

Note

Oxidation of thiocyanate by iron(V) in alkaline medium

Virender K. Sharma^{a,*}, Donald B. O'Connor^b, Diane Cabelli^c

^a Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, FL 32901, USA

^b Department of Chemistry, University of Texas at Austin, Austin, TX 78712, USA

^c Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, NY 11973, USA

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Abstract

The oxidation of thiocyanate by iron(V) (Fe(V)) was studied as a function of pH in alkaline solutions by a premix pulse radiolysis technique. The rates decrease with an increase in pH. The rate law for the oxidation of SCN⁻ by Fe(V) was obtained as $-d[\text{Fe(V)}]/dt = k_{10}\{[\text{H}^+]^2/([\text{H}^+]^2 + K_2[\text{H}^+] + K_2K_3)}[\text{Fe(V)}][\text{SCN}^-]$, where $k_{10} = 5.72 \pm 0.19 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, $\text{p}K_2 = 7.2$, and $\text{p}K_3 = 10.1$. The reaction precedes via a two-electron oxidation, which converts Fe(V) to Fe(III). Thiocyanate reacts approximately $10^3\times$ faster with iron(V) than does with iron(VI).

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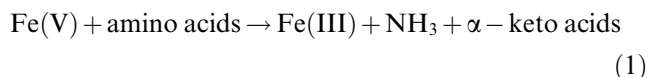
Keywords: Iron(V); Oxidation; Thiocyanate; Pulse radiolysis

1. Introduction

There has been increasing interest in higher oxidation states of iron (Fe(IV), Fe(V), and Fe(VI)) because of their unusual solid-state structures and electronic properties [1–4]. In aqueous solutions, the highly oxidized irons have shown a potential as an alternate for battery cathodes, oxidant for organic synthesis, and an intermediate in Fenton reactions and biological transfer processes [5–8]. Ferryl (Fe^{IV}=O) and perferryl (Fe^V=O) units have been postulated in several iron–dioxygen systems [9]. Recently, structural evidences for the reactive intermediates having an Fe^{IV}=O unit in the activation of dioxygen by nonheme iron enzymes were given [10]. Fe(V) and Fe(IV) are frequently postulated as intermediates in the oxidation of inorganic and organic substrates by Fe(VI) [11–20]. Despite the proposed involvement of these oxidation states of iron in numer-

ous reactions, sporadic information is available on the fundamental properties of Fe(V) and Fe(IV) in the absence of a specialized ligand system (Fe^VO₄³⁻ and Fe^{IV}O₄⁴⁻) in aqueous solution [21,22].

A limited number of studies on the oxidations by Fe(V) in its simple state as an oxyanion (Fe^VO₄³⁻) in aqueous solution have been conducted [23–27]. It has been suggested that Fe(V) oxidizes amino acids and carboxylic acids by a two-electron step (Eq. (1)).



The rates for the oxidation of carboxylic acids by Fe(V) depend on the nature of substituent group at the α -carbon atom of the acids and decrease in the order of $\alpha\text{-C-NH}_2 > \alpha\text{-C-OH} > \alpha\text{-C-H}$ [23–25].

We have used a premix pulse radiolysis technique to study the reaction of Fe(V) with thiourea and cyanide [26,27]. Similar to previous studies on Fe(V), the reaction of Fe(V) and thiourea appear to occur via a concerted two-electron oxidation. However, in studying a reaction of cyanide with Fe(V) in alkaline solution, we

* Corresponding author. Tel.: +1 321 674 7310; fax: +1 321 674 8951.

E-mail address: vsharma@fit.edu (V.K. Sharma).

found for the first time the spectroscopic evidence for sequential one-electron reductions of Fe(V) to Fe(III) by cyanide; Fe(V) is one electron reduced to Fe(IV), which is subsequently one-electron reduced to Fe(III) by cyanide. The results also showed that Fe(V) and Fe(IV) are much more reactive than Fe(VI) ($k(\text{Fe(V)} + \text{cyanide})/k(\text{Fe(VI)} + \text{cyanide}) \approx 10^4$; $k(\text{Fe(IV)} + \text{cyanide})/k(\text{Fe(VI)} + \text{cyanide}) \approx 10^2$).

