

Iron(VI) and Iron(V) Oxidation of Thiocyanate

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Thiocyanate (SCN^-) is used in many industrial processes and is commonly found in industrial and mining wastewaters. The removal of SCN^- is required because of its toxic effects. The oxidation of thiocyanate (SCN^-) by environmentally friendly oxidants, Fe(VI) and Fe(V), has been studied anaerobically using stopped-flow and premix pulse radiolysis techniques. The stoichiometry with Fe(VI) was determined to be $4\text{HFeO}_4^- + \text{SCN}^- + 5\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3 + \text{SO}_4^{2-} + \text{CNO}^- + \text{O}_2 + 2\text{OH}^-$. The rate law for the oxidation of SCN^- by Fe(VI) was found to be $-d[\text{Fe(VI)}]/dt = k_{11} \{ [\text{H}^+]/([\text{H}^+] + K_{a,\text{HFeO}_4}) \} [\text{Fe(VI)}][\text{SCN}^-]$ where $k_{11} = 2.04 \pm 0.04 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ and $pK_{a,\text{HFeO}_4} = 7.33$. A mechanism is proposed that agrees with the observed reaction stoichiometry and rate law. The rate of oxidation of SCN^- by Fe(V) was approximately 3 orders of magnitude faster than Fe(VI). The higher reactivity of Fe(V) with SCN^- indicates that oxidations by Fe(VI) may be enhanced in the presence of appropriate one-electron-reducing agents. The results suggest that the effective removal of SCN^- can be achieved by Fe(VI) and Fe(V).

Introduction

Thiocyanate (SCN^-) is widely used in a variety of industrial processes such as manufacturing of thiourea, photofinishing, metal separation, and electroplating (1). The manufacture of coke from coal results in SCN^- in water effluent streams where its concentrations range from 100 to 1500 mg/L (2, 3). Thiocyanate is commonly found in mining wastewater where the interaction of free cyanide (CN^-) with sulfur forms SCN^- (4). One of the primary treatment methods of CN^- -rich effluents from gold-ore concentrators involves the use of sulfur dioxide to convert CN^- to SCN^- (4). Thiocyanate is relatively less toxic than cyanide, its toxicity is a concern at elevated concentrations (5). The toxic effects of SCN^- include inhibition of halide transport to the thyroid gland, stomach, cornea, and gill as well as the inhibition of a variety of enzymes (6). A concentration greater than 150 mg/L in mammalian blood is critically dangerous (6).

The destruction of SCN^- has been studied using both biological and chemical methods (2, 5, 7–9). The activated sludge method can remove 90–99% influent SCN^- , and

aerobic biodegradation can completely convert SCN^- to ammonia, bicarbonate, and sulfate (8, 9). Chemical methods use chlorine, hydrogen peroxide, and ozone to oxidize SCN^- (2, 5, 7). The most commonly used method for removal of SCN^- in wastewater is direct alkaline chlorination or the addition of hypochlorite. This method, although adequate, has disadvantages such as chloride contamination and involvement of reactants that are hazardous and unsafe to handle (10). Alternate methods addressing environmental considerations are needed to treat SCN^- in wastewater. We herein propose the use of environmentally friendly oxidants, iron(VI) (Fe(VI)) and iron(V) (Fe(V)), for the destruction of SCN^- in aquatic environments.

Fe(VI) has properties such as high oxidizing power, selectivity, and a nontoxic byproduct Fe(III). Fe(VI) therefore has a role in cleaner (“greener”) technology for organic synthesis, “super-iron batteries”, and wastewater treatment processes (11–16). Fe(VI) is the strongest of all oxidants/disinfectants used for water and wastewater treatment (17). Moreover, ferric oxide, produced from the treatment, acts as a coagulant for removal of metals, nonmetals, and radionuclides (17, 18). Recently, we have studied oxidation of nitrogen- and sulfur-containing pollutants by Fe(VI) in aquatic environments (19–22). Most of the pollutants can be removed in seconds to minutes with formation of nonhazardous products (11). These results demonstrate the potential use of Fe(VI) to remove environmental and industrial pollutants.

