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STUDIES OF HYPERVALENT IRON

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The iron(IV), (V) and (VI) oxidation states are of great interest because of their role in catalytic oxidation/hydroxylation reactions. This report summarizes the information currently available on the kinetic and chemical properties of the water-soluble ions of FeO_4^{2-}, FeO_4^{3-} and FeO_4^{4-}, their protonated forms, and/or simple complex derivatives. The discussion includes their radiation-induced formation, decay kinetics, reactivity with other compounds, determination of their respective pK_a values as well as spectral properties.

KEY WORDS: Ferrate(IV), ferrate(V), ferrate(VI), ferryl, perferryl, pK_a values, spectra, kinetics, review.

INTRODUCTION

Interest in the ferryl (Fe(IV); Fe $= O^{2+}$) and perferryl (Fe(V); Fe $= O^{3+}$) species is of long standing since these oxidation states constitute the catalytically active states of iron in numerous biological and industrial processes. The Fe(IV)/Fe(V) moieties, whether as components of complex enzymatic active sites or simple iron complexes, can be very powerful, often stereospecific, hydroxylating agents and oxidants capable of aliphatic H abstraction and/or C–C bond scission.[1-11] While there has been great progress in identifying and characterizing the ferryl/perferryl oxidation states in numerous enzymes and in iron complexes soluble in organic solvents, little is known about simple hypervalent iron complexes in aqueous solutions.[12,13]

In nonbiological systems, formation of ferryl ions rather than hydroxyl radicals has been postulated to explain a high specificity of Fenton-type reactions (Fe(II)EDTA + H_2O_2 or O_2) carried out in neutral/alkaline aqueous solutions or in organic/aprotic solvents.[6,14-18] In some biological studies, similar conclusions were reached when addition of catalase, SOD and OH radical scavengers did not effectively suppress the damage observed in in vitro experiments involving iron complexes exposed to O_2^-.[19-20] If ferryl/perferryl iron species are indeed formed under such conditions and are the cause of biological damage, numerous pathways/mechanisms of attack can be envisioned; e.g. 1) As relatively small complexes they can diffuse to sensitive target sites; 2) as components of larger molecules they may generate new potent organic radicals that may diffuse to sensitive targets and/or induce deleterious chain reactions; 3) the iron may already be complexed to the target site where it undergoes oxidation to a hypervalent state(s) that cause the damage, etc.[20-22] This review is a short summary of what is currently known about the aqueous chemistry of the Fe(VI), Fe(V) and Fe(IV) oxy-anions and related simple complexes.

Ferrate(VI)

K_2FeO_4 of relatively high purity (98.6%) is conveniently synthesized by oxidizing $Fe(NO_3)_3$ with hypochlorite in 5–10 N KOH.[23] Crystalline K_2FeO_4 consists of tetrahedral oxyanion units (FeO_4^{2-}) which maintain their structural integrity when dissolved in aqueous solutions. The Fe–O bonds are apparently all equivalent and have a high degree of covalent character.[24]

Solutions of K_2FeO_4 are purple and are stable for several hours above pH 8–9. Experiments are conveniently carried out in the presence of phosphate, which complexes ferric iron, thus preventing the formation of ferric hydroxides which interfere with optical measurements and accelerate the decomposition of ferrate(VI). At pH $\geqslant$ 9 and 25°C the absorption spectrum of FeO_4^{2-} has a peak at 512 nm with a molar absorbance $\varepsilon = 1150\,M^{-1}cm^{-1}$ (Figure 1).[25,26] Upon protonation, the band undergoes a blue shift and a decrease in absorbance ($\lambda_{max} = 488$ nm; $\varepsilon_{488\,nm} = 480\,M^{-1}cm^{-1}$). These results are in good agreement with an earlier assignment of molar absorptivities at 505 nm: $\varepsilon(H_2FeO_4) = 30\,M^{-1}cm^{-1}$, $\varepsilon(HFeO_4^-) = 450\,M^{-1}cm^{-1}$ and $\varepsilon(FeO_4^{2-}) = 1030\,M^{-1}cm^{-1}$.[27] The UV spectrum (not shown) has a shoulder between 310 and 270 nm with an $\varepsilon(FeO_4^{2-}) \approx 280\,M^{-1}cm^{-1}$. Below 270 nm the absorbance increases continuously and reaches an $\varepsilon \approx 16{,}250\,M^{-1}cm^{-1}$ at 210 nm.[25]