Recently, we published a very detailed study of the reaction of Fe(VI) with thiocyanate [28], determining the stoichiometry of the overall reduction of Fe(VI) to Fe(III) reaction and showing the effect of pH on the mechanism. In that study we measured the rate constant for Fe(V) reaction with SCN^- at a single pH and showed it was three orders of magnitude faster than that of Fe(VI) with SCN^- . In the present paper, we have investigated the oxidation of thiocyanate (SCN^-) by Fe(V) in alkaline medium as a function of pH using a premix pulse radiolysis technique. The substrate SCN^- was chosen because it is a simple sulfur compound and is of interest in oscillating reactions, catalytic peroxidation by lactoperoxidase and other peroxidases, physiology, and industrial processes [29–32]. Additionally, the results of the present study can be compared with an earlier work on the oxidation of cyanide by Fe(V).

2. Experimental

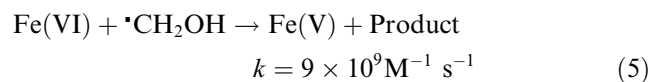
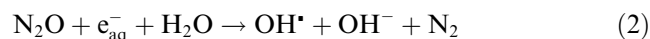
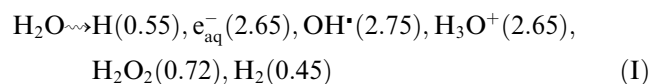
2.1. Materials

All chemicals used (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 M Ω Milli-Q water purification system. Potassium ferrate (K_2FeO_4) of high purity (98% plus) was prepared by the method of Thompson et al. [33]. The Fe(VI) solutions were prepared by addition of solid samples of K_2FeO_4 to 0.005 M $\text{Na}_2\text{HPO}_4/0.001$ M borate, pH 9.0, where solutions are most stable [33]. Phosphate serves as a complexing agent for Fe(III), which otherwise precipitates rapidly as a hydroxide that instantly interferes with the optical monitoring of the reaction and also accelerates the spontaneous decomposition of Fe(VI). A molar absorption coefficient $\epsilon_{510 \text{ nm}} = 1150 \text{ M}^{-1} \text{ cm}^{-1}$ was used for the calculation of $[\text{FeO}_4^{2-}]$ at pH 9.0 [34].

2.2. Fe(V) Kinetics

The reaction of Fe(VI) with thiocyanate occurred so rapidly under our experimental conditions [28] as to necessitate the use of a premix apparatus to study the reaction of Fe(V) with thiocyanate using pulse radiolysis. The premix pulse radiolysis apparatus 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 thiocyanate 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 pathlength) and exposed to the ionizing pulse. Typically, the time between mixing and pulsing was <2 s, sufficiently short for performing experiments. The sequence of reactions, following the electron pulse (Eq. (1)) occurring within a fraction of a microsecond [35,36] that lead to formation of Fe(V) are shown in Eqs. (2)–(5). The number in parentheses in Eq. (1) are *G* values, that is the number of radicals formed per 100 eV of energy dissipated in the aqueous solution. The solutions were saturated with N_2O and contained methanol. The H atoms are converted to hydrated electrons (Eq. (3)), which react with nitrous oxide to form hydroxyl radicals (Eq. (2)). The OH radicals react with methanol to form reducing radicals (Eq. (4)), which in turn reduces Fe(VI) to Fe(V) (Eq. (5)).



2.3. Equipment

A 4 MeV Van de Graff accelerator was used to perform kinetic studies. This produced electron pulses (<500 ns) resulting in irradiation doses of 2–15 gray in the solutions. Details of the accelerator and absorption spectrometer have been reported elsewhere [37]. 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 $\epsilon_{472 \text{ nm}} = (7950 \pm 3\%)$.

