Influence of Organic Ligands on Chromium(VI) Reduction by Iron(II)

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Iron(II) is one of the most important reductants that transforms toxic chromium(VI) to essentially nontoxic chromium(III), but the effect of iron speciation on this redox reaction is not well-understood. We determined rate constants for Cr(VI) reduction by a series of Fe(II)−organic complexes, using UV−vis spectroscopy and kinetic fitting. The experiments with 1−20 μM Cr(VI), 1−60 μM Fe(II), and 5−1000 μM organic ligand at pH 4.0−5.5 can be described with the following rate law: $-d[Cr(VI)]/dt = \sum_L k_L[Fe(II)L][Cr(VI)]$, where k_L is pH-dependent. Fe(III)-stabilizing ligands such as bi- and multidentate carboxylates and phenolates generally accelerate the reaction, whereas Fe(II)-stabilizing ligands such as phenanthroline essentially stop the reaction. The rate coefficients increase with decreasing electron reduction potential of the Fe(III)L−Fe(II)L redox couples. The relationship of log k_L versus $E_H°$(Fe(III)L) is quite linear over 10 orders of magnitude. Dissolved organic matter extracted from the organic horizon of a forested spodosol shows qualitatively the same behavior as the investigated carboxylates. The presence of organic ligands leads to soluble Cr(III) and Fe(III) complexes. These results are important in DOC-rich soils and natural waters with respect to Cr(VI) reduction rates, the mobility of the products, and the reoxidation probability of newly reduced Cr(III), e.g., by naturally occurring manganese oxides.

Introduction

The advantageous chemical and technical properties of chromium are reflected in a wide range of industrial applications, e.g., in the stainless steel, galvanic, refractory, leather, pigment, and chemical industry (*1*, *2*). The worldwide annual mining of chromite (FeCr$_2$O$_4$) has exceeded a level of 10 million tons (*2*), and as a result of the extensive use, waste disposal and natural water contamination have become important environmental problems (*3*, *4*). The hexavalent chromates HCrO$_4^-$ and CrO$_4^{2-}$ exhibit a high mobility in many soils and groundwaters, and are of concern for the quality of drinking water. Cr(VI) is toxic to humans, animals, plants, and microorganisms (*1*, *2*, *5*, *6*). Trivalent chromium is much less toxic and even essential in human and animal nutrition. Cr(III) tends to associate with solid phases and is quite immobile in the environment.

For these reasons, Cr(VI) reduction processes are a major focus of the environmental chemistry of chromium. Important reductants in natural systems are organic compounds and divalent iron (*7*−*9*). Cr(VI) reduction in the presence of natural organic material and Fe(II) has been observed by several research groups. Studies have been conducted with different soils and natural waters, e.g., acidic subsoils (*10*), alkaline soils (*11*), wetland soils (*12*), alluvial river sands (*13*), aquifer material (*14*−*16*), and water of a seasonally anoxic lake (*17*) and an estuary (*18*). Fe(II) may also be an important reductant of Cr(VI) in aerosols and atmospheric droplets (*19*).

In many environmental compartments, organic compounds are quantitatively the dominant reductants. However, laboratory studies have shown that they usually react slowly with Cr(VI). At near neutral pH, the majority of compounds with oxygen-containing functional groups reduce Cr(VI) with half-lives ranging from months to many years (*20*). By contrast, Fe(II) is much more reactive than organic material (*21*, *22*), but, in oxic environments, its concentration usually does not exceed the low micromolar range (*23*). Cr(VI) reductions that have been observed in field studies are probably the result of the synergistic properties of Fe(II) and organic compounds. Fe promotes the Cr(VI) reduction by natural organic material by acting as a redox catalyst (a) in thermal, abiotic reactions (*24*, *25*), (b) in anaerobic respiration by bacteria, fungi, and other organisms (*26*), and (c) in photoinduced reactions (*18*, *25*, *27*). Conversely, organic compounds influence Cr(VI) reduction by Fe(II) by enhanced (reductive) weathering of Fe-bearing minerals (*14*, *25*, *28*) and by Fe(II) complexation (this paper).

The marked pH dependence of Cr(VI) reduction by Fe(II) has been explained by the high reactivity of Fe(II)−hydroxo complexes (*21*, *22*). Hydroxo ligands stabilize Fe(III) and make Fe(II)(OH)$_x^{2-x}$ a much better reductant than hexaquo Fe^{2+}. We expect that other, Fe(III)-stabilizing ligands also accelerate the Cr(VI) reduction by Fe(II). This study describes kinetic experiments performed with various organic ligands (citrate, oxalate, salicylate, tartrate, nitrilotriacetate, and 1,10-phenanthroline) and with a water extract of the organic horizon of a spodosol. Low-molecular weight DOC, partly in the form of the first four mentioned compounds, is released during the microbial decomposition of biomass and as exudates from plant roots (*29*). Oxalate has been found in soil water at concentrations as high as 25−1000 μM (*30*). Carboxylates and phenolates are commonly occurring functional groups in higher-molecular weight organic compounds such as fulvic and humic acids (*29*). Some of these compounds may be present in waste disposal sites.

The objective of the kinetic experiments was to measure rate constants for the reaction of Cr(VI) with Fe(II)−organic complexes and to develop a linear free energy or Marcus relation (*31*), similar to the one reported for Fe(II) oxygenation (*32*), and to the trends observed for Fe(II) oxidation by Co(III) and Ce(IV), respectively (*33*). We discuss the results of some previous studies on Cr(VI) reduction by Fe(II) complexes (ligands 2,2′-bipyridine, cyanide, ferrocene, and 1,10-phenanthroline) that, however, were all conducted under more acidic conditions at pH <3 (*34*−*36*).

In principle, Fe(II) is a potent agent for the remediation of Cr(VI)-contaminated sites and the treatment of industrial waste (*4*, *15*, *37*, *38*). Important for the evaluation of a remediation strategy is the knowledge of the Cr(III) products, mainly regarding mobility and reoxidation probability, e.g., by manganese(III,IV) (hydr)oxides (*39*−*47*). There is UV−vis spectroscopic evidence that soluble Cr(III) compounds are formed in the presence of organic ligands (*27*).

