reacts quickly with O_2 (*18*)

$$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2 \quad (7)$$

which, depending on pH, results in the formation of either the superoxide radical, $O_2^{\bullet-}$, or the hydroperoxyl radical, $HO_2^{\bullet}$ (Table 2). Once the superoxide radical is formed, the formation of H_2O_2 and $OH^{\bullet}$ in the ferrioxalate system proceeds as described in eqs 2−4. Importantly, the exclusion of O_2 via bubbling with N_2 (g) has been shown to effectively curb the production of $O_2^{\bullet-}$ and the subsequent formation of H_2O_2 (*14*).

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TABLE 1. Appearance/Disappearance Rates of Constituents in Irradiated Solutions

varying condition	constant conditions[a]	μM h^{-1} -d[As(III)]/dt	d[C_3H_6O]/dt[b]	d[H_2O_2]/dt	-d[H^+]/dt
pH					
7	17.4 μM As(III)	14 (4)[c]		15 (10)	0 (0)
6	18 μM Fe(III)	91		193	902
5		118 (21)		259 (13)	630 (261)
4		157		794	1279
3		255 (16)		861 (37)	1236 (60)
[As(III)] (μM)					
1.3	pH 5.0	12 (2)		229 (17)	542 (59)
9.3	18 μM Fe(III)	66 (4)			
17.4		118 (21)		259 (15)	630 (261)
135		174 (2)		261 (16)	369 (42)
1350		157 (6)		nd[d]	892 (30)
13500		218 (22)		nd	833 (63)
[As(III)] (μM)					
0	pH 5.0		147 (10)	170 (6)	1123 (44)
135	18 μM Fe(III)	16 (5)	74 (5)	260 (20)	1052 (19)
1350	13.5 mM 2-propanol	61 (10)	63 (9)	nd	948 (35)
13500		196 (15)	47 (8)	nd	953 (65)
[Fe(III)] (μM)					
0.02	pH 5.0	0.5 (0.2)		2.6 (0.5)	0 (0)
0.1	135 μM As(III)	3.3 (0.2)		3.3 (0.2)	0 (0)
0.2		4.9 (1.2)		2.8 (0.5)	0 (0)
1.8		156 (11)		48 (16)	102 (37)
$KClO_4$ (M)					
0.01	pH 5.0 18 μM Fe(III) 17.4 μM As(III)	127 (12)		237 (17)	761 (62)
Hyalite					
sunlight	pH 5.0	5.6 (0.3)		bd[e]	24 (7)
QTH lamp	18 μM As(III) 18 μM Fe(III)	3.7 (0.2)		bd	0 (0)

[a] All solutions were prepared in 0.01 M KCl with the exception of experiments where 0.01 M $KClO_4$ was used, and all solutions contained 1 mM oxalate, with the exception of the Hyalite natural water samples. [b] C_3H_6O = 2-propanone. [c] Values in parentheses are standard errors of triplicate analyses. [d] nd = not determined; concentrations > 1350 μM As(III) interfere with H_2O_2 measurement. [e] bd = below detection.

The photochemical production of $OH^\bullet$ free radicals in natural waters either via DOC or oxalate pathways may contribute to As(III) oxidation occurring in surface waters of lakes, oceans, and rivers. Consequently, the objectives of this study were to (i) evaluate oxidation rates of As(III) in irradiated ferrioxalate solutions as a function of pH, (ii) identify probable mechanisms of photochemical As(III) oxidation, and (iii) evaluate the oxidation of As(III) in a representative natural water containing dissolved organic C (DOC). Results indicate that the photochemical oxidation of As(III) in ferrioxalate solutions can be rapid (half-lives ranging from 0.01 to 1 h) and that photochemical oxidation of As(III) may also be important in natural waters containing Fe(III) and DOC.

Experimental Section

Reacting Solutions. Reaction mixtures (total volume = 0.2 or 0.4 L) were prepared under a red safelight in a 1.0 L glass vessel via the sequential addition of analytical grade KCl, $FeCl_3$, $K_2C_2O_4$, and NaH_2AsO_3 stock solutions (fresh NaH_2AsO_3 stock solutions prepared every 3 days). All solutions were prepared in a background of 0.01 M KCl or $KClO_4$, and the concentration of initial oxalate in the reaction vessels was kept constant at 1 mM. With the exception of experiments designed to determine the influence of Fe(III) concentration, experiments were conducted at 18.0 μM Fe(III). At these ratios of oxalate:Fe(III), over 99% of the total soluble Fe(III) existed as oxalate complexes, of which the trioxalato species was dominant (Figure 1a). The distribution of aqueous species was estimated using GEOCHEM (*19*), using equilibrium constants for soluble Fe(III)-complexes as presented by Zuo and Hoigne (*14*). Precipitation of Fe(III) in the presence of oxalate was precluded since solid-phase Fe(III) was not observed in any ferrioxalate solutions ranging from pH 3 to 7. However, precipitation of $Fe(OH)_{3(s)}$ was allowed in calculations conducted with no oxalate, using a log $K = 3.54$ for the reaction $Fe(OH)_3(s) + 3H^+ = Fe^{3+} + 3H_2O$ (*20*).

