Light-Induced Oxidation of Aqueous Chromium(III) in the Presence of Iron(III)

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Oxidation of Cr(III) to toxic Cr(VI) by Mn(IV) or Mn(III) species has been identified as probably the only important oxidation pathway in soils, aquatic bodies, and atmospheric environments. We observed ready oxidation of Cr(III) in Fe-(III) solutions in light at pH 3.2−4.4. Further kinetic study of this oxidation was performed in sunlight as well as in black light under controlled conditions (e.g., pH 3.2, 20°C). Quantum yields of Cr(VI) formation at 356 nm were 0.020−0.046 for initial levels of 50−800 μM Cr(III) and 200 μM Fe-(III). The Cr(VI) formation reached steady state in 0.5 h (6 μM, [Cr(III)]$_0$: 50 μM; 10 μM, [Cr(III)]$_0$: 200 μM; [Fe(III)]$_0$: 200 μM). The best linearity found only for log[Cr(III)] vs t in the first 1 or 1.5 min of the reaction suggests apparent first-order kinetics for the disappearance of Cr(III) at 356 nm over the period; afterward, it failed to comply with any regular rate law. The Cr(III) oxidation decreased at high initial levels of Cr(III) or Fe(III) and upon removal of O$_2$, and it was found to be very limited at pH <2.5 or pH >5.0. Cr-(III) was hypothesized to be oxidized to Cr(VI) by •OH radicals from photolysis of FeOH^{2+} complexes (estimated $k_{\text{•OH+Cr(III)}} = 8.3 \times 10^7$ M^{-1} s^{-1}); Cr(VI) also was reduced by the formed Fe(II) and intermediates such as HO$_2$. This study suggests that light-induced oxidation of aqueous Cr-(III) in the presence of Fe(III) would be one potential pathway for the oxidation of Cr(III) to toxic Cr(VI), more possibly in atmospheric waters or in acidic surface waters with low dissolved organic carbon content; it would not be expected to occur in surface soils because of their universal association with organic carbon.

Introduction

Oxidation of Cr(III) in natural environments has received attention because of the toxicity of Cr(VI) (*1−3*). All of this attention has involved oxidation by oxidized Mn, most of it in soil systems (*3−9*). There has been almost no recognition of the free radical mechanism that occurs in light in the presence of soluble Fe(III) (*10, 11*). Chromium(III) also is present in atmospheric waters and aerosols because of emission from anthropogenic source (60−70%) as well as natural sources (30−40%) (*12*). In the atmosphere, Cr transformation mainly involves soluble Cr(III) and Cr(VI) species because the pH of atmospheric aqueous media is commonly found at 2−5 (*12, 13*). As in soils and aquatic bodies, oxidation of Cr(III) to Cr(VI) by Mn(IV) or Mn(III)

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species also was identified to be probably the only important oxidation pathway in atmospheric environments (*12*). Yet, there were suggestions in this paper (*12*) that trace metals could react with free radicals such as HO$_2$, O$_2^-$, and •OH, and these reactions could proceed fairly rapidly, possibly leading to a steady state between Cr(III) and Cr(VI); these reactions, however, were not included in the comprehensive chemical kinetic mechanism for atmospheric Cr because of a lack of kinetic information.

Bartlett and James (*9, 10*) and recently Zhang (*11*) observed that oxidation of aqueous Cr(III) occurred at easily measured levels at pH 3.2−4.4 in the presence of Fe(III) and in light. This finding could be important for Cr cycling in ambient environments where Fe(III) species are commonly present. However, our knowledge of the kinetics of this light-induced Cr(III) oxidation is lacking, and the mechanism is only partially understood (*10, 11*). This paper reports our kinetic investigation into light-induced oxidation of aqueous Cr(III) in the presence of Fe(III) and discusses possible environmental implications for Cr cycling.

Experimental Section

Materials. All reagents were of analytical grade and used as received. The working series of FeCl$_3$ solutions of 1, 2, 4, and 8 mM were obtained through 1:25 dilution of a stock series of 25 mM in 1.0 M HCl, 50 mM in 0.8 M HCl, 100 mM in 0.6 M HCl, and 200 mM in 0.6 M HCl, respectively. The stock solutions stayed stable more than 1 month. The pH 3.2 Fe-(III) solutions directly used in the experiments were freshly prepared by 1:50 dilution of the working series. The Cr(III) solutions of 1, 2, 4, 8, and 20 mM were made from a stock solution of 100 mM CrCl$_3$ in 0.6 M HCl. Because of the detection limit of the Cr(VI) method used (0.1−0.3 μM) (*14*), the lowest initial levels of Cr(III) (50 μM) and Fe(III) (100 μM) were so chosen that reliable data could be obtained to study the initial kinetics.

The light-induced oxidation of Cr(III) appeared to be kinetically unrepeatable at pH >3.2, which was found to be caused mainly by the rapid Fe(III) hydrolysis in diluted solutions (*11*). As a result, throughout this study except when its effect was being studied, the pH was adjusted to 3.2 with HCl or KOH to exclude the possible complications caused by hydrolysis of Fe(III) as well as by Cr(III) (*6*). Additional electrolytes were avoided to prevent the kinetic effect of complexation of Fe(III).