In the present study, we have studied Fe(VI) and Fe(V) oxidation of SCN^- under anaerobic conditions. The rates of oxidation of SCN^- by Fe(VI) were determined as a function of pH (7.61–10.35) and temperature (5–45 °C). The reactivity of Fe(V) with SCN^- was studied at pH 10.1 to compare its reactivity with Fe(VI) and to understand the mechanism of SCN^- oxidation.

Experimental Section

Materials. All chemicals (Sigma, Aldrich) were of reagent grade or better and were used without further purification. Solutions were prepared with water that had been distilled and then passed through an 18 MΩ Milli-Q water purification system. Potassium ferrate (K_2FeO_4) of high purity (98% plus) was prepared by the method of Thompson et al. (23). The Fe(VI) solutions were prepared by addition of solid samples of K_2FeO_4 to deoxygenated 0.005 M Na_2HPO_4 /0.001 M borate at pH 9.0, a pH at which the solutions are most stable (12). A molar absorption coefficient of $\epsilon_{510 \text{ nm}} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$ was used for the calculation of $[\text{FeO}_4^{2-}]$ at pH 9.0. Thiocyanate solutions were prepared in 0.01 M phosphate buffers to obtain desired pH of the reaction mixtures. Anaerobic solutions were prepared in a glass apparatus in which they were purged of oxygen with nitrogen.

Stoichiometry. The stoichiometric experiments were carried out by mixing equal volumes ($5 \times 10^{-3} \text{ L}$) of deoxygenated Fe(VI) and SCN^- solutions together. The experiments were performed at pH 9.0 where Fe(VI) is most stable and the effect of its spontaneous decomposition is insignificant (12). The concentration of SCN^- was kept at $1.25 \times 10^{-4} \text{ M}$ and Fe(VI) concentrations ranged from $4.6 \times 10^{-5} \text{ M}$ to $5.08 \times 10^{-4} \text{ M}$. Thiocyanate concentrations were determined before and after mixing with Fe(VI) using High Performance Ion Chromatography (HPIC) (16, 17). Two products of the reactions of Fe(VI) with SCN^- , cyanate and sulfate, were also analyzed by using HPIC (16, 17). The stoichiometry of the cyanide reaction with Fe(VI) under anaerobic conditions was determined by keeping cyanide

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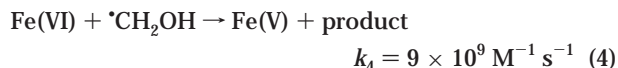
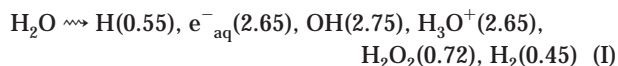
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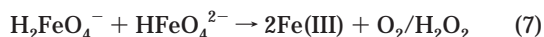
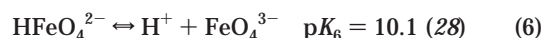
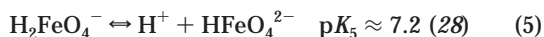
constant at 1.25×10^{-4} M and varying the Fe(VI) concentration. Cyanide concentrations before and after the reaction were determined using an Orion cyanide specific electrode (model number 94-06) with an Orion model 601A pH/mV digital meter. Cyanate, a product of the reaction, was determined by HPIC (16). Dissolved oxygen was determined using a YSI electrode.

Fe(VI) Kinetics. Kinetic studies were carried out under anaerobic conditions using a Rapid Kinetic Accessory (Applied Photophysics, UK), attached to a UV/vis diode array spectrophotometer (Hewlett-Packard model 8452A) (24). Kinetic runs were acquired and interpreted using OLIS Diode Array software (On-Line Instrument Systems Inc.), which had been interfaced with the diode array spectrophotometer. In the experiments, Fe(VI) solutions at pH 9.0 were mixed in 1:1 volume ratio with 0.01 M phosphate buffers at the desired pH. The temperature of the reactions was controlled within ± 0.01 °C by an isothermal circular bath (Fisher Scientific). With our kinetic system, we were able to determine the rates of the reaction at 15 °C only in the pH range of 7.61–10.35. The reactions were too rapid at pH values lower than 7.61.