The spontaneous decomposition of ferrate(VI) in water is accompanied by oxygen evolution.[27,28] In alkaline solutions over half of the O_2 is generated from the FeO_4^{2-} anion while in 1 M acid essentially 100% comes from H_2O.[28] earlier studies of ferrate(VI) decomposition have shown that the overall process is acid catalyzed and proceeds by mixed first- and second-order decay kinetics that involve the various protonated forms of FeO_4^{2-}:[27]

$$H_2FeO_4 \rightleftharpoons H^+ + HFeO_4^- \qquad pK_1 = 3.5 \qquad (1, -1)$$

$$HFeO_4^- \rightleftharpoons H^+ + FeO_4^{2-} \qquad pK_2 = 7.8 \qquad (2, -2)$$

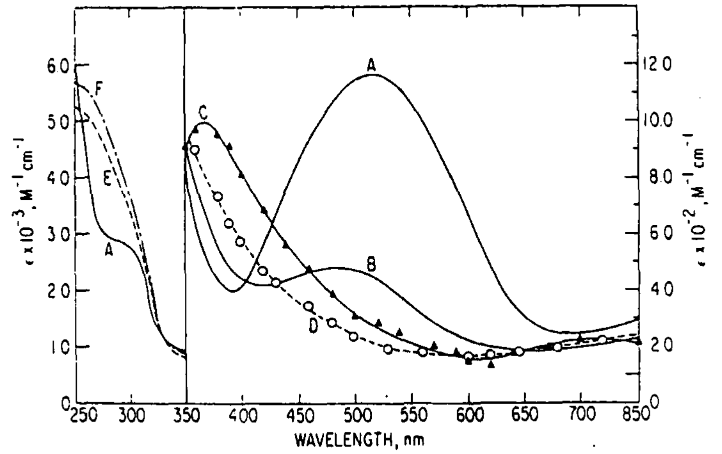

FIGURE 1 UV and Visible absorption spectra of Fe(V) and Fe(VI) anions in 0.1 M phosphate at 25°C; ref.[26].
(A) FeO_4^{2-}, pH $\geqslant$ 9.0;
(B) $HFeO_4^-$, pH = 6.3;
(C) $HFeO_4^{2-}$, pH = 9.0 (▲);
(D) $H_2FeO_4^-$, pH = 6.3 (○);
(E) $HFeO_4^{2-}$, pH = 9.0 (----) UV range; (F) FeO_4^{3-}, pH = 11.2 (— — —) UV range.

The observed decomposition rates increase by 6–7 orders of magnitude when the pH is decreased from 9 to 2.5. Depending upon the pH and experimental conditions, the end products of these reactions are either Fe(III)/Fe(II) ions/complexes or various iron hydroxides.

That the ferrate(VI) species are strong oxidizing agents is apparent from the reduction potentials of the FeO_4^{2-}/Fe^{3+} couples, which are, in acid and alkaline solutions,[29]

$$FeO_4^{2-} + 8H^+ + 3e^- \longrightarrow Fe^{3+} + 4H_2O \qquad E^0 = +2.20\,V \qquad (3)$$

$$FeO_4^{2-} + 4H_2O + 3e^- \longrightarrow Fe(OH)_3 + 5OH^- \qquad E^0 = +0.72\,V \qquad (4)$$

A selection of rate constants, that illustrate the reactivity of FeO_4^{2-} with various organic compounds, is given in Table I.

Ferrate(V)

Ferrate(V) is conveniently generated from ferrate(VI) by reduction with either the hydrated electron or select organic radicals:[26,30]

$$Fe^{VI} + e^-_{aq} \longrightarrow Fe^{V} \qquad k = 2.0 \times 10^{10}\,M^{-1}s^{-1} \qquad (5)$$

$$Fe^{VI} + CO_2^- \longrightarrow Fe^{V} + CO_2 \qquad k = 3.5 \times 10^{8}\,M^{-1}s^{-1} \qquad (6)$$

$$Fe^{VI} + (CH_3)_2\dot{C}OH \longrightarrow Fe^{V} + (CH_3)_2CO \qquad k = 3.0 \times 10^{9}\,M^{-1}s^{-1} \qquad (7)$$

$$Fe^{VI} + CH_3\dot{C}HOH \longrightarrow Fe^{V} + CH_3CHO \qquad k = 8.0 \times 10^{9}\,M^{-1}s^{-1} \qquad (8)$$