Procedures. Experiments in sunlight were conducted with simultaneous duplication at near noontime under a clear October sky (44.30° N, ~374 W m^{-2} at 300−500 nm, 20−22 °C). The solutions tested (8 mL each) were placed inside capped polycarbonate tubes (1.4 cm in diameter, 7 cm high, ~80−90% UV transmission), which were held approximately perpendicular to the sun rays. Experiments in 356 nm light were performed in a dark chamber at a constant temperature of 20 °C. A black-ray lamp (UVP INC, model XX-5L, 78 W) with two parallel light tubes (45 cm long, 2.3 cm in diameter, 3.2 cm apart, maximum intensity at 356 nm) was suspended horizontally 8.5 cm above the bench surface where irradiance values of ~1.1 W m^{-2} at 356 nm and of ~21.3 W m^{-2} at 356 ± 10 nm were measured using a Li-Cor, LI-1800 spectroradiometer. Treatment solutions of a final volume of 10 mL (0.6 cm in depth) were obtained by placing 0.5 mL of the working series of the Fe(III) or Cr(III) solutions along with distilled water into acid-washed polyethylene beakers. Each time, four beakers in a set were placed under the lamp tubes. The photoexposure was started by uncovering the beakers and then was blocked by recovering them at the end of the
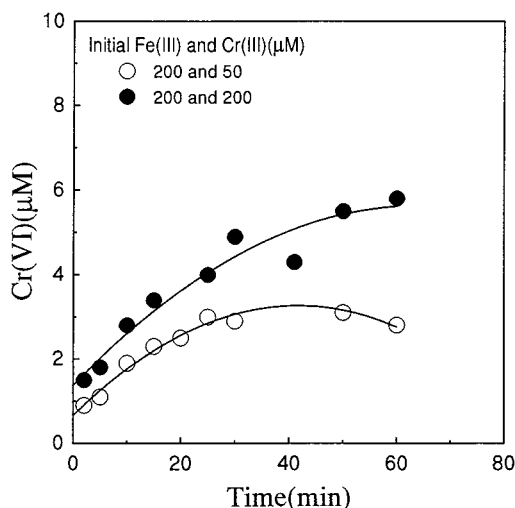
FIGURE 1. Oxidation of aqueous Cr(III) in the presence of Fe(III) in the noon sunlight of late October (44.30° N, ~374 W m^{-2} at 300−500 nm, 20−22 °C). The mean values of the standard deviations for Cr(VI) concentrations are 0.5 (0.14−2.3) for 50 μM Cr(III) and 1.2 (0.21−2.3) for 200 μM Cr(III).

desired exposure. Samples were analyzed immediately after the exposure. Concentrations of Cr(VI) and Fe(II) were found to remain stable during the time required for the analysis. In some experiments, O$_2$ was removed by bubbling N$_2$ into the solutions for 12 min before and during the photoexposure.

Determinations. Cr(VI) and Fe(II) were determined spectrophotometrically using diphenylcarbazide (*14*) and dipyridyl (*15*), respectively. Mean values of Cr(VI) and Fe(II) concentrations of 2−4 replicates of the kinetic experiments are reported. The intensity of the light absorbed in the solutions was measured using the ferrioxalate actinometry according to Parker (*16*). To do this, we exposed a 10-mL solution of 10 mM FeCl$_3$ and 30 mM K$_2$C$_2$O$_4$ in 0.1 M HCl to the 356 nm light for 5, 8, and 10 s and obtained a value of 18.2 ± 1.5 (μM s^{-1}) for the initial photolysis rate with a relative error of 8.3%. The light intensity was calculated to be 14.9 μEinstein L^{-1} s^{-1} at 356 nm by dividing the initial rate (18.2 ± 1.5 μM s^{-1}) by 1.22, the quantum yield provided by Parker (*16*). The pH was measured with a combination electrode (Corning, XE-L series) connected to a digital ionanalyzer (Orion Research, model 601A).

Calculations. Initial rates (R_i, in μM s^{-1}) of Cr(VI) and Fe(II) formation were obtained using the slopes of linear least-squares regression lines of the concentrations of Cr(VI) or Fe(II) at 15, 30, and 45 s versus the corresponding time intervals. Quantum yields (Φ) of Cr(VI) and Fe(II) or •OH formation were calculated according to the following equations (*17*):

$$\Phi = \text{initial rate/intensity of light absorbed} = R_i/I_a \quad (1)$$

$$I_a = 2.303\epsilon D[\text{Fe(III)}]_0 I_0 \quad (2)$$

where I_a is the corresponding intensity of the light absorbed by FeOH^{2+} at 356 nm (μEinstein L^{-1} s^{-1}), ϵ is the decadic absorbance coefficient of FeOH^{2+} complex (300 M^{-1} cm^{-1}), D is the light path length (0.6 cm), [Fe(III)]$_0$ is the initial concentration of Fe(III) (M), and I_0 is the total light intensity in the 10-mL tested solution obtained by the ferrioxalate actinometry (14.9 μEinstein L^{-1} s^{-1}). The overall errors for the initial rates and quantum yields were about 15−20%.

Results and Discussion

Oxidation of Cr(III) in Sunlight. Formation of Cr(VI) in the presence of 200 μM initial Fe(III) was observed for 50 and
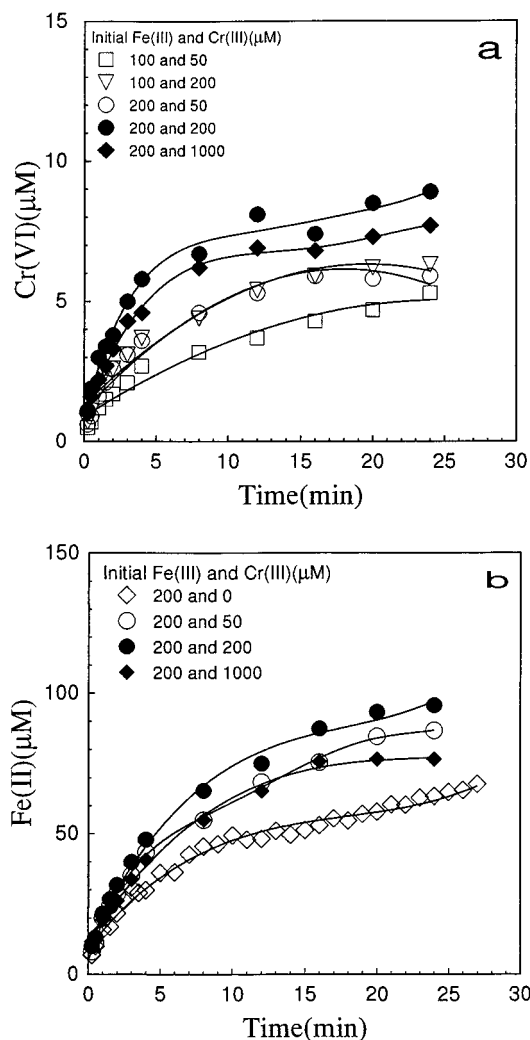