Experimental Section

Chemicals. All chemicals were at least reagent grade and were used as supplied [from Merck, K$_2$CrO$_4$, (NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O, FeCl$_3$·6H$_2$O, acetic acid (100%), sodium acetate, ammonium acetate, potassium oxalate, salicylic acid, nitrilotriacetic

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acid, diphenylcarbazide, H_2SO_4 (95−97%), HCl (32%), NH_3 (25%), Titrisol HCl (0.1−1 M), and NaOH (0.1−1 M); and from Fluka, KCl, citric acid, D-(−)-tartaric acid, 1,10-phenanthroline, ferrozine, and NaOH (32%)]. Solutions were prepared with 18 MΩ water (Q-H_2O grade Barnstead Nanopure). The experiments were carried out in HCl-cleaned glassware.

Soil Extract. Soil samples were collected from the organic horizons O_e and O_a [intermediately (hemic) and highly (sapric) decomposed organic matter] of a ferric−humic spodosol in Guberwald/Eigenthal (Switzerland). The 10 cm thick horizons had a pH(H_2O) of ≈3.1 and an organic matter content of ≈83 g/100 g (48). An extract of organic matter was obtained from 20 g of field-moist soil using 50 mL of Nanopure water for 2 h. Afterward, the suspension was filtered using water-cleaned cellulose nitrate filters (0.45 μm from Satorius). The resulting, yellow-brown filtrate had a pH of 4.8. The DOC content was 53.6 ± 0.6 mg/L, measured with a Shimadzu 5000 analyzing system.

Experiments. The kinetic experiments were performed by rapid mixing (<5 s) of equal amounts of a pH-buffered Fe(II)−ligand solution with a Cr(VI) solution in a 5 cm quartz cell. The UV−vis absorbance of the Fe(III) products forming during the reaction was directly recorded at a specific wavelength, as described below.

All solutions contained 0.01 M KCl for a defined ionic strength and 1 mM acetate buffer to maintain a constant pH of 4.5−5.5. Solutions of pH 4.0 were unbuffered. The initial pH was adjusted with HCl or NaOH. The pH drift during the experiments was always less than 0.05 unit, indicating a sufficient buffer capacity. A constant temperature of 23 ± 3 °C was maintained by circulating thermoregulated water through a cooling jacket surrounding the spectrophotometer cell holder. With citrate, we performed additional experiments at 13 ± 1 and 31 ± 2 °C.

Fe(II)−ligand solutions were always freshly prepared by dilution of stock solutions of 0.01−0.1 M ligand and 0.001−0.1 M Fe(II) with pH 1−3 (H_2SO_4). The Fe(II)−ligand solution (7.5 mL) was immediately transferred to a 5 cm optical cell. The cell was placed into the spectrophotometer, and the recording of an absorbance versus time curve was started (Uvikon 860/Kontron and Cary 1E/Varian). A short time later, 7.5 mL of a Cr(VI) solution was added to the cell. In the experiments with the soil extract, we added a small volume of Cr(VI) to the buffered Fe(II)−soil extract solution. The solutions were stirred in the cell. At the end of the reaction, we recorded a full absorption spectrum. Most experiments were performed in duplicate.

Initial concentrations are listed in Table 1. In most solutions, the concentrations did not satisfy the usual excess condition for the classical kinetic analysis. The criteria for the selected reaction conditions were environmentally relevant concentration ranges, the desired speciation of Fe-(II), the measuring range of the analytical method (UV−vis), the duration of the experiments, and the prevention of other, interfering redox reactions. Fe(II) oxygenation was always small compared to oxidation by Cr(VI) except for NTA where oxygenation was prevented by using Ar-sparged solutions. Control experiments without Fe(II) showed no detectable reduction of Cr(VI) or Fe(III) by the organic acids on the time scale of the experiments (10−60 min). All experiments were performed in the dark, and the light intensity of the spectrophotometer was too small to cause measurable photochemical Fe(III) reduction.

The monitoring wavelength was chosen so that the molar absorption coefficients of the forming Fe(III) complexes were large, those of Cr(VI) small, and those of all other species essentially zero (310 nm for citrate, oxalate, tartrate, and the soil extract, 300 nm for NTA, and 500 nm for salicylate; full spectra from 200 to 700 nm were recorded for 1,10-phenanthroline). Figure 1 illustrates the spectra of different

TABLE 1. Initial Micromolar Concentrations and pH Conditions of All Experiments, $T = 23 \pm 3$ °C

ligand	Cr(VI)	Fe(II)	pH
citrate			
10,[a] 15, 20, 25	3.3	10	5.0
5, 10, 20, 50	1	3	5.0
10	1	3, 5, 10, 15	5.0
10	1, 1.2, 1.5, 2, 5	3	5.0
10	1	3	4.0, 4.5, 5.0, 5.5
nitrilotriacetate			
5, 10, 20	0.5	1.5	5.0
oxalate			
100	20	10, 20	5.0
50, 100	10	20	5.0
100	5	10	5.0
50, 100, 200	2	5	5.0
100	10	20	4.0, 4.5, 5.0, 5.5
200	2	5	4.0, 4.5, 5.0, 5.5
1,10-phenanthroline			
1000	20	60	5.0
salicylate			
1000	3.3, 10, 20	10	5.0
1000	10	10	4.0, 4.5, 5.0, 5.5
tartrate			
100, 200, 500	10	30	5.0
200	10	30	4.0, 4.5, 5.0, 5.5
soil extract			
10.7, 21.4, 42.9[b]	20	60[c]	4.9
21.4[b]	20	60[c]	4.6, 4.9, 5.3

[a] T = 13 ± 1, 23 ± 3, and 31 ± 2 °C. [b] mg/L DOC. [c] All Fe(II) added.

Fe(III) complexes, $HCrO_4^-$, and CrO_4^{2-}. Typical absorbance versus time curves are depicted in Figure 2.

Analytical Methods. Spectra recorded at the end of the experiments allowed the determination of remaining $HCrO_4^-$, CrO_4^{2-}, and total Fe(III). These concentrations were extracted by multicomponent fitting of the measured spectrum with the spectra of the components (Figure 1) (21). As component spectra for Fe(III), we used spectra of Fe(III)−ligand mixtures with similar concentrations and pHs as in our experiments. We double-checked these measurements in a number of experiments with colorimetric methods, using diphenylcarbazide (DPC) for Cr(VI) (49) and ferrozine for Fe(II) (50). Different Cr(III) species could be separated and determined semiquantitatively with capillary zone electrophoresis (51).