Fe(V) Kinetics. The reaction of Fe(VI) with SCN^- was too fast under the required experimental conditions to study the reaction of Fe(V) with SCN^- using standard pulse radiolysis; the reactants are mixed and held in a reservoir from which the pulsing cell is automatically filled. Therefore, a premix pulse radiolysis apparatus was used which consists of two 30-cm³ glass syringes mounted in a double syringe drive. The Fe(VI) solution (0.001 M borate/0.005 M phosphate; pH 9.0) in one syringe was mixed with the SCN^- solution (0.10 M phosphate buffer; 0.7 M methanol) of the other syringe. Both solutions were saturated with nitrous oxide; $[\text{N}_2\text{O}] = 0.026$ M. The mixed solution was promptly injected into the optical cell (2.5-cm path length) and exposed to the ionizing pulse. Typically, the time between mixing and pulsing was < 2 s, sufficiently short to minimize the effect of Fe(VI) + SCN^- reaction on the Fe(V) + SCN^- reaction. The sequence of reactions following the electron pulse (eq I) occurred within a fraction of a microsecond (25, 26) and lead to the formation of Fe(V) (eqs 1–4). The numbers in parentheses in eq I are *G* values (27), the number of radicals formed per 100 eV of energy dissipated in the aqueous solution.



In near neutral and alkaline pH ranges, Fe(V) goes through equilibria (eqs 5 and 6) and its decay is predominantly second order (eqs 7 and 8) (27, 28).



In the presence of thiocyanate, Fe(V) decay becomes first-order and depends on thiocyanate concentration. Typically,

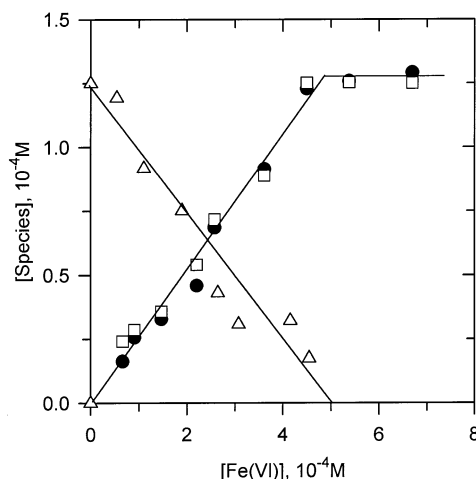


FIGURE 1. A plot of SCN^- consumption and products formed versus $[\text{Fe(VI)}]$ at pH 9.0 (initial $[\text{SCN}^-] = 1.25 \times 10^{-4}$ M; \triangle SCN^- ; \square SO_4^{2-} ; \bullet CNO^-).

thiocyanate concentrations were varied in the range of 0.043–0.407 M. The reactions were followed at 380 nm where Fe(V) has a maximum absorbance.

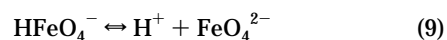
A 4 MeV Van de Graff accelerator produced electron pulses (< 500 ns) resulting in irradiation doses of 2–15 Gy in the solutions. Details of the accelerator and absorption spectrometer have been reported elsewhere (29). The thiocyanate dosimeter (0.01 M KSCN, 0.026 M N_2O , pH 5.5) was used as a calibrant taking $G(\text{SCN})_2^- = 6.13$ (radicals/100 eV) and $\epsilon_{472 \text{ nm}} = (7950 \pm 3\%)$ (27).

Results and Discussion

Stoichiometry and Reaction Products. Figure 1 shows the concentration of consumed SCN^- and generated sulfate (SO_4^{2-}) and cyanate (CNO^-), as two products of the reaction of SCN^- with Fe(VI) under anaerobic conditions at pH 9.0. The decrease in the amount of SCN^- concentration was nearly equal to the amount of sulfate and cyanate formed. The slopes of the resulting lines were as follows: -0.24 ± 0.02 , 0.26 ± 0.02 , and 0.27 ± 0.02 for SCN^- , SO_4^{2-} , and CNO^- , respectively. This indicates a stoichiometric conversion of SCN^- to SO_4^{2-} and CNO^- ions at all Fe(VI) concentrations with a stoichiometry of 4:1 (Fe(VI): SCN^-). Fe(III) was the final product of Fe(VI) reduction, and the gas produced in the reaction was identified as oxygen.