In one set of experiments at pH 5.0, initial As(III) concentrations were varied from 1.3 μM to 13.5 mM As(III) to determine the rate dependence of As(III) photooxidation on initial As(III) concentration. The influence of pH on As(III) photooxidation was evaluated at pH values ranging from 3 to 7 at initial As(III) concentrations of 17.4 μM. In addition, one set of experiments was conducted at pH 5.0 in the presence of 133 μM As but at variable Fe(III) concentrations ranging from 0.02 to 18 μM.

Experimental Apparatus and Irradiation Source. Ferrioxalate reaction mixtures were exposed to light emitted from a 250 W Quartz Tungsten Halogen lamp (QTH, Oriel Instruments). The effective photon flux of the lamp between wavelengths 300−500 nm was determined to be approximately 97 μE cm^{-2} h^{-1} using ferrioxalate actinometry (*21*). The temperature of all reaction mixtures was held constant at 25 ± 2 °C with a circulating water bath connected to a jacketed reaction vessel. The pH of the reacting solutions was held constant during irradiation using an autotitrator (Radiometer, Copenhagen) operating in pH-stat mode while being constantly stirred with a Teflon bar and vigorously bubbled with compressed air. Reaction mixtures were sampled as a function of time (generally for periods up to 30 min) and analyzed for total soluble As(III), As(V), Fe(II), Fe(III), and H_2O_2 (methods discussed below). Initial rates of formation or disappearance were determined by fitting an exponential equation to the data and measuring the slope

TABLE 2. Compilation of Chemical Reactions and Corresponding Rate Constants Concerning Production and/or Consumption of Free Radical Species in Fe−As−H_2O Systems

	eq no.	k (L mol^{-1} s^{-1})	ref
As(III) Oxidations			
$H_3As^{III}O_3 + OH^\bullet \rightarrow As^{IV}(OH)_4$	(13)	8.5×10^9	(*29*)
$H_3As^{III}O_3 + O_2^{\bullet-} + H_2O + H^+ \rightarrow As^{IV}(OH)_4 + H_2O_2$		3×10^6	(*8*)
$H_3As^{III}O_3 + Cl_2^{\bullet-} + H_2O \rightarrow As^{IV}(OH)_4 + 2Cl^- + H^+$		unknown	(*7*)
$H_3As^{III}O_3$ + Fe species → ? → $H_2As^{V}O_4^-$		unknown	(*27, 28*)
As(IV) Oxidations			
$As^{IV}(OH)_4$ (+ H^+) + $O_2 \rightarrow H_2As^{V}O_4^-$ + $(HO_2^\bullet)/O_2^{\bullet-}$ + $2H^+$		1.1×10^9	(*29*)
$As^{IV}(OH)_4 + O_2 \rightarrow As^{IV}(OH)_4{-}O_2$		$\sim 1 \times 10^9$	(*29*)
$As^{IV}(OH)_4{-}O_2 \rightarrow H_2As^{V}O_4^- + (HO_2^\bullet)/O_2^- + 2H^+$		$\sim 1 \times 10^{10}$	(*29*)
2-Propanol Oxidation and Follow-Up			
$OH^\bullet + HROH \rightarrow ROH^\bullet + H_2O$		1.9×10^9	(*12*)
$ROH^\bullet + O_2 \rightarrow RO + HO_2^\bullet$		4.1×10^9 [a]	(*18*)
Ferrioxalate Photolysis and Follow-Up Reactions			
$Fe^{III}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe(II) + 2C_2O_4^{2-} + C_2O_4^{\bullet-}$	(5)	$\Phi_{Fe(III)}N_a/V$ (M s^{-1})[b]	(*15*)
$C_2O_4^{\bullet-} \rightarrow CO_2^{\bullet-} + CO_2$	(6)	2×10^6	(*17*)
$CO_2^{\bullet-} + O_2 \rightarrow O_2^{\bullet-} + CO_2$	(7)	4.2×10^9	(*18*)
$O_2^{\bullet-}/HO_2^\bullet$ Reactions			
$HO_2^\bullet \leftrightarrow O_2^{\bullet-} + H^+$		p$K_a = 4.8$	(*11*)
$2HO_2^\bullet \rightarrow H_2O_2 + O_2$	(2)	8.3×10^5	(*11*)
$HO_2^\bullet + H^+ + Fe(II) \rightarrow H_2O_2 + Fe(III)$	(3)	1.2×10^6	(*32*)
$HO_2^\bullet + Fe(III) \rightarrow O_2 + Fe(II) + H^+$		3.6×10^5	(*11*)
$HO_2^\bullet + O_2^{\bullet-} + H_2O \rightarrow H_2O_2 + O_2 + OH^-$	(16)	9.7×10^7	(*11*)
$O_2^{\bullet-} + 2H^+ + Fe(II) \rightarrow Fe(III) + H_2O_2$	(3)	1×10^7	(*32*)
$O_2^{\bullet-} + Fe(III) \rightarrow Fe(II) + O_2$		1.5×10^8	(*32*)
$H_2O_2 + Fe(III) \rightarrow O_2^{\bullet-} + Fe(II) + 2H^+$		2.6×10^{-3} pH 5	(*33*)
$^\bullet$OH Reactions			
$OH^\bullet + OH^\bullet \rightarrow H_2O_2$		5.2×10^9	(*12*)
$OH^\bullet + O_2^{\bullet-}/HO_2^\bullet \rightarrow H_2O + O_2$		6.6×10^9 pH 0.5−6.75	(*12*)
$OH^\bullet + H_2O_2 \rightarrow O_2^{\bullet-}/HO_2^\bullet + H_2O$		3.3×10^7 pH 3−5	(*33*)
$OH^\bullet + Fe(II) \rightarrow Fe(III) + OH^-$		3.2×10^8 pH 3−5	(*33*)
Fenton Reaction and $Fe(OH)^{2+}$ Photolysis			
$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^\bullet + OH^-$	(4)	63, 5.7×10^2 pH 3,5	(*34, 33*)
$Fe^{III}(OH)^{2+} + h\nu \rightarrow Fe(II) + OH^\bullet$	(10)	6.3×10^{-4}	(*26*)