Kinetic Analysis. The kinetics of the pH dependence of the Cr(VI) reduction by Fe(II) in the absence of complexing organic ligands have been described by a rate law that considers different Fe(II) complexes (21, 22):

$$-d[Cr(VI)]/dt = (k_1[Fe^{2+}] + k_2[FeOH^+] + k_3[Fe(OH)_2^0])[Cr(VI)] \quad (1)$$

analogous to Fe(II) oxidation by O_2 and by H_2O_2, respectively (52, 53). We expect that Fe(II)-complexing organic ligands influence the kinetics likewise, i.e., that Cr(VI) reduction obeys a generalized rate law of the following form:

$$-d[Cr(VI)]/dt = \sum_L k_L[Fe(II)L][Cr(VI)] \quad (2)$$

To verify this rate law and to determine constants k_L for the different ligands, we defined a kinetic model with all pertinent dissociation, complex formation, and redox reactions (Table 2, Tables I and II in the Supporting Information). Chemical
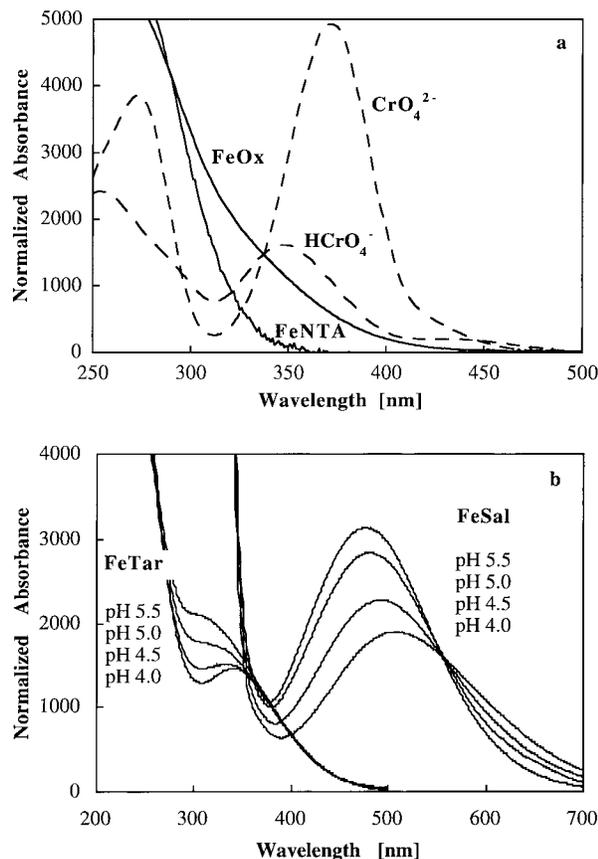
FIGURE 1. UV−vis absorption spectra of (a) 20 μM HCrO$_4^-$ at pH 2.5, 20 μM CrO$_4^{2-}$ at pH 11.5, 20 μM Fe(III) and 100 μM oxalate at pH 5.0, and 1.5 μM Fe(III) and 10 μM NTA at pH 5.0 and (b) 30 μM Fe(III) and 200 μM tartrate at different pH values and 10 μM Fe(III) and 1000 μM salicylate at different pH values, normalized to concentrations of 1 M (Cr or Fe) and path lengths of 1 cm. The normalized absorbance of 3 μM Fe(III) and 10 μM citrate at pH 5.0 is similar to that of 20 μM Fe(III) and 100 μM oxalate at pH 5.0.

equilibria are treated as forward and backward reactions with bimolecular rate constants of 10^{10} M^{-1} s^{-1} for the acid−base reactions and $>10^6$ M^{-1} s^{-1} for the complex formation reactions (*54*). The Cr(VI) to Cr(V) electron transfer is taken to be the rate-limiting step (*21, 35, 55*), whereas the subsequent reductions to Cr(IV) and Cr(III) are fast. The overall Cr(VI) reduction leads to soluble Cr(III) complexes (see Stoichiometry and Products). A fast uptake of a ligand is simulated proceeding from Cr(IV) (reaction 20). However, the ligand could be bound to Cr at another step in the reduction process without affecting the outcome. Within the time scale of the experiments, the ligand exchange of the Cr(III) complex formed is negligible (*54*).

As previously mentioned, we recorded the change in absorbance at an Fe(III)-sensitive wavelength. The following equations show that the change is proportional to the change in the total Fe(III) concentration:

$$\frac{dA}{dt} = I\left[\sum_{L}\epsilon_{Fe(III)L}\frac{d[Fe(III)L]}{dt} + \sum_{i}\epsilon_{H_iCrO_4^{i-2}}\frac{d[H_iCrO_4^{i-2}]}{dt}\right] \tag{3a}$$

$$\frac{dA}{dt} \approx I\left[\epsilon_{Fe(III)_{pH}}\frac{d[Fe(III)]}{dt} - \epsilon_{Cr(VI)_{pH}}\frac{d[Fe(III)]}{dt}\Big/R\right] \tag{3b}$$

$$\frac{dA}{dt} \approx I\left[\epsilon_{Fe(III)_{pH}} - \frac{\epsilon_{Cr(VI)_{pH}}}{R}\right]\frac{d[Fe(III)]}{dt} = I\Delta\epsilon\frac{d[Fe(III)]}{dt} \tag{3c}$$

where A is the absorbance, l is the length of the optical cell, [Fe(III)] $\approx$ [Fe(III)L] + [Fe(III)L$_2$] + [FeOH^{2+}] + [Fe(OH)$_2^+$], [Cr(VI)] = [HCrO$_4^-$] + [CrO$_4^{2-}$], $\epsilon_{sp_{pH}}$ is the molar decadic absorption coefficient of the indicated species (subscript sp) at constant pH, R means the stoichiometric ratio Δ[Fe(II)]/Δ[Cr(VI)], and $\Delta\epsilon$ is a proportionality factor [$\epsilon_{Fe(III)_{pH}} - \epsilon_{Cr(VI)_{pH}}/R$].