Fe(VI) Kinetics. The kinetic studies were carried out anaerobically under pseudo-first-order conditions with SCN^- in excess. Reactions were monitored by measuring the absorbance of Fe(VI) as a function of time at a wavelength of 510 nm. The absorbance versus time profile for Fe(VI) fits nicely to a single-exponential decay curve (inset Figure 2), indicating the reaction was first-order with respect to Fe(VI). The k_1 values for the reaction were determined at various concentrations of SCN^- at pH 9.20 and 25 °C (Table S1). The plot of k_1 versus $[\text{SCN}^-]$ was linear with correlation coefficient, $r^2 = 0.99$ (Figure 2). This suggests that the rate law for this reaction is first-order with respect to SCN^- .

The reaction rate constants were determined as a function of pH (7.61–10.35) and the rate of the reaction increases with a decrease in pH (Table 1; inset Figure 3). The protonation of thiocyanate does not occur in the pH range studied ($\text{p}K = -1.28 \pm 0.03$) (30); therefore, the dependence is related to the protonation of Fe(VI). Fe(VI) is a stronger oxidant upon protonation so the reaction rate was expected to increase.



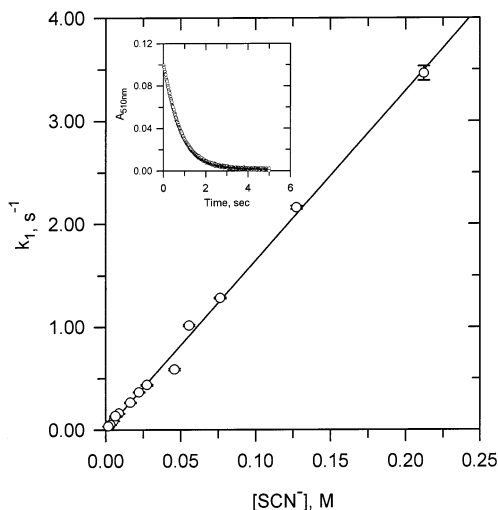


FIGURE 2. Typical plot of pseudo-first-order rate constant (k_1 , s^{-1}) versus $[SCN^-]$ of Fe(VI) oxidation of thiocyanate in 0.01 M sodium phosphate at pH 9.20 and 25 °C. Inset: The first-order decay at 510 nm of a typical Fe(VI) reaction with 0.016 M SCN^- .

TABLE 1. Fe(VI) Oxidation of SCN^- at Different pHs under Anaerobic Conditions at 15 °C

| pH | k , $M^{-1} s^{-1}$ | pH | k , $M^{-1} s^{-1}$ |
|------|-----------------------|-------|-----------------------|
| 7.61 | 687 ± 70.1 | 9.20 | 11.0 ± 0.69 |
| 8.03 | 378 ± 25.1 | 9.79 | 4.00 ± 0.41 |
| 8.44 | 168 ± 9.22 | 10.05 | 1.18 ± 0.16 |
| 8.86 | 47.4 ± 2.26 | 10.35 | 0.57 ± 0.06 |
| 8.97 | 39.2 ± 4.67 | | |

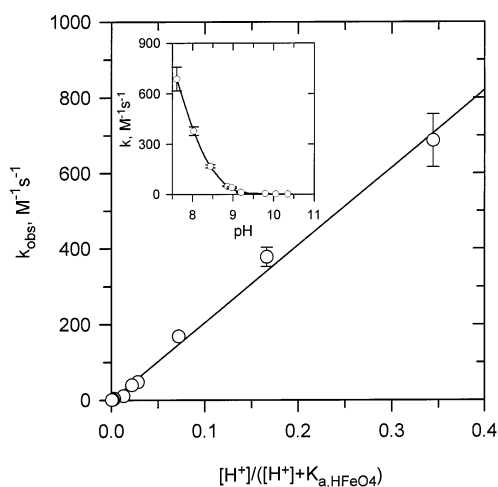


FIGURE 3. Hydrogen ion dependence on the rate of Fe(VI) oxidation of thiocyanate in 0.01 M sodium phosphate at 15 °C. Inset: Rate dependence on pH (fitted line was drawn using $k = 2.06 \times 10^3 M^{-1} s^{-1}$).