FIGURE 2. (a) Oxidation of aqueous Cr(III) in 356 nm light in the presence of Fe(III) and (b) paralleled Fe(III) photoreduction. The mean values of the standard deviations for Cr(VI) concentrations are 0.19 (0.14−0.35) for □, 0.21 (0.14−0.57) for ▽, 0.25 (0.14−0.49) for ○, 0.30 (0.21−0.57) for ●, and 0.31 (0.21−0.49) for ◆. Those for Fe(II) are 2.2 (0.3−4.2) for ◇, 1.2 (0.4−3.6) for ○, 1.7 (0.2−3.4) for ●, and 1.0 (0.2−4.5) for ◆.

200 μM initial Cr(III) in the sunlight at noon in late October (Figure 1). Formation of Cr(VI) increased with time during the first 25 min and then rose less steeply, and it also depended on the initial Cr(III) level.

Oxidation of Cr(III) in 356 nm Monochromic Light. Kinetics of Cr(VI) formation in 356 nm light (Figure 2a) was similar to that in sunlight. At the same initial level of Fe(III), 200 μM initial Cr(III) led to more Cr(VI) than 50 μM Cr(III), but a higher initial Cr(III) level (1000 μM) did not lead to more Cr(VI) than 200 μM Cr(III). The results of different treatments indicate that Cr(VI) formation depended on the initial level of both Fe(III) and Cr(III). The formation of Fe(II) paralleled the Cr(III) oxidation, and it was increased by the presence of Cr(III) (Figure 2b). A great decrease of the Cr(III) oxidation occurred in the presence of NO$_2^-$ (Figure 3), apparently caused by the strong competition of NO$_2^-$ with Cr(III) for the oxidant.

Empirical Rate Law and Reaction Order. No satisfactory overall linear relationships were found for all treatments in terms of regular rate expressions. We attributed this to the reduction of Cr(VI) by Fe(II) (*1, 18, 19*) and other reducing intermediate(s), which complicated the overall kinetics. This hypothesis is supported by our finding that Cr(VI) formation
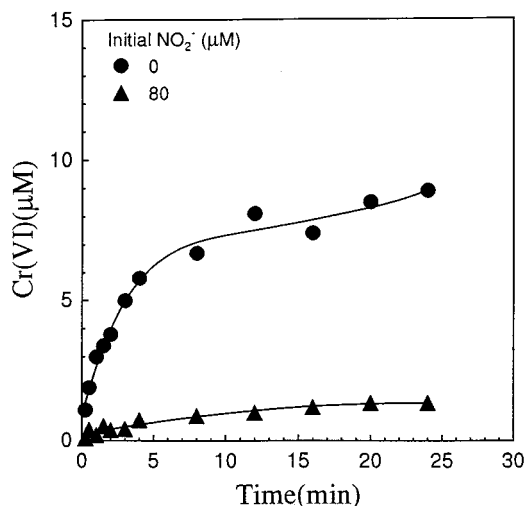
FIGURE 3. Oxidation of aqueous Cr(III) in 356 nm light in Fe(III) solutions in the presence or absence of nitrite (initial Fe(III) and Cr(III): both 200 μM).

TABLE 1. Kinetics of Oxidation of Aqueous Cr(III) in 356 nm Light in Solutions of 200 μM Initial Fe(III) As Shown by Cr(VI) Concentration Change with Photoexposure Time

initial Cr(III) (μM)	Cr(VI) change (μM) at t (min) =								
	2	4	8	12	16	20	24	40	60
50	2.6	3.6	4.6	5.3	5.9	5.8	5.9		
200	3.8	5.8	6.7	8.1	7.4	8.5	8.9	9.8	9.8

TABLE 2. Empirical Kinetics of Oxidation of Cr(III) in the Presence of Fe(III) in 356 nm Light

t (min)	Fe(III):Cr(III (μM)[a]							
	100:50		100:200		200:50		200:200	
	r^2_1[b]	r^2_2[c]	r^2_1	r^2_2	r^2_1	r^2_2	r^2_1	r^2_2
0–1[d]	0.9968	0.9692	0.9763	0.9798	0.9956	0.9874	0.9936	0.9714
0–1.5[e]	0.9716	0.9486	0.9807	0.9544	0.9943	0.9784	0.8893	0.9227
0–2[f]	0.9584	0.9430	0.9434	0.9462	0.9901	0.9776	0.8678	0.8981
0–3[g]	0.9485	0.9423	0.9142	0.8980	0.9636	0.9427	0.9052	0.9087

[a] Initial level. [b] The correlation coefficients for regression of log[Cr(III)] vs time. [c] The correlation coefficients for regression of [Cr(III)]$^{-1}$ vs time. [d] Four data points. [e] Five data points. [f] Six data points. [g] Seven data points.

reached steady state (Table 1), which could occur when the rates of Cr(VI) formation and reduction are equal to each other.

However, the kinetics of Cr(III) disappearance may be approximated by the initial kinetics in the first few minutes of the reaction when the levels of Cr(VI), Fe(II), and other intermediates were substantially low. The best correlations were found for the regression of log[Cr(III)] vs time within the first 1or 1.5 min (Table 2). We therefore inferred that the Cr(III) disappearance probably followed first-order kinetics in the beginning (Table 3), and then it deviated as the levels of the formed Cr(VI) and reductants built up.