The molar absorption coefficient for Cr(VI) [$\epsilon_{Cr(VI)_{pH}}$] was constant at a given pH. Speciation calculations for Fe(III) with each ligand showed that $\epsilon_{Fe(III)_{pH}}$ also remained constant during the reaction. For salicylate, the ligand was always in excess so that the fractions of the different Fe(III) species, mainly 1:1 and 1:2 complexes, did not change. For tartrate, the fractions of the Fe(III) species, dihydroxo and 1:1 complexes, were constant during each experiment. For NTA, most Fe(III) was speciated as FeNTA. For citrate, the main fraction was Fe citrate. In some experiments with low citrate concentrations, Fe(III) was partly present as Fe(OH)$_2^+$ at the end of the reaction. In these cases, the last data points were omitted in the kinetic analysis. For oxalate, Fe(III) was speciated as 1:2 and 1:3 complexes. The relative fractions were changing during the experiments; however, the molar absorption coefficients of the two species do not differ greatly at 310 nm (*56*).

Consequently, $\Delta\epsilon$ in each experiment could be considered constant. Relative to the origin of coordinates as defined in Figure 2a, the integration of eq 3c yields

$$\Delta A = l\Delta\epsilon[Fe(III)] \tag{4}$$

The constants k_L were obtained by fitting the absorbance versus time curves with the kinetic model in Table 2. Acuchem (*57*), a numerical integration program, was used to compute the time-dependent concentrations of all reactants. A Matlab program (*58*) and two auxiliary Pascal programs inserted initial concentrations (Table 1) and varied k_L until the sum of squared residuals from the difference between model [$\Delta A = l\Delta\epsilon[Fe(III)]$] and data was minimized for the entire set of experiments for each ligand and pH [simplex routine (*59*)]. The only two adjustable parameters were k_L and $\Delta\epsilon$ (for oxalate, two k_L's were used). For the computation of errors, we refer to the Supporting Information.

Results and Discussion

Stoichiometry and Products. From the difference between initial and final Fe(II), Fe(III), and Cr(VI) concentrations, we found overall stoichiometries R (Δ[Fe(II)]/Δ[Cr(VI)]) of $\approx$3:1 [for citrate 2.94 $\pm$ 0.61 (SD for $n = 12$ experiments), oxalate 2.96 $\pm$ 0.21 ($n = 13$), salicylate 3.07 $\pm$ 0.30 ($n = 2$), NTA 3.65 $\pm$ 0.18 ($n = 2$), and the soil extract 2.56 $\pm$ 0.18 ($n = 3$)]. Tartrate showed a different behavior, depending on pH [$R = 1.33 \pm 0.04$ at pH 4.0, 1.51 $\pm$ 0.03 at pH 4.5, 1.85 $\pm$ 0.06 at pH 5.0, and 2.07 $\pm$ 0.05 at pH 5.5 ($n = 2-4$)]. With 1,-10-phenanthroline, we did not observe any reaction.

The multicomponent fits reproduced the experimental spectra to within the signal-to-noise ratio and confirmed the formation of Fe(III)−organic complexes. With capillary zone electrophoresis (*51*), we could separate different Cr(III) complexes as products of our Cr(VI) reduction experiments: Cr(III) citrate, Cr(III) oxalate, Cr(III) bisoxalate, Cr(III) salicylate, and Cr(III) bisalicylate. We did not observe precipitation of colloids or particles. We can summarize the redox processes as follows:

$$Cr(VI) + 3Fe(II)L_w + xL = Cr(III)L_y + 3Fe(III)L_z \tag{5}$$
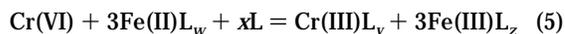
The measured stoichiometries of Δ[Fe(II)]/Δ[Cr(VI)] of $\approx$3:1 (with the exception of experiments with tartrate) were expected for the transfer of three electrons to Cr(VI) by the
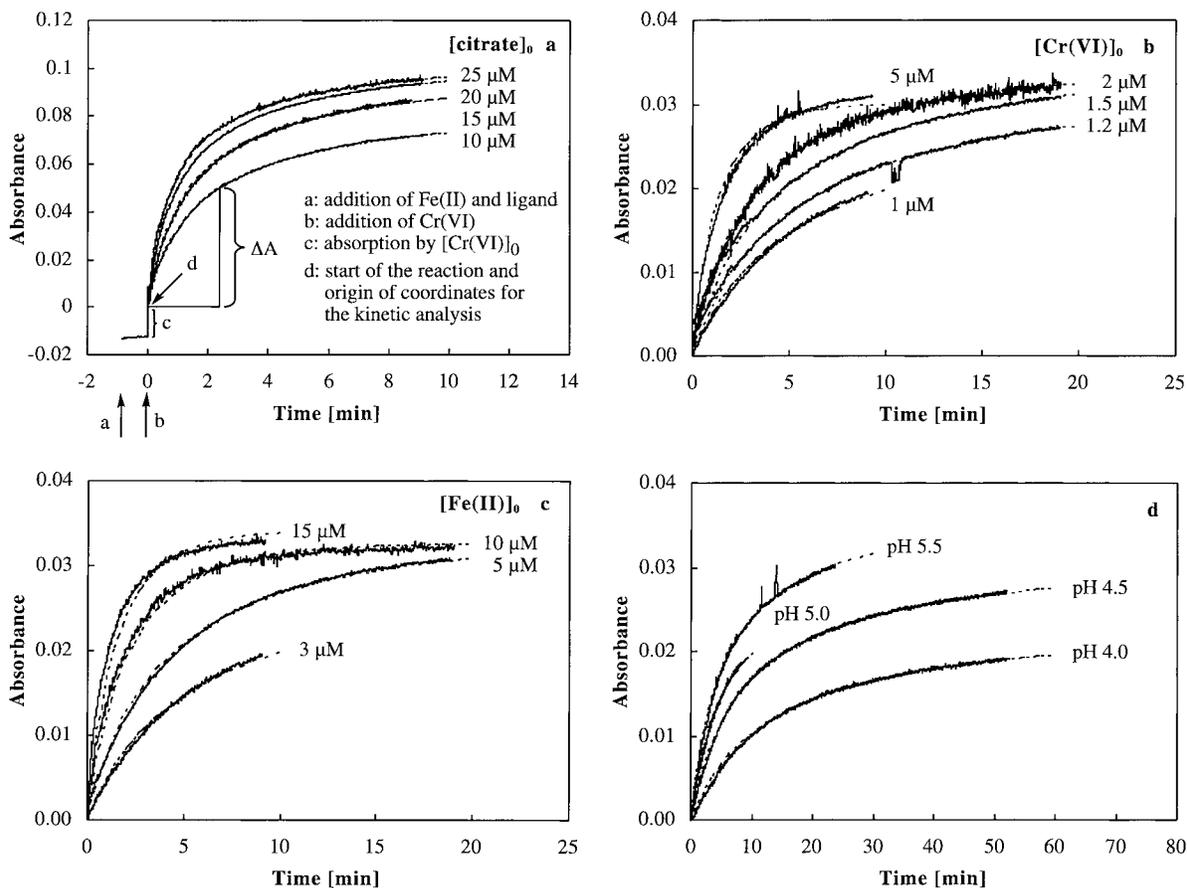
FIGURE 2. Absorption curves of Cr(VI) reduction experiments recorded at 310 nm in a 5 cm cell: (a) citrate variation [[Cr(VI)]$_0$ = 3.3 μM, [Fe(II)]$_0$ = 10 μM, [citrate]$_0$ = 10−25 μM, pH 5.0], (b) Cr(VI) variation [[Cr(VI)]$_0$ = 1−5 μM, [Fe(II)]$_0$ = 3 μM, [citrate]$_0$ = 10 μM, pH 5.0], (c) Fe(II) variation [[Cr(VI)]$_0$ = 1 μM, [Fe(II)]$_0$ = 3−15 μM, [citrate]$_0$ = 10 μM, pH 5.0], and (d) pH variation [[Cr(VI)]$_0$ = 1 μM, [Fe(II)]$_0$ = 3 μM, [citrate]$_0$ = 10 μM, pH 4.0−5.5]. The dashed lines indicate simultaneous fits using the kinetic model of Table 2 with the pH-dependent coefficient k_L (Table 3).