An increase in rates of oxidation of thiocyanate by Fe(VI) with a decrease in pH is related to faster reaction rates of the protonated forms of Fe(VI) ($HFeO_4^-$) than the ionized forms (FeO_4^{2-}). This is consistent with faster rates for the spontaneous decomposition of Fe(VI) with a decrease in pH (12, 20). The partial radical characters ($Fe^{VI} = O \leftrightarrow Fe^V - O^\bullet$) may be proton stabilized and increase the reactivity with thiocyanate. It has also been stated that $HFeO_4^-$ has a larger spin density on the oxo ligands than FeO_4^{2-} that increases the oxidation ability of protonated Fe(VI) (31).

We have determined the constants ($pK_{a,HFeO_4}$) for the dissociation of $HFeO_4^-$ (eq 9) at different temperatures (5–

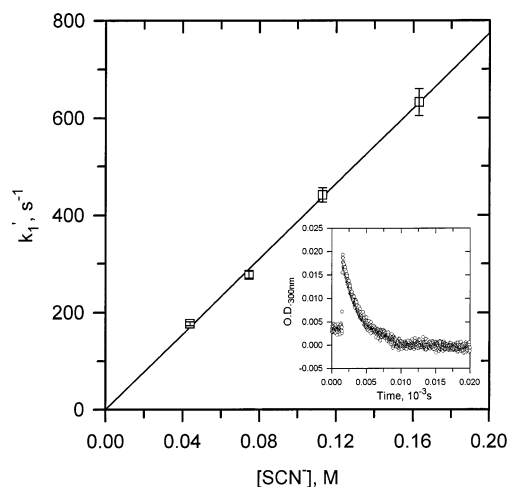


FIGURE 4. Typical plot of pseudo-first-order rate constant (k_1 , s^{-1}) versus $[SCN^-]$ of Fe(V) reaction with thiocyanate in 0.1 M sodium phosphate at pH 10.1 and 22 °C. Inset: The trace recorded at 380 nm is the example of first-order behavior of Fe(V) in reaction of Fe(VI) with thiocyanate.

45 °C) (32) which were previously unknown. The results were fitted to eq 10 ($\sigma = 0.02$ in pK_9).

$$pK_{a,HFeO_4} = 4.247 + 888.5/T \quad (10)$$

This equation gives a ΔH value for the dissociation of $HFeO_4^-$ of $17.0 \pm 0.4 kJ mol^{-1}$.

A $pK_{a,HFeO_4}$ value of 7.33 at 15 °C was used to interpret the kinetic data at different pHs. A plot of the observed second-order rate constant versus α_{HFeO_4} ($\{[H^+]/([H^+] + K_{a,HFeO_4})\}$) was found to be linear (Figure 3). The slope of $\log k$ versus $\log\{[H^+]/([H^+] + K_{HFeO_4})\}$ plot gave a value of 0.88 ± 0.04 which approximates a first-order dependence. This suggests that $HFeO_4^-$ is the reactive species of Fe(VI). The observed rate law may be written as

$$-d[Fe(VI)]/dt = k_{11}\{[H^+]/([H^+] + K_{a,HFeO_4})\}[Fe(VI)][SCN^-] = k_{11}[HFeO_4^-][SCN^-] \quad (11)$$

The slope in Figure 3 gave a value of $k_{11} = 2.06 \pm 0.04 \times 10^3 M^{-1} s^{-1}$ at 15 °C.

The reaction of Fe(VI) with SCN^- was studied as a function of temperature, 5–45 °C at pH 9.20 (Table S1). The plot of $\log k$ versus $1/T$ (K^{-1}) was linear ($r^2 = 0.99$) (Figure S1), and the activation energy was determined to be $32.7 \pm 2.1 kJ mol^{-1}$. The intrinsic activation energy calculated using the ΔH for the dissociation of $HFeO_4^-$ was $15.7 \pm 1.1 kJ mol^{-1}$.