[a] Average of three values given in ref *18*. [b] Value based on photochemical transformation of ferrioxalate. $\Phi_{Fe(III)}$ = quantum yield of Fe(III) generation (typical value ~1.2), N_a = absorbed photon flux (einstein s^{-1}) and V = volume irradiated (L).

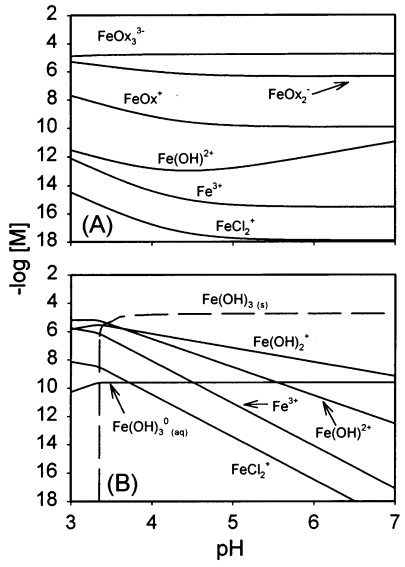

FIGURE 1. Calculated (GEOCHEM) distribution of aqueous Fe(III) species as a function of pH. Fe(III) was not allowed to precipitate in the presence of 1 mM oxalate (A), but was allowed to precipitate as $Fe(OH)_3$ (s) (dashed line) in the absence of oxalate (B). Both solutions contained 0.01 M KCl, 18 μM Fe(III), 18 μM As(III) and 10 mM KCl.

between time zero and 10 ps. The majority of irradiation experiments discussed in the current study were performed in triplicate.

Analytical Methods. Determination of As(V) was performed by adding 5 mL of reaction mixture to a 15 mL HDPE bottle containing 1 mL of 2.0 M TRIS buffer ((hydroxymethyl)-aminomethane, pH 6.0). While sparging the mixture with N_2, 1 mL of 0.025 M NaOH and 1.59 M $NaBH_4$ was added in 0.5 mL increments over 7 min to reduce As(III) to arsine gas. The sample was then sparged for an additional 7 min to purge arsine. Concentrations of As(III) were determined by difference between As(ts) and As(V) (*22, 23*) measured using continuous flow hydride generation atomic adsorption spectrometry (HG-AAS). Samples were acidified with 3 M HCl, prereduced with 1% potassium iodide (KI), and mixed with 0.6% $NaBH_4$ in 0.5% NaOH. Subsequent emission of arsine gas was quantified at 193.4 nm in a quartz cuvette immersed in an air-acetylene flame (Perkin-Elmer model 3100 atomic adsorption spectrophotometer). The detection limit for As using this method was 3.4 nM. Concentrations of H_2O_2 were determined using the *N*,*N*-diethyl-1,4-phenylenediamine method developed by Bader et al. (*24*), and concentrations of Fe(II) and Fe(III) were determined using the o-phenanthroline method (*25*).

Effect of 2-Propanol on Initial As(III) Oxidation Rate. Reaction mixtures (pH 5.0) of 0.01 M KCl, 18 μM Fe(III), 1 mM oxalate, and 13.5 mM 2-propanol and varying amounts of As(III) (0−13.5 mM) were irradiated to determine the initial rate of $OH^\bullet$ formation (when [As(III)] = 0) and to determine the effect of an $OH^\bullet$ scavenger on initial As(III) oxidation rates. These reaction mixtures were sampled as a function of time for a total of 30 min and analyzed for 2-propanone using gas chromatography (Varian Gas Chromatograph, Model 3400, Walnut Creek CA, operating under flame

ionization mode). In the presence of excess 2-propanol relative to other potential $OH^{\bullet}$ scavengers, the production of 2-propanone can be used to estimate the formation rate of $OH^{\bullet}$ (*15*)

$$R_o\,(OH^{\bullet}) = R_o\,(\text{2-propanone})/0.87 \qquad (8)$$

where R_o is initial rate (μM h^{-1}) and 0.87 represents the fraction of 2-propanol molecules attacked by $OH^{\bullet}$ that ultimately result in the formation of 2-propanone (*15*). In experiments designed to determine the effect of an $OH^{\bullet}$ scavenger on initial As(III) oxidation, ferrioxalate solutions containing three concentrations of As(III) (0.135, 1.35, and 13.5 mM) were irradiated in the presence of 13.5 mM 2-propanol. Reaction mixtures were sampled as a function of time for a total of 30 min, after which samples were analyzed for 2-propanone and As(III)/As(V) as described above.