Initial Rates and Quantum Yields. The initial rate of Cr-(VI) formation increased sharply with increasing initial Cr-(III) level ([Cr(III)]$_0$) from 50 to 100 μM, but it decreased gradually when [Cr(III)]$_0$ was raised from 100 to 800 μM. The initial rate of Fe(II) formation changed slightly with increasing [Cr(III)]$_0$ (Figure 4a). The two initial rates changed with [Fe-(III)]$_0$ in nearly the same way as with [Cr(III)]$_0$ (Figure 4b). The quantum yield for Cr(VI) formation changed with [Cr-(III)]$_0$ and with [Fe(III)]$_0$ much as the initial rate of Cr(VI)

TABLE 3. Empirical and Calculated First-Order Rate Constants (k_{exp} and k_m) for Cr(III) Oxidation in 356 nm Light in Fe(III) Solutions in the First 1 or 1.5 min

Fe(III)[a] (μM)	Cr(III)[a] (μM)	t (min)	k_{exp}[b] (s^{-1})	R^2_{exp}[c]	k_m[d] (s^{-1})	R_m^2[e]
100	50	0–1	3.8×10^{-4}	0.9968	2.3×10^{-4}	0.9999
100	200	0–1.5	1.3×10^{-4}	0.9807	2.6×10^{-4}	1.0000
200	50	0–1.5	4.6×10^{-4}	0.9943	1.9×10^{-4}	1.0000
200	200	0–1	2.7×10^{-4}	0.9936	2.7×10^{-4}	0.9998

[a] Initial level. [b] Obtained by regression of log[Cr(III)] vs time in the first 1 or 1.5 min of the reaction (four data points for 0–1 min, five data points for 0–1.5 min). [c] The correlation coefficient for regression of log[Cr(III)] vs time. [d] Pseudo-first-order rate constant calculated according to the mechanism, $k_m = \text{slope}_m \times 6.173 \times 10^{-3}$, where $\text{slope}_m = \{k_4[\cdot OH]/(2.303\epsilon DI_0 \times 10^{-6}\Phi)\}$, whose value is obtained by regression using $[Fe(III)] = \{k_4[\cdot OH]/(2.303\epsilon DI_0 \times 10^{-6}\Phi)\}\{[3Cr(III)] + (k_7/k_4)[Fe(II)]\}$, where [Cr(III)], [Fe(III)], and [$\cdot$OH] are Cr(III), Fe(III), and $\cdot$OH concentrations (μM), respectively; ϵ is the decadic molar absorbance coefficient for FeOH^{2+} complex (300 M^{-1} cm^{-1}); D is the depth of the solution exposed to the light (0.6 cm); I_0 is the intensity of the photon entering the solution (14.9 μEinstein L^{-1}s^{-1}); Φ is the quantum yield of $\cdot$OH or Fe(II) formation; k_4 is the rate constant of reaction $\cdot$OH + Cr(III) → Cr(IV) + OH $^-$. [e] The correlation coefficient for the regression to obtain slope$_m$ (four points for 0–1 min, five points for 0–1.5 min).
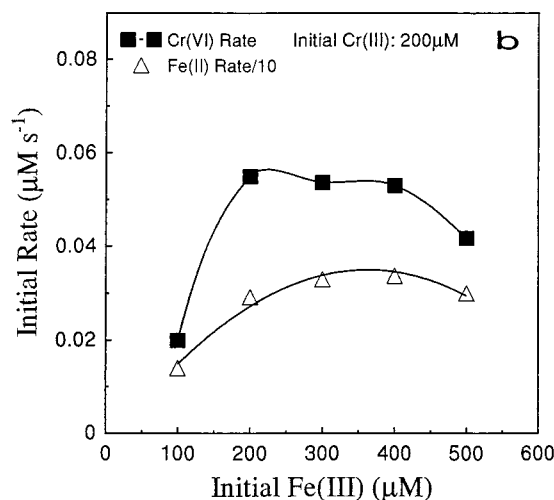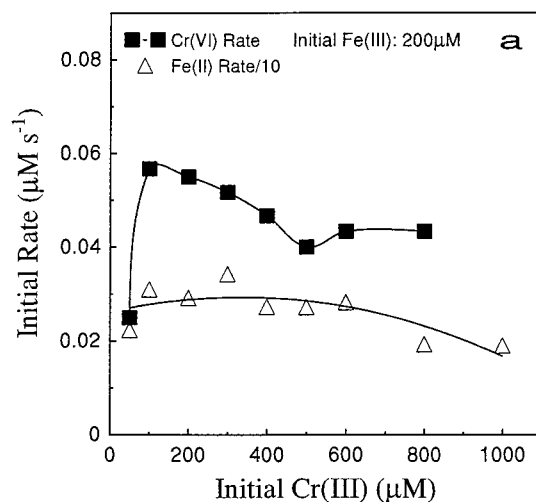

FIGURE 4. Change of initial rates of Cr(VI) and Fe(II) formation in 356 nm light with initial concentrations of (a) Cr(III) and (b) Fe(III).

formation changed with [Cr(III)]$_0$ and with [Fe(III)]$_0$ (Table 4).

These results suggest that the Cr(VI) formed was removed rapidly when [Cr(III)]$_0$ and [Fe(III)]$_0$ both, especially the latter,

TABLE 4. Quantum Yields (QY)[a] for Formation of Cr(VI) and Fe(II) or $^{\bullet}$OH in Light-Induced Oxidation of Aqueous Cr(III) in the Presence of Fe(III) at 356 nm

treatment (μM)		QY			treatment (μM)		QY		
Fe(III)	Cr(III)	Fe(II)	Cr(VI)	QY_{Fe}/QY_{Cr}	Fe(III)	Cr(III)	Fe(II)	Cr(VI)	QY_{Fe}/QY_{Cr}
200	50	0.18	0.020	9.0	100	200	0.23	0.032	7.2
200	100	0.25	0.046	5.4	200	200	0.24	0.045	5.3
200	200	0.24	0.045	5.3	300	200	0.18	0.029	6.2
200	300	0.28	0.042	6.7	400	200	0.14	0.021	6.7
200	400	0.22	0.038	5.8	500	200	0.097	0.014	6.9
200	500	0.22	0.032	6.7					
200	600	0.23	0.035	6.6					
200	800	0.16	0.035	4.6					