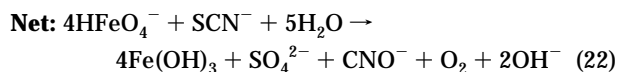
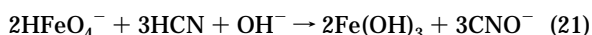
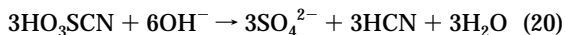
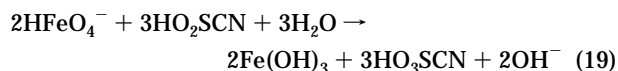
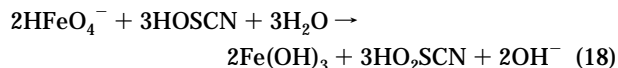
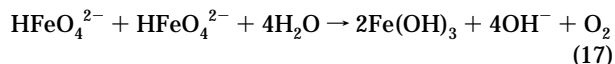
Fe(V) Kinetics. The reaction of Fe(V) with thiocyanate was measured anaerobically under pseudo-first-order conditions with SCN^- in excess. A first-order reaction with respect to Fe(V) was observed (inset Figure 4). A plot of observed first-order rate constants at various concentrations of SCN^- is shown in Figure 4. The linear relationship indicates first-order thiocyanate concentration dependence in the rate law of the reaction of Fe(V) with thiocyanate. The observed rate law can be written as

$$-d[Fe(V)]/dt = k_{12}[Fe(V)][SCN^-] \quad (12)$$

where $k_{12} = 3.63 \pm 0.12 \times 10^3 M^{-1} s^{-1}$ at pH 10.1.

Mechanism. Our stoichiometric and kinetic measurements allow us to propose a mechanism for the oxidation of SCN^- in which the oxygen addition on the sulfur center to the sulfonic acid is followed by a cleavage of the S–C bond

to give sulfate and cyanide. It is postulated that Fe(VI) is reduced to Fe(V) by SCN^- with the formation of a SCN^\bullet radical. The formation of Fe(V) via a one-electron-transfer step has been proposed in oxidations by Fe(VI) (16, 21). Recent EPR work on the reduction of Fe(VI) by substrates indicates the formation of a radical during the reaction (33, 34). A similar step has also been reported in the oxidation of SCN^- by Cr(VI) and Ni(III) in acidic solutions (35, 36).



The SCN^\bullet radical further reacts with SCN^- to form $(\text{SCN})_2^{\bullet-}$ anion radical ($k = 6.9 \pm 0.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; 297 K); reaction 14 (37). High concentrations of SCN^- in our experiments would ensure the occurrence of this reaction. The $(\text{SCN})_2^{\bullet-}$ anion radical further reacts with Fe(VI) to form Fe(V) and thiocyanogen. The rate constant for a reaction of Fe(VI) with sulfur containing thiourea radical was found to be $\approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (18); therefore, eq 15 should be of a similar order of magnitude. The formation of thiocyanogen was not detected spectrophotometrically during the reaction, probably related to its rapid hydrolysis to yield sulfenyl acid (HOSCN) (38, 39) (eq 16). A formation of an intermediate HOSCN has also been proposed in the oxidation of SCN^- by halogen-containing oxidants (38–42). Fe(V) resulting from reactions 13 and 14 can either self-decompose or react with SCN^- . The rate constant for self-decomposition at pH 9.0 is $\approx 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (27, 28) which is approximately 3 orders of magnitude higher than the rate constant for a reaction of Fe(V) with SCN^- . Under the conditions of the experiments, the half-life of the reaction 17 would be much lower than the reaction of Fe(V) with SCN^- . Therefore, a self-decomposition of Fe(V) would occur, producing oxygen as observed in our experiments (eq 17).

The zero oxidation state of sulfur in sulfenyl acid is very labile; therefore, it will be rapidly oxidized by Fe(VI) to sulfinic and sulfonic acid (HO_3SCN) (eqs 18 and 19). The sulfonic acid can hydrolyze to the products, sulfate and cyanide (eq 20) (38). Goff and Murman (43) used ^{18}O -enriched-ferrate tracer in studying oxidation of sulfite (SO_3^{2-}) by Fe(VI) to demonstrate that the oxygen is transferred from Fe(VI) to form sulfate (SO_4^{2-}), a reaction product. This observation was also successfully used to explain the kinetics of the oxidation of sulfite, thiosulfate, and selenite by Fe(VI) (44). Similarly, there is a possibility that a portion of the oxygen in sulfate in our study comes from the direct transfer of oxygen from Fe(VI) to the sulfur center of the molecule such as in reactions 18 and 19.