Oxidation of As(III): H_2O_2 and Fe(II) Dark Controls at pH 2.7. Solutions of 2.66 μM As(III) and 20 mM H_2O_2 were prepared under a red safelight and sampled as a function of time for 10 min. An equal volume solution containing either 3.6, 7.2, 17.8, or 35.8 μM Fe(II) was then added, and the reaction mixture was sampled as a function of time for an additional 20 min for a total of 30 min per experiment. Samples were analyzed for Fe(II)/Fe(III), As(III)/As(V), and H_2O_2 as described above. Both solutions were prepared at pH 2.7, had a background ionic strength of 0.01 mM KCl, and were constantly bubbled with air. Care was taken not to exceed the amount of Fe(II) in solution which upon oxidation to Fe(III) would result in the precipitation of amorphous Fe(III) hydroxide. The solubility limit of Fe(III) was estimated using a log $K = 3.54$ as described above. The maximum estimated solubility of Fe(III) at pH 2.7 was 70.5 μM, significantly greater than the concentration of Fe(II) used in this study. In one experiment, As(III) oxidation was measured in the presence of 13.5 mM 2-propanol to confirm the affect of an $OH^{\bullet}$ scavenger on the oxidation of As(III).

Photochemical Oxidation of As(III) in a Natural Water. To determine whether photochemical oxidation of As(III) may occur under sunlight conditions in natural waters containing dissolved organic C (DOC), a water sample was collected from a pristine wetland (pH = 6.5) at an elevation of 2000 m in Hyalite Canyon located 25 km south of Bozeman, MT. The natural water sample was filter-sterilized (0.22 μM) following collection, then refrigerated in an autoclaved vessel until use. The amount of DOC was determined using a DC-80 carbon analyzer (Tekmar-Dohrmann, Cincinnati, OH) and found to equal 0.86 mM C. Total and non-carbonate alkalinity were determined by titration with standardized 0.025 M HCl, using unpurged and purged ($N_{2(g)}$) samples. Since the Hyalite water sample was found to contain below detectable Fe(III) or Fe(II) (<0.45 μM), it was spiked to a concentration of 18 μM Fe(III) 1 h prior to irradiation under natural sunlight at 12 p.m., August 22, 2000. Natural sunlight intensity was measured in the photosynthetically relevant wavelengths using a quantum sensor (LiCOR, Model 190, Lincoln, NE), and total solar irradiance was measured with a solarimeter (Kipp and Zonen Model CM5, Delft, Netherlands). Experiments involving the Hyalite natural water sample were performed in duplicate, and concentrations of As(III), As(V), and H_2O_2 were determined as described previously.

Results and Discussion

Photochemical Oxidation of As(III). At pH 3.0, the oxidation of 17.4 μM As(III) in irradiated ferrioxalate solutions was complete within 10 min (Figure 2A), corresponding to an initial oxidation rate of 255 ± 16 μM h^{-1} (Table 1). The rate of As(III) oxidation in irradiated solutions decreased with increasing pH, falling to 14 μM h^{-1} at pH 7.0 (Figure 2A, Table 1). To verify that the measured oxidation of As(III) occurred as a direct result of photochemical processes resulting from the irradiation of Fe(III)-oxalate solutions, irradiated experiments were compared to appropriate dark controls (Figure 2B). The dark control containing identical concentrations of Fe(III), oxalate, and As(III) showed no oxidation of As(III) (Figure 2B) during a 30 min incubation. Further insights regarding the mechanism of As(III) oxidation were obtained from controls in the presence of H_2O_2 or Fe(III) at pH 3.0 (Figure 2B). Insignificant oxidation of As(III) was observed in dark or irradiated controls containing 300 μM H_2O_2. An additional control was performed at a higher H_2O_2:As(III) ratio of 10 mM H_2O_2 and 1.3 μM As(III), and no oxidation was observed within 10 min. The H_2O_2 controls indicated that direct oxidation of As(III) via H_2O_2 was insignificant under the current solution conditions. This is important because oxidation rates of As(III) via H_2O_2 can be significant at pH values greater than 8.0 and at high ratios of H_2O_2:As(III) (*5*).

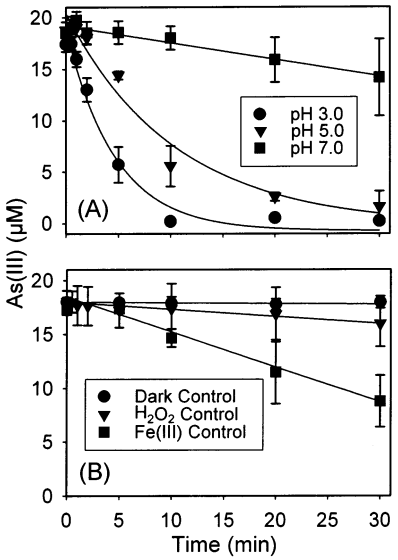

FIGURE 2. Disappearance of As(III) in (A) irradiated ferrioxalate solutions at pH 3, 5 and 7, and in (B) dark or irradiated controls (pH 3.0). Irradiated ferrioxalate solutions and the dark control contained 18 μM As(III), 18 μM Fe(III), and 1 mM oxalate. The irradiated H_2O_2 control contained 18 μM As(III) and 300 μM H_2O_2, while the irradiated Fe(III) control contained 18 μM As(III) and 18 μM Fe(III). Background ionic strength of all solutions = 0.01 M KCl.