[a] Quantum yields are obtained by dividing the initial rate (μM s^{-1}) by I_a, the corresponding intensity of the light absorbed by FeOH^{2+} complexes at 356 nm (μEinstein L^{-1} s^{-1}), $I_a = 2.303\epsilon D[\text{Fe(III)}]_0 I_0$, where ϵ is the decadic absorbance coefficient of FeOH^{2+} (300 M^{-1} cm^{-1}), D is the light path length (0.6 cm), [Fe(III)]$_0$ is the initial concentration of Fe(III) (M), and I_0 is the total irradiance intensity in the 10-mL tested solution (14.9 μEinstein L^{-1} s^{-1}).

were high. This removal can be explained very well by the reduction of Cr(VI) (e.g., by Fe(II)). Hence, our reported initial rates and quantum yields only represented the apparent values. They must be lower than the true values when [Cr-(III)]$_0$ or [Fe(III)]$_0$ was higher than 100 or 200 μM, respectively.
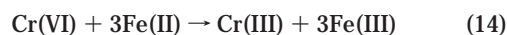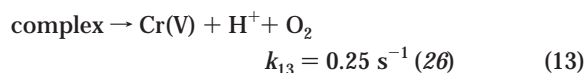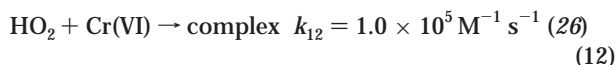
The quantum yields for Cr(VI) formation obtained in this study (0.020−0.046) are higher than the reported quantum yield for $^{\bullet}$OH formation (0.017 at 360 nm) in acidic ferric solutions (pH 4.0) (13). This is presumably due to the differences in experimental conditions, such as pH, initial Fe(III) level, light source, and experimental setup (e.g., use of an open beaker with shallow solution of a large exposed surface in this study).

Oxidant for Cr(III) Oxidation. In our control experiments, we found neither direct photolysis of aqueous Cr(III) in the absence of Fe(III) nor oxidation of Cr(III) in the presence of Fe(III) in the dark. Therefore, the oxidation was light-induced and Fe(III)-assisted.
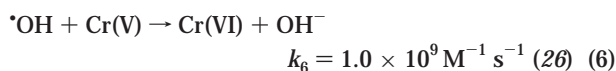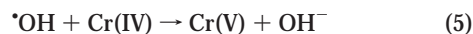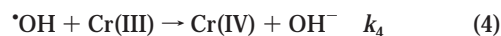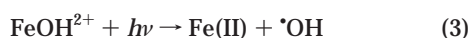
Because oxidation of Cr(III) by O$_2$ is very slow at the pH as low as 3.2 (3, 6, 8), O$_2$ could not be the oxidant for Cr(III). Aqueous Fe(III) at pH 2.5−4.5 has been well-known to undergo photolysis in light to form Fe(II) and $^{\bullet}$OH free radicals through electron-transfer absorption of the light by FeOH^{2+} complexes (13, 20), the dominant species at the pH range (13). Hence, no oxidant(s) except $^{\bullet}$OH could be present initially in the system of initially containing only Fe(III), Cr-(III), and H$_2$O (pH 3.2). $^{\bullet}$OH has been well established as the primary kinetic agent responsible for oxidation of substrates in the system of only acidic ferric solution in light (refs 17, 21−23, and references within). Furthermore, as a strong oxidant (13, 17, 20−23), $^{\bullet}$OH has been shown to be able to oxidize Cr(III) (24−26). Therefore, we consider that $^{\bullet}$OH radicals, as the dominant oxidant, acted to oxidize the Cr-(III). This is supported by our finding that Cr(VI) was detected in the solution containing Cr(III) and the Fenton reagent (Fe(II) and H$_2$O$_2$), which produces $^{\bullet}$OH radicals in the dark (27).

As seen in Table 4, the ratios of $^{\bullet}$OH to Cr(VI) quantum yields as well as of Fe(II) to Cr(VI) initial rates (see eq 1) are around 6:1 rather than 3:1 as suggested by the stoichiometry of the subsequent oxidation of Cr(III) by one-equivalent $^{\bullet}$OH. This discrepancy implies that part of the generated $^{\bullet}$OH radicals actually did not oxidize Cr(III) and must be scavenged through other pathways.

Hypothesized Mechanism. On the basis of our observations in this study, we propose the following mechanism currently as the simplest for light-induced oxidation of aqueous Cr(III) in the presence of Fe(III) in our experimental systems:

$$\text{FeOH}^{2+} + h\nu \rightarrow \text{Fe(II)} + {}^{\bullet}\text{OH} \quad (3)$$

$${}^{\bullet}\text{OH} + \text{Cr(III)} \rightarrow \text{Cr(IV)} + \text{OH}^- \quad k_4 \quad (4)$$

$${}^{\bullet}\text{OH} + \text{Cr(IV)} \rightarrow \text{Cr(V)} + \text{OH}^- \quad (5)$$

$${}^{\bullet}\text{OH} + \text{Cr(V)} \rightarrow \text{Cr(VI)} + \text{OH}^-$$
$$k_6 = 1.0 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}\ (26) \quad (6)$$

$${}^{\bullet}\text{OH} + \text{Fe(II)} \rightarrow \text{Fe(III)} + \text{OH}^-$$
$$k_7 = 5.0 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}\ (28) \quad (7)$$

$${}^{\bullet}\text{OH} + {}^{\bullet}\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad k_8 = 5.2 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}\ (29) \quad (8)$$

$${}^{\bullet}\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$$
$$k_9 = 2.7 \times 10^7\,\text{M}^{-1}\,\text{s}^{-1}\ (28) \quad (9)$$

$${}^{\bullet}\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad k_{10} = 3.1 \times 10^9\,\text{M}^{-1}\,\text{s}^{-1}\ (29) \quad (10)$$

$$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad k_{11} = 8.6 \times 10^5\,\text{M}^{-1}\,\text{s}^{-1}\ (28) \quad (11)$$