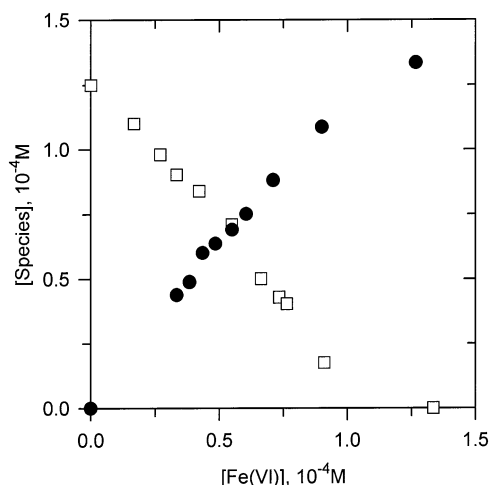


FIGURE 5. A plot of cyanide consumption and cyanate formation versus $[\text{Fe(VI)}]$ under anaerobic conditions at pH 9.0 (initial $[\text{cyanide}] = 125 \times 10^{-6} \text{ M}$; \square — cyanide; \bullet — CNO^-).

The oxidation of cyanide by Fe(VI) was studied separately under anaerobic conditions at pH 9.0. The ratio of Fe(VI) consumed to cyanide was found to be 0.85 ± 0.03 (Figure 5). A similar ratio was found in our earlier work on Fe(VI) oxidation of cyanide under an oxygenated environment. Cyanate and nitrite were the products of the reaction (17). In the present study, cyanate was the only product of the reaction, and the ratio of Fe(VI) to cyanate formation was 0.83 ± 0.03 (Figure 5). A further oxidation of cyanate under oxygenated conditions would have resulted in nitrite in a previous study (17). ^{18}O tracer study of permanganate reaction with cyanide has shown that the oxygen in cyanate comes predominantly from the oxidant (45). It is likely that HFeO_4^- is transferring the oxygen to cyanide forming cyanate in reaction 21. The observed stoichiometry of the reaction of Fe(VI) with cyanide is in reasonable agreement with the stoichiometry of the reaction 21.

The intermediates, Fe(V), SCN^\bullet , $(\text{SCN})_2^{\bullet-}$, $(\text{SCN})_2$, sulfenyl, sulfinic, sulfonic acids, and cyanide are in steady-states and the rate of the disappearance of Fe(VI) in our experiments can be written as

$$-d[\text{Fe(VI)}]/dt = 5k_{13}\{[\text{H}^+]/([\text{H}^+] + K_{a,\text{HFeO}_4})\} [\text{Fe(VI)}][\text{SCN}^-] \quad (23)$$

Equation 23 is similar to the observed rate law (eq 11) where $5k_{13} = k_{11}$. The proposed mechanism therefore suggests that reaction 13 is the rate-determining step. This is further evident from the sulfate and cyanate formation which follows the Fe(VI) to thiocyanate stoichiometry at all Fe(VI) concentrations (Figure 1).

Fe(V) reacts approximately 3 orders of magnitude faster with SCN^- than does Fe(VI) (Table 1; eq 12). This may be related to the radical nature of the Fe(V), evident from the spontaneous decomposition rate of Fe(V), $k_7 \sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (27, 28). Iron in the +5 oxidation state is a more powerful oxidant than the +6 oxidation state. This suggests that the oxidation of SCN^- by Fe(VI) may be enhanced in the presence of appropriate one-electron-reducing agents such as Fe(II) and Cu(I) (46). The radiolysis of water results in the formation of the hydrated electron and conduction band electron is formed in photocatalytic processes (47, 48). The use of the ionizing radiation technique and photocatalytic technique in the presence of Fe(VI) would therefore form Fe(V) and may have synergistic effects in the oxidation of SCN^- in aquatic environment (47, 48).

Acknowledgments

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Supporting Information Available

One table and one figure showing further results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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