reductant Fe(II) and are consistent with previous investigations on Cr(VI) reduction by Fe(II) complexes (34−36). In the tartrate experiments, Cr(V) and Cr(IV) intermediates must have reacted partly with another reductant, probably with tartrate itself. At lower pH, more of this second reductant was consumed, consistent with the pH dependence of Cr(VI) reduction kinetics with most organic compounds (20). It seems that tartrate is more easily oxidized than the other organic compounds used in this study. As one-electron oxidation potentials could not be found in the literature for all our carboxylic acids, we draw a qualitative assessment by comparing rate coefficients of the oxidation of some carboxylates by Cr(VI). Deng (20) has measured the following Cr(VI) half-lives in solutions containing 10 μM Cr(VI) and 1 mM organic acid at pH 7: tartrate, 620 d; salicylate, 1700 d; and oxalate, >4000 d. Citrate, a α-hydroxycarboxylate like tartrate, does not possess an α-hydrogen atom in the geminal position to the OH group that can be abstracted and is therefore expected to be more slowly oxidized than tartrate (60).

Reduction Kinetics. As a representative set of measurements, Figure 2a−c shows absorption curves with varying [Cr(VI)]$_0$, [Fe(II)]$_0$, and [citrate]$_0$. All three reactants accelerate the rate of Cr(VI) reduction as seen by the rate of Fe(III) production. The fits (dashed curves) are calculated with the kinetic model of Table 2, with k_L as the only fitting parameter (reaction 14). The overall reaction becomes faster with higher pH (Figure 2d) because the fraction of Fe(II) citrate increases. However, the pH dependence of the Fe(II) citrate concentration cannot fully explain the pH dependence of the reaction.

The fitting procedure yields pH-dependent coefficients k_L-(pH) (Table 3).

With the other carboxylic acids, we observed similar kinetics and obtained pH-dependent coefficients as with citrate (Table 3). To fit the experiments with oxalate, we had to include a second coefficient for the reaction of Fe(II) bisoxalate with Cr(VI) (reaction 15). Our kinetic model yielded a good agreement of fit and experimental absorption curve for all investigated reaction conditions.

In contrast to the carboxylic acids, the Fe(II)-complexing ligand 1,10-phenanthroline (mainly a 1:3 complex) essentially stopped the reaction. At pH 5, the absorption spectrum did not change within 15 weeks. A similar effect was found by Anderson et al. (14) in batch experiments with material from a mildly reducing sand and gravel aquifer, where the addition of phenanthroline or bipyridine stopped the reduction of Cr(VI).

In the kinetic model of Table 2, we postulate three subsequent reduction steps (reactions 14, 15, 19, and 21) with a rate-limiting electron transfer from Cr(VI) to Cr(V). This is consistent with recent studies of the pH dependence of Cr(VI) reduction by Fe(II) (21, 22) and earlier kinetic studies with the ligands 2,2′-bipyridine, cyanide, ferrocene, and 1,-10-phenanthroline at pH <3 (34−36). The reported rate laws are first-order in $HCrO_4^-$ and Fe(II)L$_x$, with pH-dependent, second-order rate coefficients. There was no influence by the oxidation product, Fe(III).

The influence of temperature was investigated with citrate. We observed a slight temperature dependence with a rate

TABLE 2. Kinetic Model[a]

				K (M or M^{-1})
		Dissociation Reactions		
1	Fe^{2+}	$=$	$FeOH^+ + H^+$	$2.34 \times 10^0/10^{10}$ [b]
2	$FeOH^+$	$=$	$Fe(OH)_2 + H^+$	$7.24 \times 10^{-2}/10^{10}$ [b]
3	Fe^{3+}	$=$	$FeOH^{2+} + H^+$	$3.89 \times 10^7/10^{10}$ [b]
4	$FeOH^{2+}$	$=$	$Fe(OH)_2^+ + H^+$	$2.29 \times 10^6/10^{10}$ [b]
5	H_xL	$=$	$H_{x-1}L + H^+$	K_a [c]
		Complex Formation Reactions		
6	$Fe^{2+} + L$	$=$	$Fe(II)L$	K_1 [d]
7	$Fe(II)L + L$	$=$	$Fe(II)L_2$	K_2 [d]
8	$Fe(II)L_2 + L$	$=$	$Fe(II)L_3$	K_3 [d]
9	$Fe^{2+} + HL$	$=$	$Fe(II)HL$	K [d]
10	$Fe^{3+} + L$	$=$	$Fe(III)L$	K_1 [d]
11	$Fe(III)L + L$	$=$	$Fe(III)L_2$	K_2 [d]
12	$Fe(III)L_2 + L$	$=$	$Fe(III)L_3$	K_3 [d]
13	$Fe^{3+} + HL$	$=$	$Fe(III)HL$	K [d]