$$\text{HO}_2 + \text{Cr(VI)} \rightarrow \text{complex} \quad k_{12} = 1.0 \times 10^5\,\text{M}^{-1}\,\text{s}^{-1}\ (26) \quad (12)$$

$$\text{complex} \rightarrow \text{Cr(V)} + \text{H}^+ + \text{O}_2$$
$$k_{13} = 0.25\ \text{s}^{-1}\ (26) \quad (13)$$

$$\text{Cr(VI)} + 3\text{Fe(II)} \rightarrow \text{Cr(III)} + 3\text{Fe(III)} \quad (14)$$
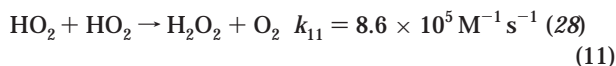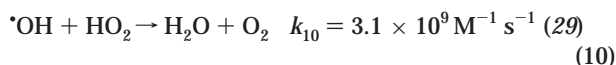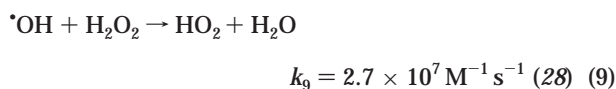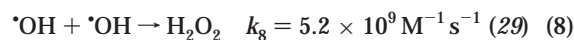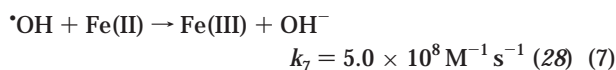
This mechanism consists of oxidation of Cr(III) (reactions 3−6), subsequent reduction of Cr(VI) by Fe(II) and HO$_2$ (reactions 12−14), and other possible fates of $^{\bullet}$OH radicals (reactions 7−11). A general kinetic expression can be written as

$$d[\text{Cr(VI)}]/dt = \text{rate}_{\text{formation}} - \text{rate}_{\text{reduction}} \quad (15)$$

Oxidation of Cr(III). The oxidation of Cr(III) is considered to consists of three subsequent steps (reactions 4−6) because $^{\bullet}$OH is a one-equivalent oxidant. Redox reactions between Cr(III), Cr(IV), and Cr(V) and disproportionation of Cr(IV) or Cr(V) also might occur. However, these reactions are not included in the mechanism because of uncertainties on the roles of these reactions in one-equivalent Cr redox reactions (18, 26, 30).

The rate of Cr(VI) formation can be derived using the rate laws of reactions 3−12 without considering the Cr(VI)
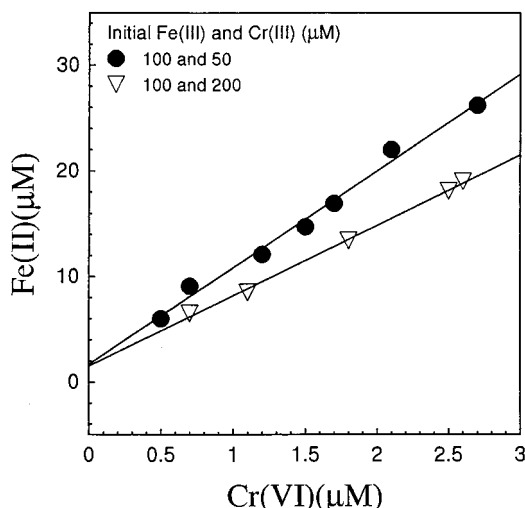
FIGURE 5. Positive linear relationships between [Fe(II)] and [Cr(VI)] in the first 4 min of the reaction (R^2: 0.9903 for ● and 0.9952 for ▽). The mean values of the standard deviations for Cr(VI) concentrations are 0.10 (0.07–0.21) for ● and 0.13 (0.07–0.21) for ▽. Those for Fe(II) are 0.6 (0.3–0.8) for ● and 0.8 (0.3–0.8) for ▽.

reduction. Hence

$$d[Cr(III)]/dt = -k_4[^{\bullet}OH][Cr(III)] = -k_m[Cr(III)] = -d[Cr(VI)]/dt \quad (16)$$

Under the steady-state assumption, we can obtain the following equation:

$$(2.303\epsilon DI_0 \times 10^{-6}\Phi)[Fe(III)] - k_7[^{\bullet}OH][Fe(II)] - 3k_4[^{\bullet}OH][Cr(III)] - 2k_{10}[^{\bullet}OH][HO_2] - k_9[^{\bullet}OH][H_2O_2] = 0 \quad (17)$$

which can be rearranged as

$$[Fe(III)] = \{k_4[^{\bullet}OH]/(2.303\epsilon DI_0 \times 10^{-6}\Phi)\}\{3[Cr(III)] + (k_7/k_4)[Fe(II)] + 2(k_{10}/k_4)[HO_2] + (k_9/k_4)[H_2O_2]\} \quad (18)$$

Assuming, initially, $3[Cr(III)] + (k_7/k_4)[Fe(II)] \gg 2(k_{10}/k_4)[HO_2] + (k_9/k_4)[H_2O_2]$, then

$$[Fe(III)] = \{k_4[^{\bullet}OH]/(2.303\epsilon DI_0 \times 10^{-6}\Phi)\}\{3[Cr(III)] + (k_7/k_4)[Fe(II)]\} \quad (19)$$

$$slope_m = \{k_4[^{\bullet}OH]/2.303\epsilon DI_0 \times 10^{-6}\Phi\} \quad (20)$$

$$k_m = k_4[^{\bullet}OH] = slope_m \times 2.303\epsilon DI_0 \times 10^{-6}\Phi = slope_m\Phi \times 6.173 \times 10^{-3} \quad (21)$$

where [Cr(III)], [Fe(III)], and [$^{\bullet}$OH] are Cr(III), Fe(III), and $^{\bullet}$OH concentrations (μM), respectively; k_4 is the rate constant of reaction 4; k_m is the calculated pseudo-first-order rate constant; ϵ is the decadic molar absorbance coefficient of FeOH^{2+} complexes (300 M^{-1} cm^{-1}); D is the depth of the solutions exposed to the light (0.6 cm); I_0 is the intensity of the photon entering the solution (14.9 μEinstein L^{-1} s^{-1}); Φ is the quantum yield of $^{\bullet}$OH or Fe(II) formation (Table 4); slope$_m$ is defined as in eq 20, whose values can be obtained by linear least-squares regression according to eq 19 for different treatments.

