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Ferrates: Synthesis, Properties and Applications in Water and Wastewater Treatment

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AQUEOUS HIGH OXIDATION STATE IRON: GENERATION AND REACTIVITY

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The higher oxidation states of iron (Fe(VI) and Fe(V) in particular) have been shown to be strongly oxidizing in enzymatic systems, where they can carry out aliphatic hydrogen abstraction. In addition, they have been postulated as intermediates in Fenton-type systems.[1] Fe(VI) itself is relatively stable and has been shown to have potential as an oxidant in the so-called "green" treatment of polluted waters. By contrast, Fe(V) is a relatively short-lived transient when produced in aqueous solution in the absence of strongly bonding ligands other than hydroxide, a feature that has limited studies of its reactivity. Fe(VI) has been proposed to be useful in battery design[2] and a very interesting study suggested that ferrate may be able to oxidize insoluble chromium to chromate and thus serve to remove chromium contamination in the Hanford radioactive waste tanks.[3]

We have been interested in the study of the reactivity of high valent aquo iron states with inorganic substrates in order to look at the degradation of pollutants in water. Fe(V) can be generated very easily in the presence of excess Fe(VI) through the use of reducing radicals generated in pulse radiolysis according to the following scheme:

$$H_2O \text{ -\textbackslash/\textbackslash/\textbackslash}\rightarrow \ H(0.55),\ e_{aq}^-(2.65),\ OH(2.75),\ H_2O_2(0.72),\ H_2(0.45)$$

$$e_{aq}^- + Fe(VI) \rightarrow Fe(V) \qquad (1)$$

$$H + OH^- \rightarrow e_{aq}^- + H_2O \qquad (2)$$

$$OH/O^- + ROH \rightarrow H_2O/OH^- + {}^{\cdot}ROH \qquad (3)$$

$Fe(VI) + {}^{\cdot}ROH \rightarrow Fe(V) + Product$ (4) $k_4 = 9 \times 10^9\ M^{-1}s^{-1}$

In the course of studying Fe(V) reactivity with a substrate, the intrinsic reactivity of Fe(VI) with the substrate (or the alcohol used to generate the alcohol radical that reduces Fe(VI) to Fe(V); reaction 4) presents a complication. This can be limited through the use of a premix device. The premix pulse radiolysis apparatus consists of two glass syringes mounted in a double syringe drive. The Fe(VI) solution in one syringe is mixed with the alcohol and substrate solution in the other syringe. The mixed solution is promptly injected into the optical cell and exposed to an ionizing pulse.

In Figure 1 we show the visible spectral features of Fe(VI) and Fe(V). By using a fast premixing apparatus synchronized with the accelerator pulse, experiments can be carried out to measure the reactivity of Fe(V) with a substrate. Alternately, if the concentration of the substrate is increased such that the substrate now reacts with the OH radical, then the reaction between Fe(VI) and an oxidized substrate radical can be measured (reactions 5 and 6). Finally, conditions can be adjusted by eliminating the addition of alcohol. Here, the electron reduces the Fe(VI) to Fe(V) and the substrate is oxidized by the OH radical (reactions 2 and 5), leading to the reaction between Fe(V) and a radical substrate.

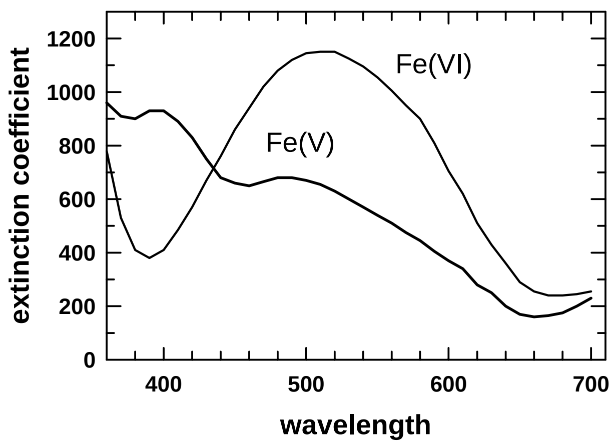

Figure 1: Visible spectra of Fe(V) and Fe(VI) in aqueous basic solution.

$S + {}^{\cdot}OH \rightarrow S_{ox} + H_2O/OH^-$ (5)

$Fe(VI) + S_{ox} \rightarrow Fe(V) + P$ (6)

$Fe(V) + S_{ox} \rightarrow Products$ (7)

Here, we discuss the basic chemistry of ferrate(V) and highlight its reactivity with cyanide, thiocyanate, copper cyanide, bisulfite and thiosulfate. This allows a discussion of one-electron versus two-electron processes and shows some of the kinetic parameters in the use of high oxidation state iron as an oxidant for inorganic pollutants.

Thiocyanate (SCN-) is used in processes such as the manufacture of thiourea, metal separation and electroplating as well as being formed in mining wastewater. Ferrate(V) reacts with thiocyanate via a two-electron pathway[4] with no observable Fe(IV) formation. As has been seen generally, the reaction of Fe(V) with SCN^- is significantly more rapid than that of Fe(VI) with SCN^-; with a rate constant that is over two orders of magnitude faster.[4]

Cyanide is also a polluting byproduct of the mining industry and so the reactivity of high oxidation state iron with cyanide is also of great interest. The experiments on the reduction of Fe(V) by cyanide demonstrate sequential one-electron reductions of Fe(V) to Fe(IV) to Fe(III) in aqueous media, where the order of reactivity is k(Fe(V)) > k(Fe(IV)) > k(Fe(VI)).[5] That the Fe(V) reaction is faster than the FeIV) reaction with CN^- lends support to the two-electron pathway observation with SCN^- and further suggests that ferrate(VI) oxidations may be accelerated in the presence of one-electron or two-electron reducing substrates, where the reactive high valent iron species is either Fe(V) or Fe(IV).

Metal cyanide complexes are also found in mine tailings and the reactivity of copper cyanide and zinc cyanide complexes with high valent iron species will also be addressed.[6] Here, the effect of the metal on reactivity is of primary interest and the results will be contrasted with earlier studies on cyanide alone.

Finally, we have begun examining Fe(V) reactivity with sulfite (SO_3^{2-}) and thiosulfate ($S_2O_3^{2-}$). In both systems, a 2-electron pathway to Fe(III) was observed. The reactions of Fe(VI) with the two sulfur radicals were both ca 10^8 $M^{-1}s^{-1}$. However, the reaction of Fe(V) with the two different ions were separated by an over an order of magnitude, with SO_3^{2-} reacting at $4x10^4$ $M^{-1}s^{-1}$ while $S_2O_3^{2-}$ reacted with Fe(V) at $1.8x10^3$ $M^{-1}sec^{-1}$.

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