				k (M^{-1} s^{-1})
		Redox Reactions		
14	$Fe(II)L + Cr(VI)$	$\rightarrow$	$Fe(III)L + Cr(V)$	k_{L1}?
15	$Fe(II)L_2 + Cr(VI)$	$\rightarrow$	$Fe(III)L_2 + Cr(V)$	k_{L2}?
16	$Fe^{2+} + Cr(VI)$	$\rightarrow$	$Fe^{3+} + Cr(V)$	0.34
17	$FeOH^+ + Cr(VI)$	$\rightarrow$	$FeOH^{2+} + Cr(V)$	1.41×10^5
18	$Fe(OH)_2^0 + Cr(VI)$	$\rightarrow$	$Fe(OH)_2^+ + Cr(V)$	2.84×10^9
19	$Fe(II)L + Cr(V)$	$\rightarrow$	$Fe(III)L + Cr(IV)$	$>10^8$
20	$Cr(IV) + L$	$\rightarrow$	$Cr(IV)L$	$>10^8$
21	$Fe(II)L + Cr(IV)L$	$\rightarrow$	$Fe(III)L + Cr(III)L$	$>10^8$

[a] For constants and references for reactions 1–13, see Tables I and II in the Supporting Information; for reactions 16–18 (21); constants of reactions 19–21 are non-rate-determining. [b] K is given as quotient of the kinetic constants for the forward reaction (s^{-1}) and backward reaction (M^{-1} s^{-1}), respectively. [c] Backward reaction with a k of 10^{10} M^{-1} s^{-1}. [d] Forward reaction with a k of $>10^6$ M^{-1} s^{-1}.

FIGURE 3. Absorption curves of Cr(VI) reduction experiments recorded at 310 nm [[Cr(VI)]$_0$ = 20 μM, [Fe(II)]$_0$ = 60 μM, [DOC of soil extract]$_0$ = 10.7–42.9 mg/L, pH 4.6–5.3]. (Inset) Observed constants obtained from the rate law $-d[Cr(VI)]/dt = k_{obs}[Cr(VI)]$ [Fe(II)], assuming a 3:1 stoichiometry.

FIGURE 4. Second-order rate coefficients k_L at pH 5.0 as a function of the reduction potential $E_H°$ (volts) of the corresponding Fe(III) complexes. Rate law of $-d[Cr(VI)]/dt = k_L[Fe(II)L][Cr(VI)]$.

coefficient at 31 °C about twice that at 13 °C, similar to the kinetics with free and hydroxo Fe(II), respectively (22).

Experiments with the soil extract yielded results similar to those with the carboxylic acids. The soil extract alone did not lead to a measurable reduction of Cr(VI) within 30 min [20 μM Cr(VI) and 43 mg/L DOC (pH 5)]. When Fe(II) was added (60 μM), we observed a fast reaction. Increasing DOC concentrations as well as higher pH values accelerated the redox process (Figure 3). We attribute this to the complexation of Fe(II) with oxygen ligands that make it a better reductant. DOC (1 mg/L) from the organic horizon of this spodosol has about the same reactivity as 1 mg/L tartrate. DOC is a complex mixture of compounds, and the observed rate is the sum of the different reactivities of a whole series of Fe(II) complexes.

Linear Free Energy Relation. As mentioned in the Introduction, we expected a relation between log k_L and the free molar energy of the first electron transfer ($\Delta G° = -F \{E_H°(Cr(VI)) - E_H°(Fe(III)L)\}$). One-electron reduction potentials $E_H°$ of Fe(III)–Fe(II) redox couples are listed in Table III of the Supporting Information. Unfortunately, the pH-dependent one-electron reduction potential of Cr(VI) is not
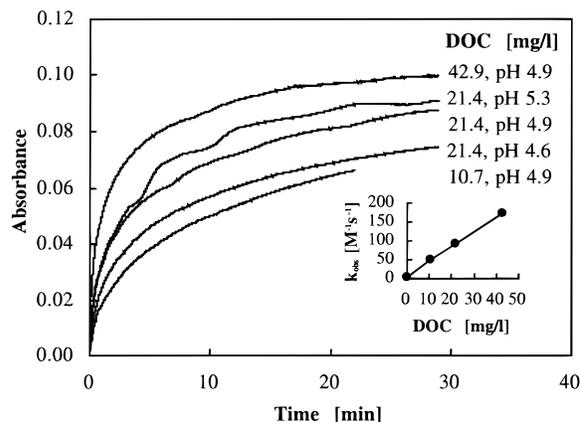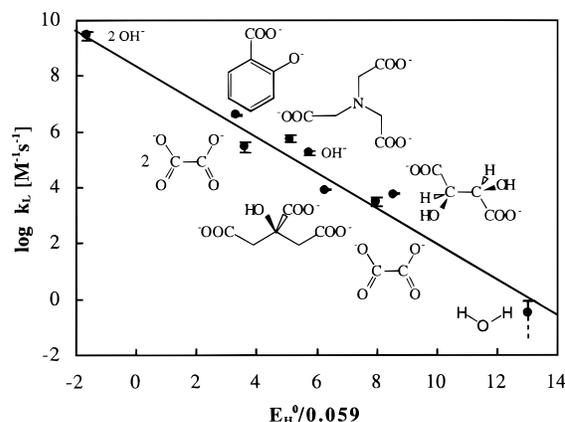
known, but is constant at a given pH. In Figure 4, the values of log k_L at pH 5 are plotted versus $E_H°$(Fe(III)L). The correlation is quite linear over several orders of magnitude ($r^2 = 0.98$).

Birk (35) applied Marcus theory to kinetic data of Cr(VI) reduction by cyano- and 2,2′-bipyridine–Fe(II) complexes at pH <3. The rate coefficients at constant pH correlated with the Fe(III) reduction potential [reactivity, Fe(II)CN$_6^{4-}$ > Fe(II)bipCN$_4^{2-}$ > Fe(II)bip$_2$CN$_2$]. Wehrli (32) reported a linear free energy relationship (LFER) for the oxygenation of aquo-, hydroxo-, and adsorbed Fe(II). Elovitz and Fish (61), who studied the kinetics of Cr(VI) reduction by substituted phenols, also found a linear correlation of the second-order rate constants with the half-wave potentials of the phenols.