The irradiated control experiment conducted at pH 3.0 containing only Fe(III) and As(III) yielded an As(III) oxidation rate of approximately 13 μM h^{-1} (Figure 2B), roughly 5% of the As(III) oxidation rate observed in the presence of Fe(III) and oxalate (Table 1). The oxidation of As(III) in the absence of oxalate may be due to the production of $OH^{\bullet}$ from photoreduction of Fe(III)

$$Fe^{III}(OH)^{2+} + h\nu \rightarrow Fe(II) + OH^{\bullet} \qquad (10)$$

where $Fe(OH)^{2+}$ is an important photoreactive species in acidic solutions (Figure 1B) (*26*). Although photochemical reactions with $Fe(OH)^{2+}$ may represent a significant contribution to As(III) oxidation at low pH, the rate of As(III) oxidation was considerably faster (20 times) in the presence of ferrioxalate complexes. Emett and Khoe (*7*) suggested that $Cl_2^{\bullet-}$ may be a potential oxidant of As(III) in Fe(III) and Cl^- containing solutions. However, the concentration of $FeCl_2^+$ was 2−3 orders of magnitude lower than $Fe(OH)_2^+$ under conditions employed here (Figure 1). Furthermore, the rate of As(III) oxidation was identical in experiments where $KClO_4$

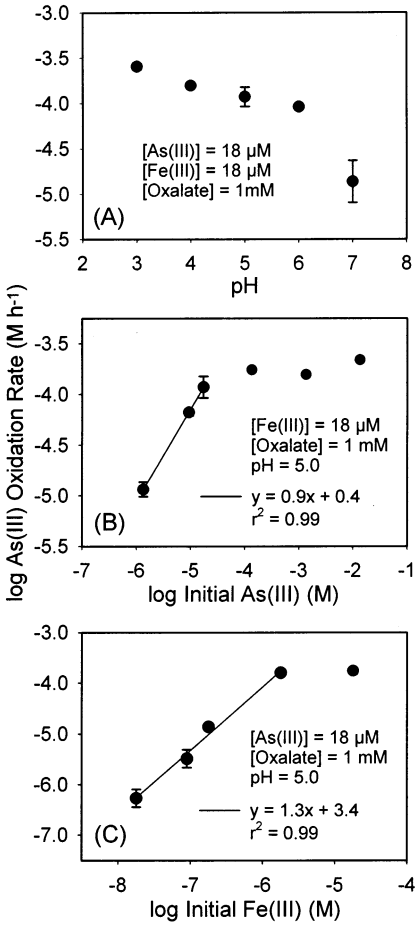

FIGURE 3. Log initial rates of As(III) oxidation (M h^{-1}) as a function of pH (A), initial As(III) (B), and initial Fe(III) (C). All experiments were performed in 0.01 M KCl; experiments reported in (B) and (C) were conducted at pH = 5.0.

was substituted as a background electrolyte (Table 1), ruling out $Cl_2^{\bullet-}$ as an important oxidant of As(III).

As(III) Oxidation Rate Dependence on pH. The rate of photochemical As(III) oxidation in the ferrioxalate system was highly pH dependent (Figure 3A) with initial oxidation rates ranging from 255 ± 16 μM h^{-1} at pH 3.0, to 14 ± 4 μM h^{-1} at pH 7.0. The measured production rate of H_2O_2 also declined with increasing pH (Table 1), which is consistent with results from previous work in ferrioxalate systems (*14*). This pH dependence reflects the mechanism of H_2O_2 formation via $HO_2^{\bullet}/O_2^{\bullet-}$, where at pH values below 4.8 (pK_a for $HO_2^{\bullet}$), $HO_2^{\bullet}$ is the dominant species favoring the formation of H_2O_2 via both eqs 2 and 3. At higher pH, $O_2^{\bullet-}$ becomes the dominant species, which is thought to react more quickly with Fe(III) to form O_2 as opposed to reacting with Fe(II) to form H_2O_2 (Table 2). Although H_2O_2 is not the species directly responsible for the oxidation of As(III), the formation rate of free radical $OH^{\bullet}$ is proportional to the formation rate of H_2O_2 (eq 4).

Oxidation Rate Dependence on Initial As(III) and Fe(III). The rate of As(III) oxidation was evaluated as a function of initial As(III) concentration under constant solution conditions [Fe(III) = 18 μM, pH = 5.0, oxalate = 1 mM] and found to be approximately first-order with respect to As(III) from 1.3 to 17.4 μM initial As(III) (Figure 3B). Under the reaction conditions employed in this study, the oxidation rate of As(III) plateaued at concentrations of As(III) ≥ 135 μM. Clearly, As(III) was a limiting reactant at low initial As(III) concentration, whereas the production of oxidant from photochemical processes limited the reaction rate at high initial As(III) concentrations. Under constant solution conditions resulting in constant H_2O_2 production rates (Table 1), the psuedo-first-order rate expression describing the oxidation rate dependence on initial As(III) can be written

$$-\mathrm{d[As(III)]}/\mathrm{d}t = k_{\mathrm{As-obs}}[\mathrm{As(III)}]^x \qquad (11)$$

where in this study, the fitted values of x and $k_{\mathrm{As-obs}}$ were 0.90 and 2.31 h^{-1}, respectively. The apparent rate constant ($k_{\mathrm{As-obs}}$) is a lumped parameter containing information related to the initial reaction conditions, such as light intensity and initial concentrations of Fe(III), oxalate, and O_2(g).