As the precursors of the above organic radicals react relatively slow with ferrate(VI), (See Table I), pulse radiolysis studies above pH 8 are feasible *in situ*. Studies in more acidic solutions, where Fe(VI) becomes unstable, are feasible if stable ferrate(VI) solutions are rapidly premixed with appropriate buffers before they are pulse irradiated. A premixing apparatus with a dead time of 5–7 seconds is sufficient to work at pH ⩾ 6.

The absorption spectra of FeO_4^{3-} and its various protonated forms are shown in

TABLE I
Rate constants for reactions of FeO_4^{2-} with some organic compounds and several free radicals in phosphate/borate buffers, (0.1–0.2 M), at 25°C.

Compound	pH	k, $M^{-1}s^{-1}$	Ref.
DPTA	10.5	8.53×10^{-4}	25
ethanol	10.5	1.47×10^{-3}	25
2-propanol	10.4	6.00×10^{-2}	26
formate	10.5	2.33×10^{-2}	25
NADH	11.0	7.70×10^{1}	25
phenol	9.0	8.00×10^{1}	32
glycine	8.0	1.00×10^{2}	27
O_2^-	10.5	5.70×10^{3}	25
p-hydroquinone	9.0	2.00×10^{5}	32
ascorbic acid	10.0	1.30×10^{6}	32
CO_2^-	10.0	3.50×10^{8}	25
$(CH_3)_3COH$	10.4	3.00×10^{9}	26
CH_3CHOH	10.4	8.00×10^{9}	26

Figure 1. While the visible spectrum of FeO_4^{3-} ($\lambda_{max} = 368$ nm; $\varepsilon_{368\,nm} = 990\,M^{-1}cm^{-1}$) is virtually indistinguishable from the spectrum of the monoprotonated derivative $HFeO_4^{2-}$, the UV spectrum shows definite absorbance differences e.g. $\varepsilon_{270\,nm} = 5{,}300\,M^{-1}cm^{-1}$ for FeO_4^{3-} while $\varepsilon_{270\,nm} = 4700\,M^{-1}cm^{-1}$ for $HFeO_4^{2-}$. Further protonation, that is, formation of $H_2FeO_4^-$, causes the band to blue shift with a concomitant decrease in absorbance; compare C and D in Figure 1.[26]

The changes in absorbance and in the kinetic decay rates with pH were used to determine the corresponding equilibria between the different ferrate(V) forms:

$$H_3FeO_4 \rightleftharpoons H_2FeO_4^- + H^+ \qquad pK_1 = ? \qquad (9, -9)$$

$$H_2FeO_4^- \rightleftharpoons HFeO_4^{2-} + H^+ \qquad pK_2 = 7.5 \qquad (10, -10)$$

$$HFeO_4^{2-} \rightleftharpoons FeO_4^{3-} + H^+ \qquad pK_3 = 10.1 \qquad (11, -11)$$

The pK_1 could not be determined in these experiments because of an inadequate dead time of the premixer. Depending upon the pH the ferrate(V) species decay, by first- and/or second-order order kinetics:

$$-d[Fe(V)]/dt = 2k_{obs}[Fe(V)]^2 + k_f[Fe(V)] \qquad (I)$$

While first-order kinetics dominate in alkaline solutions, the second-order reactions become rate controlling at pH $\leqslant$ 11. The decay of ferrate(V) as a function of pH is illustrated in Figure 2. The solid line was calculated using the corresponding K_2, K_3, k_1-k_4 and equation (II):