Rearrangement of eq 19 considering the mass balance for Fe and for Cr leads to positive proportion of [Fe(II)] to [Cr(VI)]. This agrees well with the kinetics observed (Figure 5). We also can use eq 21 to calculate the values of k_m using the

parameters obtained in this study and from the literature (Table 3), except for k_4, which has to be treated as an adjustable parameter because of the uncertainties on its reported values (24–26). The k_4 value that generates the best agreement between the calculated (k_m) and empirical rate constants (k_{exp}) can be found, by the best fit method, to be 8.3×10^7 M^{-1} s^{-1}, which is close to 1.35×10^8 M^{-1} s^{-1} (pH $\approx$ 1), indirectly estimated from the literature (29), and also close to another reported value, 3.1×10^8 M^{-1} s^{-1} (25). The fact that our obtained k_4 value is lower than 1.0×10^{10} M^{-1} s^{-1}, $k(^{\bullet}OH + NO_2^-)$ (28), is consistent with our observation of a great decrease of Cr(VI) in the presence of NO$_2^-$ (Figure 3). These agreements indicate that the mechanism for the Cr(III) oxidation is acceptable. Using eq 19 and assuming [Fe(II)]$_0 = 0$, we also can estimate the initial steady-state $^{\bullet}$OH concentrations as being 5.5×10^{-11} and 2.2×10^{-12} μM for 50 and 200 μM initial Cr(III) with 200 μM initial Fe(III), respectively, which are close to the typical steady-state concentration of $^{\bullet}$OH in sunlit atmospheric water drops (10^{-14} and 10^{-12} M) (22).

Reduction of Cr(VI). The formed Cr(VI) could be reduced through several pathways depending on the actual level of the reductant involved as well as the rate constant of the reaction. Our experiments suggest that the Fe(II) formed could be an important reductant. Kinetics of the reduction of Cr(VI) by Fe(II) has received much research (1, 18, 19). By using eqs 15 and 16 (rate$_{formation}$), the rate law of eq 12, and the reported rate equation for Cr(VI) reduction by Fe(II) (18) at steady state where $d[Cr(VI)]/dt = 0$, we can obtain

$$[Cr(VI)]_{steady} = [Cr(III)]_0/(1 + k[Fe(II)]_{steady}/k_4[^{\bullet}OH] + k_{12}[HO_2]/k_4[^{\bullet}OH]) \quad (22)$$

where $k = 4400[H^+]$ M^{-2} s^{-1} + $3.0 \times 10^5[H^+]^2$ M^{-3} s^{-1} (pH = 2) (18) and $k_4[^{\bullet}OH]$ can be obtained using eq 21.

Without considering reaction 12 (i.e., assuming $k_{12} = 0$), the calculation of [Cr(VI)]$_{steady}$ for 200 and 50 μM initial Cr(III) in the presence of 200 μM initial Fe(III) yields values of 89.8 and 21.8 μM, respectively, which are higher than the observed values of 9.8 and 5.9 μM, respectively. This could be due to the low value of k in eq 22. By using the rate equations of Espenson (pH 1–2) (18), of Buerge and Hug (pH >4.4) (1), and of Fendorf and Li (pH >6, in aerated aqueous solution) (19), we estimated the initial rates of the reduction of Cr(VI) by Fe(II) at pH 2–6 to be about 8.2×10^{-4} (18), 1.2×10^{-5} (1), and 6.5×10^{-2} μM s^{-1} (19), respectively, which are either much lower or even higher than the initial rates for the light-induced Cr(III) oxidation obtained in this study ($2.0–5.5 \times 10^{-2}$ μM s^{-1}). This discrepancy or uncertainty seems to suggest that other pathway(s) might be involved.

As a result, we include in the mechanism reaction 12 ($k_{12} = 1.0 \times 10^5$ M^{-1} s^{-1}, relatively high). By assuming [HO$_2$] = 2.2×10^{-8} and 6.6×10^{-9} M in eq 22, respectively, which appears reasonable, we can obtain exactly the same observed values for [Cr(VI)]$_{steady}$. However, which pathways were actually dominant in the Cr(VI) reduction remains uncertain before further study to clarify the kinetics of Cr(VI) reduction by Fe(II) at pH 2–4, which should be conducted in the dark to avoid the light-induced oxidation of Cr(III) in the presence of Fe(III). H$_2$O$_2$ also might reduce Cr(VI), but the reaction is rather slow (10^3 M^{-1} s^{-1}) (26).

Other Possible Fates of $^{\bullet}$OH Radicals. Reactions 7–11 are considered to be the major alternative paths that could competitively consume $^{\bullet}$OH, making the quantum yield for Cr(VI) formation lower than one-third of that for $^{\bullet}$OH formation. Part of the $^{\bullet}$OH could oxidize Fe(II) back to Fe(III) via reaction 7 (20, 31). In the presence of Cr(III), its oxidation could make $^{\bullet}$OH less available for the oxidation of Fe(II) and thus lead to the observed increase of Fe(II) (Figure 2b).
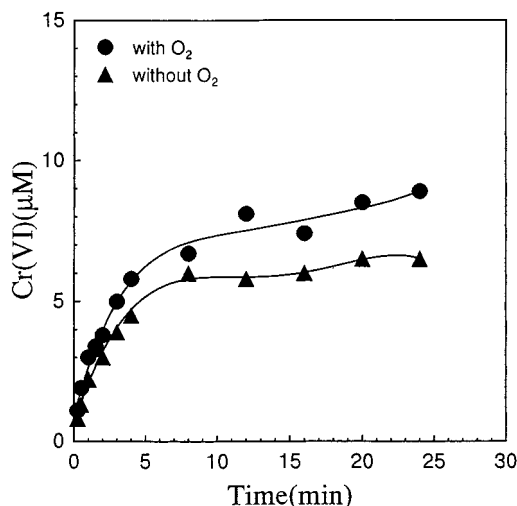
FIGURE 6. Effect of removal of dissolved O_2 by purging the solutions with N_2 gas on the oxidation of aqueous Cr(III) in 356 nm light in the presence of Fe(III) (initial Fe(III) and Cr(III): both 200 μM). The mean values of the standard deviations for Cr(VI) concentrations are 0.30 (0.21–0.56) for ● and 0.20 (0.12–0.77) for ▲.