The dependence of As(III) oxidation rate on the initial concentration of Fe(III) was tested under constant initial solution conditions of pH = 5.0, As(III) = 134 μM, and 1 mM oxalate (Figure 3C). The rate of As(III) oxidation increased with increasing concentrations of initial Fe(III) from 0.02 to 18 μM; however, the initial rate plot (log R_o vs log $[Fe(III)]_o$) was linear only over the range from 0.02 to 1.8 μM Fe(III) ($\log[Fe(III)]_o = -7.75$ to -5.75). Under constant solution and irradiation conditions, this relationship can also be described using a pseudo-first-order rate expression

$$-\mathrm{d[As(III)]}/\mathrm{d}t = k_{\mathrm{Fe-obs}}[\mathrm{Fe(III)}]^z \qquad (12)$$

where $k_{\mathrm{Fe-obs}} = 1475\ h^{-1}$ and $z = 1.24$ over the range of initial Fe(III) concentrations from 0.02 to 1.8 μM. Again, the apparent rate constant, $k_{\mathrm{Fe-obs}}$ is a lumped rate parameter dependent on the initial reaction conditions of the irradiated ferrioxalate solutions. The influence of initial Fe(III) on the oxidation rate of As(III) during irradiation of ferrioxalate solutions is consistent with previous work showing that higher concentrations of Fe(III) result in increasing photolysis rates of oxalate with corresponding increases in H_2O_2 production (*14*).

Mechanism of Photochemical Oxidation of As(III). Although H_2O_2 is not the important species responsible for the rapid oxidation of As(III) observed in the current study, H_2O_2 is a necessary reactant for the formation of the strong oxidant, $OH^{\bullet}$. Hislop and Bolton (*15*) used 2-propanol as a $OH^{\bullet}$ scavenger and measured the subsequent formation of 2-propanone to study the reactions responsible for the formation of $OH^{\bullet}$ in irradiated ferrioxalate solutions. Likewise, we conducted a series of experiments in the absence and presence of excess 2-propanol (13.5 mM) where As(III) ranged from 0 to 13.5 mM. In irradiated ferrioxalate solutions containing no As(III) and 13.5 mM 2-propanol (pH 5.0), the production rate of 2-propanone was found to be 147 ± 10 μM h^{-1} (Table 1), corresponding to an $OH^{\bullet}$ production rate of 169 μM h^{-1} (eq 9). Under identical solution conditions containing 13.5 mM As(III) and 0 mM 2-propanol, the maximum rate of As(III) oxidation was 218 ± 22 μM h^{-1} (Table 1). These results suggest an approximate 1:1 mole ratio of $OH^{\bullet}$ produced to As(III) oxidized. To further examine the role of $OH^{\bullet}$, rates of 2-propanone formation and As(III) oxidation were quantified in competition experiments containing both As(III) and 2-propanol as $OH^{\bullet}$ scavengers. At ratios of 2-propanol:As(III) > 10, the rate of As(III) oxidation decreased compared to the maximum rate observed in the absence of 2-propanol (218 μM h^{-1}, Figure 4). However, at equimolar [As(III)] and [2-propanol] = 13.5 mM, the rates of As(III) and 2-propanol oxidation were 196 μM h^{-1} and 47 μM h^{-1}, respectively, yielding a rate ratio of 4.2 (Table 2). The rate constants for the oxidation of As(III) and 2-propanol by $OH^{\bullet}$ have been estimated to be 8.5×10^9 and 1.9×10^9 L mol^{-1} s^{-1} (Table 2), respectively, yielding a ratio of rate constants of 4.5. These data show clearly that As(III) and 2-propanol compete for $OH^{\bullet}$ and that the relative rates of As(III) versus 2-propanol oxidation are consistent with the values of reported rate constants for these two species. Hug

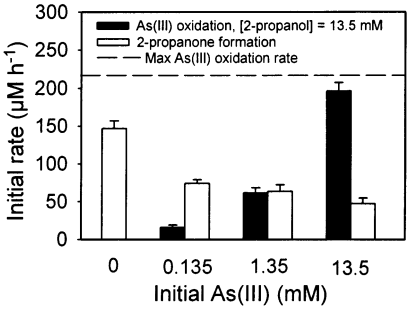

FIGURE 4. Oxidation rate of As(III) and formation rate of 2-propanone (μM h^{-1}) as a function of initial [As(III)] in the presence of 13.5 mM 2-propanol (conditions: 1 mM oxalate, 18 μM Fe(III), 0.01 M KCl, pH 5.0). Dashed line represents the maximum As(III) oxidation rate observed in the absence of 2-propanol.

