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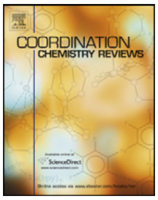

Review

Ferrate(VI) and ferrate(V) oxidation of organic compounds: Kinetics and mechanism

Virender K. Sharma*

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

Contents

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ABSTRACT

This review presents a critical assessment of the kinetics and mechanisms of the oxidation of organic compounds, X (organosulfur compounds, amines, phenols, alcohols, hydrocarbons, ascorbate, and pharmaceuticals) by ferrate(VI) ($Fe^{VI}O_4{}^{2-}$) and ferrate(V) ($Fe^{V}O_4{}^{3-}$). The rate constants (k_{app}, $M^{-1}\,s^{-1}$) of reactions of these compounds with ferrate(VI) and ferrate(V) usually decrease with increase in pH in alkaline media and the species-specific rate constants were evaluated from pH-dependent kinetics. The rate constants for the reactions of $HFe^{VI}O_4{}^{-}$ and $HFe^{V}O_4{}^{2-}$ with X were correlated with $1-e^-$ and $2-e^-$ reduction potentials in order to understand the mechanisms of the reactions. Ferrate(V) generally oxidizes compounds by a $2-e^-$ transfer step. The reactions of ferrate(VI) with compounds may be characterized most commonly by (i) a $1-e^-$ transfer step from Fe(VI) to Fe(V), followed by a $2-e^-$ transfer to Fe(III) as the reduced product ($Fe^{VI} \rightarrow Fe^{V} \rightarrow Fe^{III}$), and (ii) $2-e^-$ transfer steps ($Fe^{VI} \rightarrow Fe^{IV} \rightarrow Fe^{II}$). Oxygen-atom transfer to the compounds may occur through involvement of either ferrate(VI) or ferrate(V) in the oxidations carried out by ferrate(VI). Hammett-type relationships of reactions provided additional information on intermediates involved in oxidation processes and proposed mechanisms are consistent with the oxidized products of the reactions. Oxidation of biological species by ferrate(VI) is also briefly presented.

1. Introduction

High-valent iron-oxo species have been involved in numerous chemical, biological, and environmental reactions [1–10]. For example, high-valent iron-oxo complexes of heme and non-heme iron ligands have been suggested as the active oxidants in

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* Tel.: +1 321 674 7310; fax: +1 321 674 8951.
E-mail address: vsharma@fit.edu

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biological oxidation reactions [8,11–22]. The oxidation states of iron centers and the structures of ligands determine the reactivities of high-valent iron complexes [1,2,5,8,21,23–28]. Numerous oxo-iron(IV) model complexes exhibiting intermediate S = 1 spin states have been prepared in the last decade to further the understanding of the reaction mechanisms of the catalytic cycles of many non-heme enzymes [8,29,30]. Similar studies on S = 2 spin state iron(IV) complexes are also progressing [8,23,31,32]. Recent work on oxo-iron(IV) complexes has shown that reactivity was also affected by the binding of inactive metal ions at the iron-oxo centers [33–35]. The role of oxo-iron(V) in the oxidation of organic molecules has also been explored by studying mixtures of iron complexes and H_2O_2 [36–39]. In the tetraamido macro ligand (TAML) environment, oxo complexes of iron(IV) and iron(V) have been generated and characterized [40–44]. More recently, variable-temperature mass spectrometry (VT-MS) was utilized to demonstrate the formation of an oxo-iron(V) complex in the Fe(II) complex-H_2O_2 system [45]. In addition to studies of high-valent iron-oxo complexes, high-valent iron-nitrido-complexes have also been generated and characterized [46–48]. Studies of these complexes may increase our understanding of the role of high-valent iron species in the chemistry of enzymes. For example, the Fe(V)-nitrido complex produces ammonia in reaction with water under reducing conditions, which may have implications for the chemistry of nitrogenase [47].

In the past decade, there has been an increasing interest in tetraoxy high-valent iron anions, commonly called ferrates (e.g. ferrate(VI), $Fe^{VI}O_4{}^{2-}$ and ferrate(V), $Fe^{V}O_4{}^{3-}$) in aqueous solution due to their importance in high energy density rechargeable batteries, in cleaner ("greener") technology for organic syntheses, in environmentally friendly water and wastewater treatment processes [49–56,56–72]. Ferrate(V) has also been used as the perferryl model to study the chemistry of ferryl species with different organic substrates [73–75]. Knowledge of ferrate redox chemistry is still progressing and increasing our understanding of electron-transfer and oxygen-transfer mechanisms [76,77]. This review summarizes the current knowledge on the oxidation of organic compounds by ferrate(VI) and ferrate(V) in aqueous solution. Initially, synthesis and characterization of ferrate(VI) and ferrate(V) are briefly presented, followed by a summary of the current knowledge on their oxidation reactions with various organic molecules in aqueous systems.