TABLE 3. Second-Order Rate Coefficients k_L (M^{-1} s^{-1}) at Different pH, $T = 23 \pm 3$ °C[a]

complex	k_L(pH 4.0)	k_L(pH 4.5)	k_L(pH 5.0)	k_L(pH 5.5)
Fe citrate[b]	$(1.0 < 1.1 < 1.3) \times 10^5$	$(2.2 < 2.4 < 2.5) \times 10^4$	$(7.6 < 8.1 < 8.6) \times 10^3$	$(2.8 < 3.1 < 3.4) \times 10^3$
Fe NTA			$(4.0 < 5.5 < 7.8) \times 10^5$	
Fe phen$_3$			$<2.0 \times 10^{-5}$	
Fe oxalate	$(0.0 < 7.9 < 19) \times 10^3$	$(0.0 < 3.8 < 8.7) \times 10^3$	$(2.1 < 3.2 < 4.4) \times 10^3$	$(0.0 < 1.1 < 2.3) \times 10^3$
Fe oxalate$_2$	$(0.3 < 2.9 < 7.0) \times 10^6$	$(4.2 < 9.8 < 18) \times 10^5$	$(1.8 < 2.9 < 4.0) \times 10^5$	$(1.0 < 1.8 < 2.8) \times 10^5$
Fe salicyl.	$(3.0 < 3.3 < 3.7) \times 10^7$	$(4.6 < 4.9 < 5.2) \times 10^6$	$(3.6 < 3.8 < 4.2) \times 10^6$	$(2.0 < 2.2 < 2.4) \times 10^6$
Fe tartrate	$(1.8 < 2.0 < 2.1) \times 10^4$	$(8.5 < 9.0 < 9.5) \times 10^3$	$(5.4 < 5.7 < 6.0) \times 10^3$	$(4.2 < 4.6 < 5.0) \times 10^3$

[a] Rate law of $-d[Cr(VI)]/dt = k_L[Fe(II)L][Cr(VI)]$. The meaning of the errors is described in the Supporting Information. [b] At 13 ± 1 and 31 ± 2 °C (pH 5.0), we measured coefficients of 6.0×10^3 and 1.2×10^4 M^{-1} s^{-1}, respectively. These values are based on the equilibrium constants of Tables I and II of the Supporting Information.
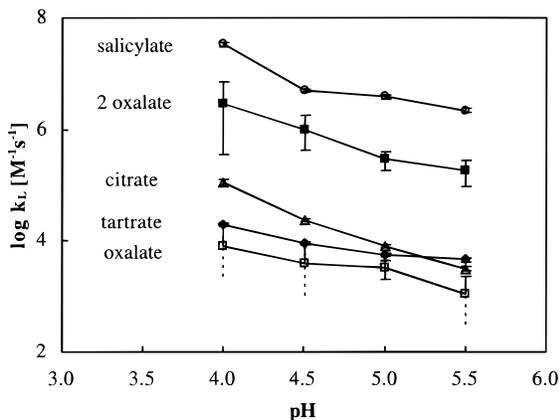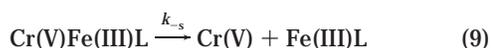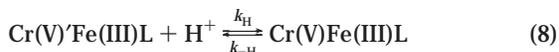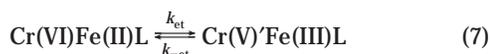
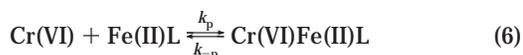**FIGURE 5.** pH dependence of the second-order rate coefficients k_L. Rate law of $-d[Cr(VI)]/dt = k_L(pH)[Fe(II)L][Cr(VI)]$.

Figure 4 allows a rough estimate of the rate coefficient for the reaction of a given Fe(II) complex with Cr(VI), provided that $E_H°(Fe(III)L)$ is known or can be calculated from Fe(II) and Fe(III) complex formation constants. Fe(II) complexes with Fe(III)-stabilizing ligands such as bi- and multidentate carboxylates or phenolates have low $E_H°(Fe(III)L)$ values and are very reactive. On the other hand, they often make up only a small fraction of Fe(II) speciation. The product of rate coefficient times concentration is the key factor that determines the importance of an Fe(II) species in the rate law for Cr(VI) reduction. For example, in an experiment with 5 μM Fe(II) and 200 μM oxalate at pH 5, about 33% of Cr(VI) is reduced by Fe(II) monooxalate and 67% by Fe(II) bisoxalate, while with 1.5 μM Fe(II) and 20 μM NTA at pH 5, 99.9% of the reaction proceeds from Fe(II)NTA and only 0.06% from Fe(II)NTA$_2$ [calculations with an estimated k_L-(Fe(II)NTA$_2$) of $\approx 1.4 \times 10^7$ M^{-1} s^{-1}]. Such considerations explain why in the case of oxalate we had to include a reaction with Fe(II) bisoxalate, and why with the other ligands, higher than 1:1 complexes could be omitted in the kinetic analysis. In any case, k_L cannot exceed the value for a diffusion-controlled bimolecular reaction of $\approx 10^{10}$ M^{-1} s^{-1}.

pH Dependence and Reaction Mechanism. The pH dependence of the rate coefficients k_L is depicted in Figure 5. The k_L's of all Fe(II) carboxylates show a marked, positive dependence on [H$^+$]. This result can be compared to the rate laws that have been found for most investigated Cr(VI) reductants (20). Apparently, reaction 14 (and 15) in Table 2 is not an elementary reaction. We suggest a sequence of (elementary) steps:

$$Cr(VI) + Fe(II)L \underset{k_{-p}}{\overset{k_p}{\rightleftharpoons}} Cr(VI)Fe(II)L \qquad (6)$$

$$Cr(VI)Fe(II)L \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} Cr(V)'Fe(III)L \qquad (7)$$

$$Cr(V)'Fe(III)L + H^+ \underset{k_{-H}}{\overset{k_H}{\rightleftharpoons}} Cr(V)Fe(III)L \qquad (8)$$

$$Cr(V)Fe(III)L \overset{k_{-s}}{\longrightarrow} Cr(V) + Fe(III)L \qquad (9)$$

Cr(VI) and Fe(II)L form an encounter complex which can either dissociate or undergo an electron transfer with formation of a successor complex. The back electron transfer might compete with the dissociation of the successor complex which occurs after addition of a proton that stabilizes the Cr(V) product.