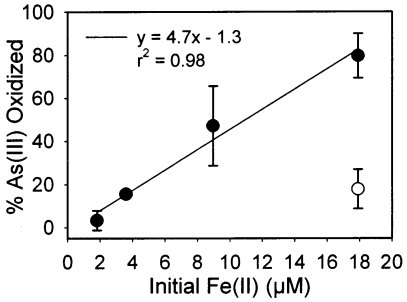

FIGURE 5. Percent of As(III) oxidized (●) as a function of Fe(II) in the presence of 1.35 μM initial As(III) and 10 mM initial H_2O_2 in the dark at pH 2.7 (Fenton's Reaction). Oxidation of As(III) in the presence of 13.5 mM 2-propanol is shown (○) at Fe(II) = 18 μM.

et al. (*8*) recently suggested that $OH^\bullet$ was not the dominant oxidant of As(III) in Fe(III)-citrate solutions at pH 7.0; however, results presented here suggest that $OH^\bullet$ is the dominant oxidant of As(III) in the ferrioxalate system at pH 5.0.

To further verify the importance of $OH^\bullet$ in the oxidation of As(III), experiments were conducted in the dark containing only Fe(II) and H_2O_2 (Fenton's Reaction) as an alternative method of generating reactive $OH^\bullet$ species. When solutions containing variable concentrations of Fe(II) (2−18 μM) were added to an equal volume of solution containing 2.7 μM As(III) and 20 mM H_2O_2, maximum As(III) oxidation rates were achieved within 2 min (Figure 5) (no oxidation of As(III) by H_2O_2 occurred in the 10 min prior to mixing). However, the oxidation of As(III) was inhibited in the presence of 13.5 mM 2-propanol, yielding approximately 10% oxidation of As(III) compared to 80% in the absence of 2-propanol (Figure 5). These data suggest that although $OH^\bullet$ is responsible for the significant majority of As(III) oxidation during the Fenton reaction, other oxidants hypothesized to form via both the thermal and photo-Fenton reaction (*27*, *28*) may oxidize As(III) as well.

As mentioned above, oxidation of As(III) in irradiated ferrioxalate solutions and in dark reactions containing Fe(II)/H_2O_2 likely occurs as a result of attack by the $OH^\bullet$ free radical, which is generated by the reduction of H_2O_2 with Fe(II) (eq 4). Klaning (*29*) proposed the following elementary reaction mechanism describing the oxidation of As(III) by $OH^\bullet$

$$H_3As^{III}O_3 + OH^\bullet \rightarrow H_4As^{IV}O_4 \qquad (13)$$

where the product, As(IV), is rapidly oxidized by a secondary oxidant such as O_2 to yield As(V) (Table 2). The summary reaction describing the oxidation of one mole of As(III) to As(V) (two electron transfer) at pH 5.0 by one mole of $OH^\bullet$

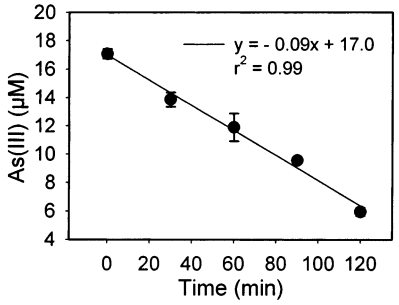

FIGURE 6. Disappearance of As(III) in the presence of 0.86 mM dissolved organic C (Hyalite natural water) upon exposure to sunlight (photosynthetically active radiation = 1538 ± 22.6 μE m^{-2} s^{-1} and total solar irradiance = 787.4 ± 11.0 W m^{-2}). Initial conditions: 18 μM As(III), 18 μM Fe(III), pH 5.0.

and an additional oxidant, such as O_2 or Fe(III), can be described as

$$H_3AsO_3^{\ 0} + OH^\bullet + O_{2(g)} \rightarrow H_2AsO_4^{\ -} + O_2^{\bullet -} + 2H^+ \qquad (14)$$

$$H_3AsO_3^{\ 0} + OH^\bullet + Fe^{III}(C_2O_4)_3^{\ 3-} = H_2AsO_4^{\ -} + Fe(II) + 2H^+ + 3C_2O_4^{\ 2-} \qquad (15)$$

It is important to note that the As(III) oxidation steps proposed in reactions 14 and 15 generate H^+. This is in apparent conflict with the pH dependence discussed in Figure 1, where the oxidation of As(III) clearly increases with increasing concentration of H^+. Furthermore, the observed H^+ consumption rates necessary to maintain constant pH during irradiation experiments show that the overall irradiation process consumes H^+ (Table 1). The primary proton consuming reactions in the ferrioxalate system relate directly to the formation of H_2O_2 via reactions 2 and 3 and to the formation of $OH^\bullet$ via reaction 4.