$$k_1(H_2FeO_4^- + H_2FeO_4^-) = 9.0 \times 10^7\,M^{-1}s^{-1}$$

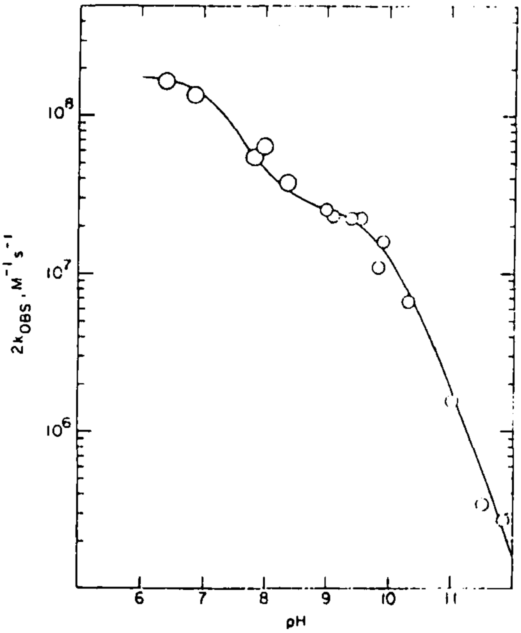

FIGURE 2 k_{obs} as a function of pH for the bimolecular decay of ferrate(V) in 1 mM phosphate/borate buffer at 25°C.[26] For computation of the solid line see text.

$$
\begin{aligned}
k_2(H_2FeO_4^- + HFeO_4^{2-}) &\approx 3.0 \times 10^7\,M^{-1}s^{-1} \\
k_3(HFeO_4^{2-} + HFeO_4^{2-}) &\approx 1.5 \times 10^7\,M^{-1}s^{-1} \\
k_4(HFeO_4^{2-} + FeO_4^{3-}) &= 1.0 \times 10^7\,M^{-1}s^{-1} \\
k_{obs}\cdot[Fe^V]^2 &= k_1[H_2FeO_4^-]^2 + k_2[H_2FeO_4^-][HFeO_4^{2-}] \\
&\quad + k_3[HFeO_4^{2-}]^2 + k_4[HFeO_4^{2-}][FeO_4^{3-}] \qquad \text{(II)}
\end{aligned}
$$

The studies show that the Fe(V) ions decay first to a longer lived transient ($t_{1/2}$ = seconds) which has, at pH $\geqslant 9$, a broad peak near 500 nm ($\varepsilon = 500\,M^{-1}cm^{-1}$) and in more acid solutions (pH 6–8), an absorbance band below 350 nm. The decay products of the long-lived transient have very broad absorbances in the near UV and visible range and are presumed to be ferric hydroxides. An analysis for hydrogen peroxide of both pulse and steady state irradiated samples gave a 75% yield of the amount expected from the decomposition of ferrate(V) by reaction (12):

$$Fe^V \longrightarrow Fe^{III} + H_2O_2 \qquad (12)$$

The second-order decay appears to involve mutual reduction rather than disproportionation reactions. Two alternate schemes are being offered, to explain the experimental observations.

Scheme I (2nd Order Mechanism) suggests that the oxide ligands are being oxidized to hydrogen peroxide in the rate-determining step, followed by further fast oxidation/reduction steps that yield two molecules of an Fe(III)-peroxo complex which ultimately hydrolyzes to iron(III) hydroxides and hydrogen peroxide:

$$2\text{-}\overset{|}{\underset{|}{Fe}}{}^V{=}O \xrightarrow{\text{slow}} [\text{-}\overset{|}{\underset{|}{Fe}}{}^{IV}(O_2^{2-})\overset{|}{\underset{|}{Fe}}{}^{IV}\text{-}] \xrightarrow[H_2O]{\text{fast}} 2Fe^{III}(O_2^{2-}) \qquad (13)$$

$$Fe^{III}(O_2^{2-}) + H_2O \longrightarrow [Fe^{III}(OH)_m^n] + H_2O_2 \qquad (14)$$

The direct formation of a peroxide bond by reaction between oxide ligands would be compatible with substantial free-radical character of the ligand. Protonation may enhance this by reducing resonance delocalization, implying that addition of an electron to the ferrate structure may greatly increase the radical character of the iron-oxygen bond which resonates between the forms $Fe^V{=}O \leftrightarrow Fe^{IV}\text{-}O^{\cdot}$.