Consideration of reaction 7 is also supported by the decrease of the quantum yield for Fe(II) with the decreasing of [Cr-(III)]$_0$ from 100 to 50 μM (Table 4).

The net result of reactions 8–11 is the formation of H_2O and O_2 from ·OH radicals. This hypothesis is strongly supported by our finding that purging the system with N_2 gas led to a decrease in Cr(VI) formation (Figure 6), because continuous removal of O_2 could promote the scavenging of ·OH via reactions 8–11 and make ·OH less available for the oxidation of Cr(III). This mechanism is further supported by our observation of a great increase of Fe(II) in the absence of Cr(III) when the system was purged with N_2 gas (*11*), because without the purging, Fe(II) would be effectively oxidized by ·OH to Fe(III) via reaction 7. Incidentally, reactions 8–11 also provide a mechanistic explanation of the observed effect of removal of O_2.

Considering $d[Cr(VI)]/dt = k_6[·OH][Cr(V)] = k_4[·OH][Cr-(III)]$, substitution of related rate expressions in eq 17 followed by its rearrangement leads to

$$d[Fe(II)]/dt{:}d[Cr(VI)]/dt = 3 + 2(k_{10}/k_6)[HO_2]/[Cr(V)] + (k_9/k_6)[H_2O_2]/[Cr(V)] \quad (23)$$

Assuming $2(k_{10}/k_6)[HO_2]/[Cr(V)] \gg (k_9/k_6)[H_2O_2]/[Cr(V)]$, as $k_{10} > k_9$, it follows that

$$d[Fe(II)]/dt{:}d[Cr(VI)]/dt \approx 3 + 6[HO_2]/[Cr(V)] > 3 \quad (24)$$

This accounts for our observation that ratios of Fe(II) to Cr-(VI) initial rates or quantum yields are larger than 3. If further assuming that $[Cr(V)] = 2[HO_2]$, then $d[Fe(II)]/dt{:}d[Cr(VI)]/dt \approx 6$.

Effect of pH. Our research showed that the light-induced Cr(III) oxidation could proceed fairly rapidly at pH about 3.2–4.4 (*9, 10*, this study). But the Cr(III) oxidation was found to be significantly limited at pH below 2.5 or above 5.0 (Table 5). The observed pH effect probably results from lowered availability of ·OH caused by lowered $FeOH^{2+}$ level (*13*) and from faster Fe(III) hydrolysis at higher pH. The increase in rate of Cr(VI) reduction by Fe(II), both at low and at high pH (*1, 19*), also could be responsible for part of the pH effect. At pH > 4, Cr(III) may react with Fe(III) to form $FeCr(OH)_n$ polymer or precipitate (*7*).

Environmental Implications. This study shows that Cr-(III) can be readily oxidized to Cr(VI) in light in acidic Fe(III)

TABLE 5. Effect of pH on Oxidation of Aqueous Cr(III) in 356 nm Light in the Presence of Fe(III) As Shown by Cr(VI) Concentration Change with Photoexposure Time[a]

	Cr(VI) change (μM) at t (s) =				
pH	15	30	60	120	180
2.5	0.2	1.0	0.5	0.8	0.8
3.4	2.4	3.7	5.3	6.6	7.2
5.0	0.2	0.3	0.6	1.1	1.3

[a] Initial Fe(III): 250 μM; initial Cr(III): 100 μM.

solutions by ·OH radicals from photolysis of $FeOH^{2+}$ complexes. The rate constant of the reaction of Cr(III) with ·OH was estimated to be 8.3×10^7 M^{-1} s^{-1}. The Cr(VI) formation reached steady state, about 6 μM ([Cr(III)]$_0$: 50 μM) and 10 μM ([Cr(III)]$_0$: 200 μM), within 0.5 h ([Fe(III)]$_0$: 200 μM). This finding appears to support the suggestion (*12*) of free radical-mediated steady state between Cr(III) and Cr(VI).

The basic requirements for light-induced oxidation of Cr-(III) in the presence of Fe(III) are sunlight, a pH of about 2.5–4.5, and soluble Fe(III) species, which are present ubiquitously in polluted atmosphere as well as in soils and aquatic bodies. Photolysis of $FeOH^{2+}$, the major Fe(III) species at pH 2.5–5, has been considered as one important source of ·OH radicals in ambient environments (*13, 22*). However, in light and in the presence of organic matter in surface soils, the Fe(III)-catalyzed photochemical reduction of Cr(VI) by organic acids will predominate in Cr cycling in most soils (*11, 32*). But, in atmospheric waters, which have the pH commonly found at 2–5 (*12, 13*) and much less dissolved organic carbon (DOC) (*33*), and in some acidic surface waters with DOC nearly depleted, we would expect that the light-induced Cr(III) oxidation could be one potentially important pathway for Cr(III) to become oxidized to Cr(VI). This study also suggests that ·OH radicals from other sources, such as gas-to-droplet transfer of ·OH (*13*), may oxidize Cr(III). The ready oxidation of Cr(III) to Cr(VI) in light in the presence of Fe(III) indicates the need to further examine the kinetic mechanism of Cr cycling in the ambient atmospheric waters or some acidic surface waters, with particular consideration of the photoredox involving Fe(III), organic acids, and free radicals.

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