With steady-state assumptions for [Cr(VI)Fe(II)L], [Cr-(V)'Fe(III)L], and [Cr(V)Fe(III)L], it is possible to establish a relation between the pH-dependent coefficients k_L and the

above scheme:

$$\frac{1}{k_L} = a + \frac{b}{[H^+]} \qquad (10)$$

where a and b are pH-independent terms. The proposed mechanism is consistent with the observed pH dependence (Figure 5).

Our results cannot differentiate between inner-sphere and outer-sphere electron transfer. There are arguments in support of outer-sphere (62). The observed rates are partly faster than the ligand exchange on Fe(II). The latter is close to the H$_2$O exchange rate of $\approx 3 \times 10^6$ s^{-1} (54) because it is likely to be a dissociative interchange mechanism (63). There is a good overlap for the formation of an encounter complex between the occupied t_{2g} orbital of Fe(II) and the vacant e orbital of Cr(VI) along the edges of the octaeder and the tetraeder, respectively.

Thus far, we did not consider Cr(VI) speciation in the rate law. The dominant Cr(VI) fraction in our experiments was always HCrO$_4^-$ ($>$88%). The observed pH dependence could therefore not be explained in terms of changing Cr(VI) speciation.

Environmental Significance. This study provides a quantitative understanding of Cr(VI) reduction by Fe(II) in DOC-rich environments. While it has been recognized that micromolar Cr(VI) and Fe(II) react within minutes to hours to mainly insoluble products above pH 3, it is shown here that the presence of carboxylates and phenolates can lead to greatly accelerated reaction rates and to formation of complexed soluble Cr(III). In light of the different mobilities and stabilities of Cr(III) products, kinetic rate constants that allow an estimation of the partitioning into different products are highly relevant.

In Cr(VI)-contaminated environments, all available Fe-(II) will readily be consumed, but may not be sufficient to remove all Cr(VI). Continued natural release of Fe(II) is often connected to the presence of organic matter (see the Introduction). Thus, slow formation of soluble Cr(III) complexes can be expected to occur in DOC-rich systems when Cr(VI) is reduced by forming Fe(II) complexes. Except at low pH, natural organic material reduces Cr(VI) at a slow rate. The fate of Cr(VI) is then mainly affected by hydrogeology and sorption and by slow release of Fe(II).

In remediation procedures of Cr(VI)-contaminated, DOC-rich environments that envision addition of Fe(II), or in situations where DOC-rich water flows through "reactive barriers", the formation of mobile Cr(III) complexes might be possible. An intentional formation of soluble Cr(III) by addition of an organic ligand could be advantageous for avoiding precipitation of Cr(III) and Fe(III) hydroxides, which could lead to a limited accessibility of either the Cr(VI) (inclusion in pores) or the reduced iron (surface passivation of iron filings) (64).

Cr(III) complexes can remain soluble in soils for quite a long time (42) and could be transported to regions with manganese concretions, whereas solid precipitates are essentially immobile in soils and aquifers. However, in more mixed compartments such as surface waters, particulate Cr-(III) and Mn(III/IV) might also come into contact.

According to most previous laboratory studies, Cr(III) oxidation by manganese oxides proceeds more slowly in the presence of low-molecular weight organic compounds. Johnson and Xyla (44) found a clear decrease in the Cr(III) oxidation rate when salicylic acid was added to a manganite (γ-MnOOH) suspension. Nakayama et al. (45) did not observe any Cr(III) oxidation in seawater containing citric acid and an excess of manganite, while in the absence of citric acid, γ-MnOOH oxidized Cr(III). In suspensions of a manganese-rich Aquic Udorthent soil, James and Bartlett

reported oxidation rates decreasing in the following order: freshly precipitated $Cr(OH)_3$ > Cr citrate > aged $Cr(OH)_3$ in citrate > aged $Cr(OH)_3$ (*43*).

Most field studies show an enhanced Cr(VI) reduction with lower pH (*14, 43*). This does not contradict to our results (Figures 2d and 3), which show increasing rates with pH at a given total Fe(II) concentration due to higher fractions of Fe(II) in the form of organic complexes. Under natural conditions, the total Fe(II) concentration is generally higher at lower pH which leads, possibly together with a higher reactivity of organic material, to an overall more efficient Cr(VI) reduction at lower pH. The release of Fe(II) by (reductive) dissolution of Fe-bearing minerals is catalyzed by protons and organic compounds (*14, 25, 28, 65*). Low pH is often correlated with a high content of organic material because of the inhibited microbiological decomposition activity.

Any attempt at modeling Cr(VI) reduction in environmental systems is challenging and requires an understanding of reaction pathways and of relevant rate constants. The LFE relationship (Figure 4) might be useful in estimating the kinetics of Cr(VI) reduction processes by Fe(II) in homogeneous systems such as atmospheric or surface waters and in the treatment of Cr(VI)-containing wastewater. The relative reactivities of different Fe(II) species are probably also transferable to the reduction of other contaminants such as halogenated hydrocarbons or nitrobenzenes.

Solid phases such as clay minerals or metal oxides will have a strong influence on Cr(VI) reduction by Fe(II). The speculations differ about the relative reactivity of dissolved, adsorbed, and structural Fe(II) (*12–14, 65–67*) and of dissolved or adsorbed Cr(VI) (*68–70*). Further studies on the factors affecting Cr(VI) reduction and product distribution are important in understanding the transport and long-term behavior of Cr in the environment.

Acknowledgments

Supporting Information Available

Thermodynamic data, error computation of k_L, and sums of squared residuals as a function of k_L (5 pages) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the Supporting Information from this paper or microfiche (105×148 mm, $24\times$ reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St. NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, names of authors, inclusive pagination, volume number, and issue number) and prepayment, check or money order for $15.00 for photocopy ($17.00 foreign) or $12.00 for microfiche ($13.00 foreign), are required. Canadian residents should add 7% GST. Supporting Information is also available via the World Wide Web at URL http://www.chemcenter.org. Users should select Electronic Publications and then Environmental Science and Technology under Electronic Editions. Detailed instructions for using this service, along with a description of the file formats, are available at this site. To download the Supporting Information, enter the journal subscription number from your mailing label. For additional information on electronic access, send electronic mail to si-help@acs.org or phone (202) 872-6333.

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