3. Results and discussion

Initially, spectral studies of thiocyanate reaction with Fe(V) were performed at pH 10.67. 1.00×10^{-4} M Fe(VI) and 1×10^{-3} M thiocyanate solutions were mixed and pulse irradiated. Kinetic traces and spectra obtained following the pulse are shown in Fig. 1. These spectra manifest the decay of Fe(V) ($\lambda_{\text{max}} = 380$ nm) during the reaction. The characteristic spectrum of

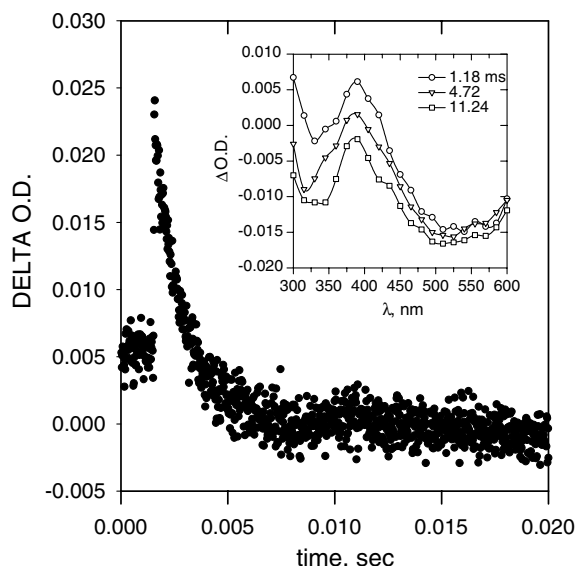
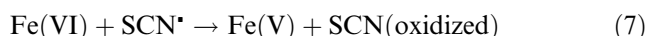
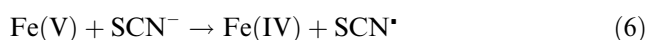


Fig. 1. Kinetic traces and spectra obtained upon pulse radiolysis of solutions (pH 10.67) during Fe(V) oxidation of SCN^- .

Fe(IV) ($\lambda_{\text{max}} = 430 \text{ nm}$) [21] was not observed in the experiments. As discussed in the earlier publication [34], the OD_{∞} of the Fe(V) reaction with thiocyanate was the same as that of Fe(V) spontaneous decay, indicating that reaction between Fe(V) and thiocyanate was stoichiometric and there was no chain decomposition of Fe(VI) arising from the possible free radical intermediates (Eq. (7)). The SCN^{\cdot} could have possibly reduced Fe(VI) to Fe(V) at a faster rate, $k \approx 10^9 \text{ M}^{-1} \text{ s}^{-1}$

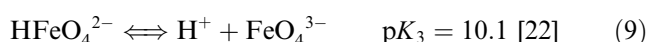
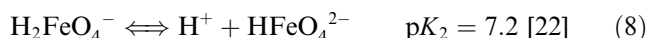


The absence of reaction 6 suggests that the reaction of Fe(V) with thiocyanate proceeds via a concerted two-electron oxidation, which converts Fe(V) to Fe(III).

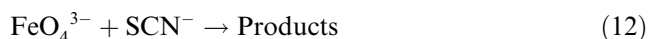
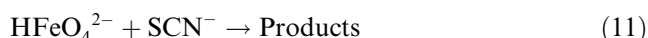
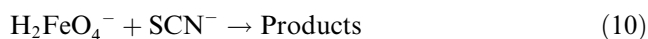
The kinetics of Fe(V) reaction with thiocyanate was studied under pseudo-order conditions with thiocyanate in excess. Reactions were monitored by measuring the absorbance of Fe(V) at 380 nm wavelength as a function of time. The disappearance of Fe(V) occurred by a first-order decay that was also first order in thiocyanate concentration. The second-order rate constants were determined as a function of pH (Table 1). The first-order

decay rates of Fe(V) with methanol at different pH were used to correct rates for reactions of Fe(V) with thiocyanate [26]. The experiments at different pH showed no change in the observed rate law. The spontaneous decay rate of Fe(V) with itself ($2k_{\text{obs}} \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$) was so fast below pH 10.1 that it contributes significantly to the studied reaction, therefore, rates were limited to $\text{pH} \geq 10.1$.