The empirical data on proton consumption at pH 3.0 in irradiated experiments suggest that 1.4 mol of H^+ was consumed per mole of H_2O_2 produced (see experiment at [As(III)] = 17.4 uM, Table 1). This ratio increases to 2.4 mol of H^+ consumed per mole of H_2O_2 produced when the pH increases to 5.0 (near the pK_a of $HO_2^\bullet$) as a result of the following reaction

$$HO_2^\bullet + O_2^{\bullet -} + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad (16)$$

where the production of OH^- increases the moles of H^+ consumed per mole H_2O_2 generated. However, at a constant pH = 5.0, the ratio of H^+ consumed per mole of H_2O_2 produced drops from 2.4 to approximately 1.4 at higher concentrations of initial As(III), consistent with the additional H^+ generated via reactions 14 and 15. In summary, the net effect of irradiating ferrioxalate solutions results in H^+ consumption; clearly the production of H_2O_2 and subsequent formation of free radical $OH^\bullet$ increases with decreasing pH. Under the solution conditions employed here, this pH dependence is responsible for higher As(III) oxidation rates at lower pH despite the fact that the suggested oxidation steps of As(III) via reactions 14 and 15 are proton generating.

As(III) Oxidation in the Presence of DOC. The rate of photoinduced oxidation of As(III) was significant in the Hyalite natural water sample containing DOC (Figure 6). At pH 5.0 and 18 μM Fe(III), rates of As(III) oxidation were 3.7 μM h^{-1} under the QTH light source and 5.6 μM h^{-1} under natural sunlight. The amount of photosynthetically relevant and total solar radiation measured at the surface of the reaction solution under sunlight was 1538 ± 22.6 μE m^{-2} s^{-1} and 787.4 ± 11.0 W m^{-2}, respectively.

TABLE 3. Comparison of Apparent Half-Lives for the Oxidation of As(III) via Abiotic and Biotic Pathways

oxidant/process	half-life (h)	ref
irradiated ferrioxalate solution (pH 5.0, 18 uM Fe(III), 17.4 uM As(III))	0.12	(this study)
irradiated hyalite sample	1.6	(this study)
O_2	8640	(*35*)
Fe(III) (pH 5.0)	227	(*4*)
H_2O_2 (pH 7.5)	38.5	(*5*)
synthetic δ-MnO_2	0.15−0.35	(*3*)
O_3	0.07	(*36*)
$TiO_{2(suspended)} + h\nu$	0.04	(*37*)
microbial oxidation	0.01, 0.3	(*22, 38*)

Although it has been hypothesized that DOC acts as a sink for $OH^\bullet$ (*30*), it has also been suggested that $O_2^{\bullet-}$ is produced directly from DOC upon irradiation (eq 1). This reaction then leads to the production of H_2O_2 and $OH^\bullet$ from $O_2^{\bullet-}$ through aforementioned mechanisms. Characterization of the Hyalite water sample revealed a noncarbonate alkalinity of 0.09 mM. This translates to 1 mole charge:10 mol C and is consistent with the range expected for aquatic DOC (*31*). The ratio of moles charge to moles Fe was 5:1 in this experiment and would have resulted in significant complexation of Fe(III) with organic functional groups (phenolic and carboxylic).

Environmental Implications. The photochemical oxidation of As(III) to As(V) has been shown to occur at significant rates in both irradiated ferrioxalate solutions and in a natural water sample containing low levels of DOC. The mechanism of As(III) oxidation in irradiated ferrioxalate solutions ranging from pH 3 to 5 appears to be due primarily to the generation of $OH^\bullet$ radicals from the reaction of H_2O_2 and Fe(II). At pH 7.0, the considerably slower rates of As(III) oxidation indicate that this mechanism is likely important, but not as pronounced, and may be supplemented by the generation of other photochemically derived oxidants, such as Fe(IV)-type species (*8*). In ferrioxalate solutions, Fe(II) and H_2O_2 are initial reaction products formed from the photochemical decomposition of ferrioxalate, which react further via the Fenton reaction to yield $OH^\bullet$. Oxidation of As(III) and inhibition by excess 2-propanol ($OH^\bullet$ scavenger) were observed in the dark Fenton reaction where $OH^\bullet$ is generated upon addition of Fe(II) and H_2O_2 without irradiation. In the natural water sample, addition of Fe(III) to native DOC resulted in lower, yet significant rates of As(III) oxidation upon irradiation. In addition to clarifying the role of $OH^\bullet$ in the oxidation of As(III), the results presented here suggest that the photochemical oxidation of As(III) may be extremely important in surface waters containing dissolved Fe(III) and DOC.

The rates of As(III) oxidation observed in the presence of irradiated ferrioxalate solutions or natural DOC are comparable to rapid rates of As(III) oxidation measured for other oxidative pathways, including inorganic electron transfer reactions and microbially mediated processes (Table 3). For example, apparent half-lives describing photochemical oxidation of As(III) in irradiated ferrioxalate solutions and in natural water containing DOC fall within the same range observed for oxidation of As(III) via microorganisms using pure cultures under log growth conditions and in suspensions containing MnO_2(s). Further, the photochemical oxidation rates observed in the current study are roughly 3−4 orders of magnitude faster than oxidation rates attainable in the presence of O_2 or H_2O_2. Although the oxidation of As(III) by H_2O_2 has been shown to be significant at pH values > 8−9 (*5*), rates at pH < 7 are likely too slow to be of significance in natural water systems. Given the ubiquity of Fe(III) and DOC in surface waters, we expect that the photochemical oxidation of As(III) represents an additional pathway responsible for As(III) oxidation in natural water systems, following mechanisms similar to those described here for irradiated ferrioxalate solutions. Future work should emphasize the potential role of photochemical processes on As(III) oxidation−reduction reactions important to As cycling in natural waters.

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