2. Synthesis and characterization

A number of alkali and alkaline earth salts of ferrate(VI) are known with the molecular formula M_2FeO_4 (M = Li, Na, K, Rb, Cs, and Ag) and $M'FeO_4$ (M′ = Ca, Ba, and Sr) [78–82]. Wet chemical, electrochemical, and dry thermal synthetic methods have been applied to prepare salts of ferrate(VI) [78,81,83,84]. In the wet chemical methods, a sodium salt of ferrate(VI) (Na_2FeO_4) is prepared by oxidizing Fe(III) with either hypochlorite or ozone under highly alkaline conditions [52,85,86]. The purity of ferrate(VI) in salts is determined by volumetric and electrochemical titration as well as by spectrophotometric methods [87–94]. The K_2FeO_4 thus produced is stable for long periods of time if it is stored under dry conditions [95,96]. However, it decomposes slowly to amorphous iron(III) hydroxide nanoparticles when exposed to moisture; the rate of decomposition depends on the humidity [95]. Because of the relatively high stability of K_2FeO_4, it has been used to prepare other salts of ferrate(VI) [81,97–101]. The electrochemical synthesis of ferrate(VI) involves the anodic oxidation of iron under strong alkaline conditions (NaOH, KOH, and a mixture of NaOH and KOH) [83,102–105]. In recent years, platinum- and boron-doped diamond electrodes have been used to oxidize iron species in alkaline solution to generate ferrate(VI) [105–109]. Ferrate(VI) also forms in the direct anodic oxidation of an iron electrode as well as by the use of an inert anode to oxidize iron species already present in the molten electrolyte [110–112].

In thermal techniques, a mixture of salts of iron and sodium (or potassium) oxides is heated to more than 400 °C to obtain salts of ferrate(VI) [78]. Intermediates (ferrate(V) and ferrate(IV)) were obtained in the synthesis of ferrate(VI) [79,80,113,114]. The decomposition of ferrate(VI) at high temperature also plays a role in the ultimate yield of the salt of ferrate(VI) by thermal synthesis [115–117]. The identification of the valence state of iron was carried out using Mössbauer spectroscopy [78–80,118–120], where isomer shift values of ferrates decreased linearly with increase in the oxidation state of iron (OS) in ferrates and are expressed by Eq. (1) [120].

$$\delta(\mathrm{mm\ s^{-1}}) = 1.084\text{–}0.326 \times \mathrm{OS} \tag{1}$$

The isomer shifts of different salts of ferrate(VI) vary very little (−0.87 to −0.91 mm/s) indicating a weak influence of the counter ions on iron bound in the oxygen tetrahedron, which is the main structural unit of all ferrates(VI). In recent years, values of the hyperfine parameters of K_2FeO_4 at very low temperatures (1.5–5 K) with and without an external magnetic field, suggest magnetic ordering at around 3.8 K [97]. The hyperfine magnetic field was found to increase from 10.6 to 13.7 T upon a decrease in temperature from 3.5 to 1.5 K [97].

Solid salts of ferrate(VI) have also been characterized by Fourier transform infrared (FTIR) spectra, which characteristically display an absorption band at ~800 cm^{-1} in the infrared region with triplet splitting [89,98,98,99,101,121,122]. A single crystal electron paramagnetic resonance (EPR) spectrum of K_2FeO_4 exhibited a marked change in *g* values with temperature variation from 2.14 at 20 K to 2.00 at 193 K. A significant difference between the absorption obtained from K_2FeO_4 and $BaFeO_4$ was observed [123]. The powder and single crystal EPR spectra of Fe(VI) in the host structures K_2MO_4 (M = Cr, S, Se) revealed the zero-field splitting parameters ($g = 1.99$) as $D = 0.10$ cm^{-1} and $E = 0.01$ cm^{-1} [123,124].

The synthesis of solid potassium ferrate(V) (K_3FeO_4) was first demonstrated by heating a mixture of KO_x and Fe_2O_3 at 750–780 °C [125,126]. Later, crystals of K_3FeO_4 were prepared by heating well ground mixtures of K_2O_2 and $KFeO_2$ (1.78:1.00, Ag-tube) for several days at 350–470 °C [127]. The oxidation of Na_3FeO_3 by oxygen yielded the sodium salt of ferrate(V). Crystals of K_3FeO_4 were orthorhombic. Isolated crystals of salts of ferrate(VI) in the form of $FeO_4{}^{2-}$ were also of space group *Pnma* with four molecules in the orthorhombic unit cell [100]. However, an organic salt of $FeO_4{}^{2-}$, $[N(CH_3)_4]_2FeO_4$, crystallized tetragonally [128]. The XANES spectra of ferrate(VI) have also been determined and a characteristic pre-edge feature of tetrahedrally coordinated ferrate(VI) was observed [128]. Recently, time-dependent DFT methodology was used to predict Fe K-pre-edge of high-valent iron species [129].

In solution, ferrate(V) has been generated by the reduction of ferrate(VI) by organic radicals ($^{\bullet}$ROH, where ROH = methanol, ethanol, isopropanol or *tert*-butanol) with diffusion-controlled rate constants [130–133]. The reactions, which occur in pulse radiolysis, can be expressed by the following scheme:

$$H_2O - /\backslash/\backslash/\backslash$$

$$\rightarrow H(0.55),\ e_{aq}{}^{-}(2.65),\ OH(2.75),\ H_2O_2(0.72),\ H_2(0.45) \qquad \mathrm{I}$$

$$N_2O + e_{aq}{}^{-} + H_2O \rightarrow OH + OH^{-} + N_2 \tag{2}$$

$$H + OH^{-} \rightarrow e_{aq}{}^{-} + H_2O \tag{3}$$

$$OH/O^{-} + ROH \rightarrow H_2O/OH^{-} + {}^{\bullet} \tag{4}$$

$$Fe(VI) + {}^{\bullet}ROH \rightarrow Fe(V) + Product \tag{5}$$