The rate of the reaction increases with a decrease in pH (Table 1). The protonation of thiocyanate does not occur in the pH range studied ($\text{p}K = -1.28 \pm 0.03$ [38]), therefore, the dependence is related to protonations of Fe(V) (Eqs. (8) and (9))



The three forms of Fe(V) react with thiocyanate (Eqs. (10)–(12)).



The rate of disappearance of Fe(V) can be given by

$$-\text{d}[\text{Fe(V)}]/\text{d}t = k_{10}[\text{H}_2\text{FeO}_4^-][\text{SCN}^-] + k_{11}[\text{HFeO}_4^{2-}][\text{SCN}^-] + k_{12}[\text{FeO}_4^{3-}][\text{SCN}^-] \quad (13)$$

The substitutions of equilibria of Fe(V) (Eqs. (8) and (9)) gives the following equation:

$$-\text{d}[\text{Fe(V)}]/\text{d}t = \{(k_{10}[\text{H}^+]^2 + k_{11}K_2[\text{H}^+] + k_{12}K_2K_3)/Z\}[\text{Fe(V)}][\text{SCN}^-], \quad (14)$$

$$\text{where } Z = [\text{H}^+]^2 + K_2[\text{H}^+] + K_2K_3$$

The empirical fit of the observed second-order rate constants suggest that second and third terms of Eq. (14) are not needed to fit the data. This is supported by a plot of second-order rate constants with respect to HFeO_4^{2-} i.e. $\{[\text{H}^+]/([\text{H}^+] + K_3)\}$, which was found non-linear (inset Fig. 2). The rate constants can be explained by considering H_2FeO_4^- is the only reactive species of Fe(V). Moreover, a plot of the observed second-order rate constants versus $\{[\text{H}^+]^2/([\text{H}^+]^2 + K_2[\text{H}^+] + K_2K_3)\}$ was also found to be linear (Fig. 2). This further suggests rates are dependent on concentration of H_2FeO_4^- in the reaction solution. The observed rate law may be written as

$$-\text{d}[\text{Fe(V)}]/\text{d}t = k_{10}\{[\text{H}^+]^2/([\text{H}^+]^2 + K_2[\text{H}^+] + K_2K_3)\}[\text{Fe(V)}][\text{SCN}^-] \quad (15)$$

The slope in Fig. 2 gave a value of $k_{10} = 5.7 \pm 0.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Table 1
Oxidation of thiocyanate by Fe(V) at different pH values at 22 °C

pH	$k \text{ (M}^{-1} \text{ s}^{-1}\text{)}$
10.10	3630 ± 121
10.46	1162 ± 43.3
10.67	513 ± 10.8
10.95	104 ± 2.14
11.20	63.7 ± 1.29

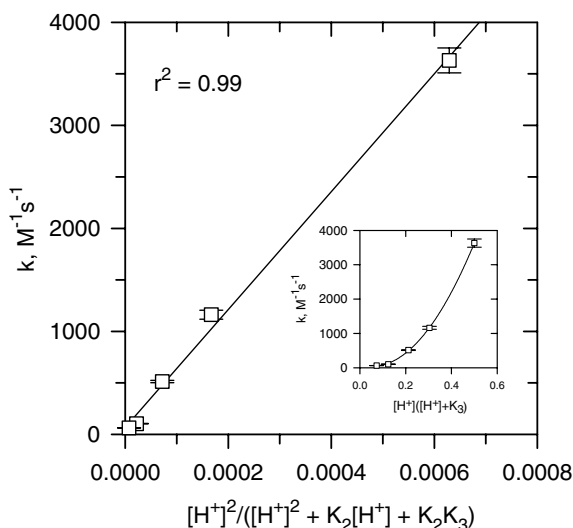


Fig. 2. Hydrogen ion dependence on the rate of Fe(V) oxidation of thiocyanate in 0.1 M sodium phosphate at 22 °C.