Scheme II (1st Order Mechanism) suggests that hydrogen peroxide is formed from oxide ligands of iron, in which case the rate-limiting step would involve hydration of ferrate(V) followed by reductive elimination of peroxide from cis oxide or hydroxide e.g.

$$FeO_4^{3-} + 2H_2O \longrightarrow [Fe^V(OH)_4(O)_2]^{3-} \qquad (15)$$

$$[Fe^V(OH)_4(O)_2]^{3-} \longrightarrow [Fe^{III}(OH)_4(O_2^{2-})]^{3-} \qquad (16)$$

$$[Fe^{III}(OH)_4(O_2^{2-})]^{3-} \longrightarrow Fe^{III}(OH)_m + H_2O_2 \qquad (17)$$

Although it is possible that the tetrahedral structure of the parent FeO_4^{2-} ion is retained on the timescale on which Fe(VI) is reduced to Fe(V), one cannot rule out that the tetrahedral structure is unstable with respect to higher coordination. For example, the protonated forms of Fe(V) may have a lower activation barrier for the rearrangement for a four to six-coordination structure. The degree of hydrolysis for an octahedral ferrate(V) species is unknown but it is probably extensive for the high oxidation state in alkaline solution.

FERRATE(IV)

Ferrate(IV) complexes with simple inorganic ligands such as OH^- or $P_2O_7^{4-}$ can be prepared from the corresponding parent complexes by oxidation with OH radicals ($k_{19} = 8.5 \times 10^7\,M^{-1}s^{-1}$; $k_{20} = 7.8 \times 10^7\,M^{-1}s^{-1}$):[30,32]

$$H_2O \xrightarrow{N_2O} OH \tag{18}$$

$$Fe(OH)_4^- + OH \longrightarrow FeO(OH)_n^{2-n} + H_2O/OH^- \tag{19}$$

$$[(P_2O_7)_2Fe^{3+}OH]^{6-} + OH \longrightarrow [(P_2O_7)_2Fe^{IV}O]^{6-} + H_2O \tag{20}$$

Preliminary results suggest that an alternative method for generating Fe(IV) is by a consecutive two-step reduction of Fe(VI) utilizing the hydrated electron and alcohol radicals. While these experiments require a relatively strict control of the ratios of $[e_{aq}^-]/[(CH_3)_2COH]/[FeO_4^{2-}]$, they are not untenable:

$$H_2O \longrightarrow e_{aq}^- + OH \tag{21}$$

$$OH + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O \tag{22}$$

$$Fe^{VI} + e_{aq}^- \longrightarrow Fe^{V} \tag{23}$$

$$Fe^{V} + (CH_3)_2\dot{C}OH \longrightarrow Fe^{IV} + (CH_3)_2CO \tag{24}$$

The spectra of $FeO(OH)_n^{2-n}$ and $[(P_2O_7)_2Fe^{IV}O]^{6-}$ are similar ($\lambda_{max} = 430\,nm$, $\varepsilon = 1200\,M^{-1}cm^{-1}$); see Figure 3.[31] The $FeO(OH)_n^{2-n}$ transient has been studied only in strong alkaline solutions where it decays by first-order kinetics ($k_{decay} = 2 \pm 1\,s^{-1}$; 1 M NaOH, 25°C).

The ferryl pyrophosphate complex has been studied at pH 10, where its parent complex has been well characterized. The charge of -6, assigned to the ferryl pyrophosphate complex, is being used here as a convenience to balance the equations and does not represent the true charge on this species since its degree of protonation and/or ion pairing is yet unknown. It disappears by a second-order process with formation of ferric pyrophosphate and molecular oxygen ($L = P_2O_7^{4-}$):[31]

$$2L_2Fe^{IV}O^{6-} \longrightarrow L_2FeOOFeL_2^{12-} \tag{25}$$

$$L_2FeOOFeL_2^{12-} + 2H_2O \longrightarrow 2L_2Fe^{III}OH^{6-} + H_2O_2 \tag{26}$$

$$L_2Fe^{IV}O^{6-} + H_2O_2 \longrightarrow L_2Fe^{III}OH^{6-} + O_2^- + H^+ \tag{27}$$

$$L_2Fe^{IV}O^{6-} + O_2^- + H^+ \longrightarrow L_2Fe^{III}OH^{6-} + O_2 \tag{28}$$

Reaction (25) appears to be the major pathway with a rate constant $k_{25} = 1.0 \times 10^6\,M^{-1}s^{-1}$ at high $[L_2Fe^{III}]_{total}$, where both reactions (27) and (28) have a minimal effect on the decay rate. If one assumes that k_{26} is of the order of $10^2\,s^{-1}$