A comparison of the reactivity of Fe(V) and Fe(VI) with thiocyanate is shown in Fig. 3. Fig. 3 also gives comparison of rate constants for oxidations of thiocyanate and cyanide by Fe(V) and Fe(VI). Fe(V) is approx-

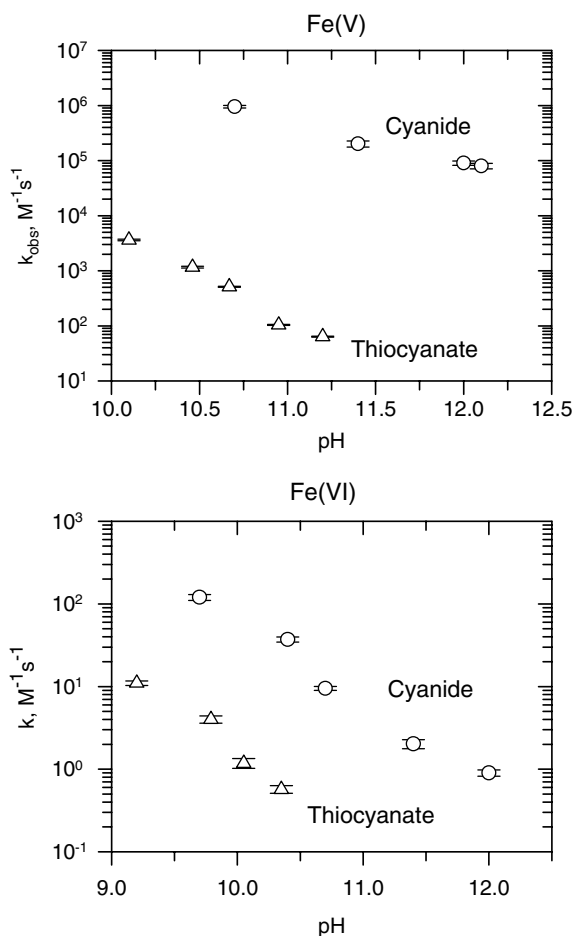


Fig. 3. Oxidation of thiocyanate and cyanide by Fe(VI) and Fe(V).

imately three orders of magnitude more reactive than Fe(VI). The bimolecular decomposition rates of Fe(V), $k \approx 10^7 \text{ M}^{-1} \text{ s}^{-1}$, suggest the radical nature of Fe(V) species [22]. This radical character of Fe(V) ($\text{Fe}^{\text{V}} = \text{O} \leftrightarrow \text{Fe}^{\text{IV}}-\text{O}^\bullet$) may be responsible for higher reactivity of Fe(V).

The oxidations of thiocyanate and cyanide by higher oxidation states of iron occur faster at a lower pH (Fig. 3). Recent spin density calculations suggested that the protonated Fe(VI) species (HFeO_4^-) has a larger spin density on the oxo ligands than the deprotonated (FeO_4^{2-}) species [39]. This would result in higher oxidation power of protonated Fe(VI) and thus higher reactivity at a lower pH.

The rates for reactivity of Fe(VI) and Fe(V) with thiocyanate are lower than those of cyanide (Fig. 3). Cyanide has two species ($\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$; $\text{p}K = 9.3$ [40]) in the pH range of this study. The protonated cyanide (HCN) would decrease the electrorepulsion between negatively charged Fe(VI) and Fe(V) species (e.g. Eq. (8)) and contributes to higher reactivity of cyanide. Moreover, activation energy for the oxidation of cyanide by Fe(VI), $\Delta E^\ddagger = 38.9 \pm 1.0 \text{ kJ mol}^{-1}$ was found to be higher than $\Delta E^\ddagger = 32.7 \pm 2.1 \text{ kJ mol}^{-1}$ for thiocyanate [34,41]. Less favorable activation energies of the reactions may also contribute to the slower rates for the oxidation of SCN^- .

4. Conclusions

The rate law for the reaction of Fe(V) with thiocyanate showed a first-order dependence on Fe(V) and SCN^- . Reduction of Fe(V) to Fe(III) by SCN^- proceeds by a two-electron process. The reactivity of diprotonated Fe(V) species, H_2FeO_4^- with thiocyanate could account for the increase in rate with decreasing pH. Fe(V) reacts approximately three orders of magnitude faster with thiocyanate than does Fe(VI). The observed rates for oxidation of thiocyanate by Fe(V) are lower than that of cyanide reaction with Fe(V).

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