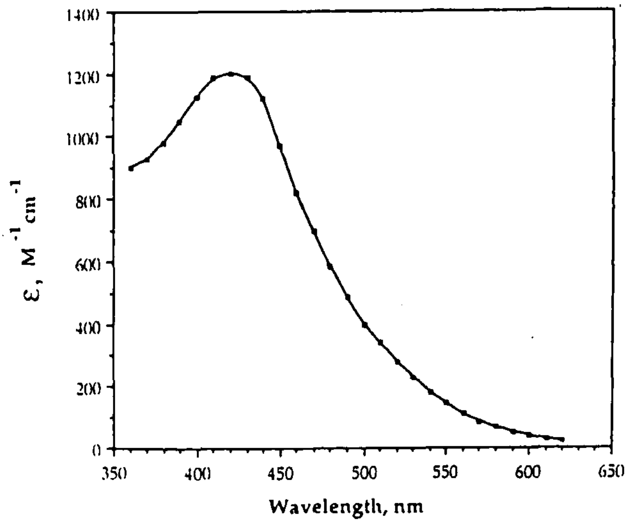

FIGURE 3 Spectrum of $[(P_2O_7)_2Fe^{IV}O]^{6-}$ in 0.1 M pyrophosphate, pH 10.0, 25°C.

TABLE II
Rate constants for reactions of Fe(IV) pyrophosphate with some divalent pyrophosphate complexes (L_mM^{2+}; $L = P_2O_7^{4-}$) determined under pseudo first-order conditions in 0.1 M pyrophosphate at pH 10.[31]

$[L_mM^{2+}]$	k, $M^{-1}s^{-1}$
Mn^{2+}	1.2×10^6
Fe^{2+}	1.6×10^6
Co^{2+}	5.5×10^5
Ni^{2+}	$< 4.0 \times 10^2$
Cu^{2+}	$< 4.0 \times 10^2$

(c.f. the exchange rate of H_2O for $Fe(H_2O)_6^{3+}$ is $k_{exch} \approx 160\,s^{-1}$), reaction (25) becomes rate limiting under conditions where $[L_2Fe^{IV}O^{6-}]_0$ is approximately at the micromolar concentration level. An analysis for H_2O_2 in both pulse and ^{60}Co irradiated samples have shown that it is oxidized to O_2 by Fe(IV) (reactions 27 & 28) and excess ferric pyrophosphate.

That Fe(IV) pyrophosphate is a relatively strong oxidant is apparent from its rate of reaction with hydrogen peroxide ($k = 3.6 \times 10^5\,M^{-1}s^{-1}$) and a number of divalent pyrophosphate complexes listed in Table II. The estimated limits for the reduction potential at pH 10 is $1.0\,V < E^0(Fe^{IV}_{pyph}/Fe^{III}_{pyph}) < 1.35\,V$.

SUMMARY

Some comparative studies on the reactivity of the three hypervalent oxidation states of iron with other compounds show that ferrate(V) and ferrate(IV) are significantly more reactive than ferrate(VI), $(k(Fe^V + HCOO^-)/k(Fe^{VI} + HCOO^-) \approx 10^5$; $k(Fe^V + \text{ascorbate})/k(Fe^{VI} + \text{ascorbate}) > 10\text{–}100$;[32] $k(Fe^{IV}_{pyph} + H_2O_2)/k(Fe^{VI} + H_2O_2) \approx 3 \times 10^3)$. That the higher reactivity may be due to a substantial free-radical character of the Fe–O bonds in the ferryl/perferryl species is in accord with the formation of covalent bonds (H_2O_2 formation) during the bimolecular decomposition of ferrate(IV)/ferrate(V), which proceed at rates typical of radical-radical interaction.

As is apparent, some ferryl/perferryl complexes are conveniently generated and characterized in aqueous solutions by pulse radiolysis. Furthermore, careful experimental design that utilizes pulse radiolysis in combination with premixing and stopped-flow techniques allows also the study of the reactivity of small hypervalent iron complexes with substrate compounds. The results of such studies, which are carried out in isolation, should not only lead to a better understanding of the basic chemistry of these hypervalent oxidation states of iron but also to a more rational evaluation of their role in more complex systems.

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