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THE OXIDATION OF PHENOL BY FERRATE(VI) AND FERRATE(V). A PULSE RADIOLYSIS AND STOPPED-FLOW STUDY.

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Potassium ferrate, K_2FeO_4, is found to oxidize phenol in aqueous solution ($5.5 \leq pH \leq 10$) by a process which is second order in both reactants: $-d[Fe^{VI}]/dt=k_1[Fe^{VI}][phenol]$, $k_1 = 10^7 M^{-1}s^{-1}$. Product analysis by HPLC showed a mixture of hydroxylated products, principally paraquinone, and biphenols that indicate that oxidation of phenol occurs by both one-electron and two-electron pathways. The two-electron oxidant, producing both para- and ortho-hydroxylated phenols is considered to be ferrate(V) which is itself produced by the initial one-electron reduction of ferrate(VI). The rate of ferrate(V) reaction with phenol was determined by pre-mix stopped flow pulse-radiolysis and found to be $k_7 = (3.8 \pm 0.4) \times 10^5 M^{-1}s^{-1}$.

KEY WORDS: Ferrate(VI), Ferrate(V), Phenol, Phenoxyl Radical, Pulse Radiolysis.

INTRODUCTION

Hypervalent oxidation states of iron have been of great interest because of their role as oxidants and hydroxylating agents in numerous enzymatic reactions (oxygenases, catalase, myloperoxidase, horseradish peroxidase etc.) as well as in model systems.[1–3] Although these reactions and the role of Fe(IV) and Fe(V) intermediates have been studied extensively in enzymes and such complex molecules like porphyrins,[3,4] there are few examples of simpler iron complexes in these oxidation states and therefore little is known about hypervalent iron in the absence of specialized ligand systems. The toxicity of some redox active metals may arise from the production of OH radicals produced in the reaction of their reduced forms with hydrogen peroxide (Fenton-type reactions) or the involvement of their higher oxidation states.[5–7] The intermediacy of ferryl, has been proposed[8,9] and this has prompted our study of hypervalent iron species and their reactions in aqueous solutions by pulse radiolysis.[10–13] We are particularly interested in whether certain forms of high valent iron may act as hydroxylating agents for aromatic compounds.

Ferrate(VI) (K_2FeO_4) is well-characterized in the solid state and in alkaline solution as a tetrahedral ion,[14] which exchanges its oxygen ligands with water relatively slowly.[15] It has also been proposed as a potential treating agent for the destruction of pollutants in waste-water[16] which makes its reactions with common organic functionalities of general interest. However, there exist relatively few mechanistic studies of iron(VI) reactions.

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We investigate here the kinetics and mechanism of the reduction of ferrate(VI) by phenol to iron(III). The protonations, stability and absorption spectra of the intermediate ferrate(V) have previously been characterized by pulse radiolysis.[17] In the present study, we use rapid pre-mix pulse radiolysis to study its reactions with phenol and the role of Fe(V) as an intermediate in the overall reaction mechanism. Phenol has been the subject of numerous investigations and the results of studies of its reactions with the hydroxyl radical have been critical in both the design of experiments and the interpretation of the results.[18–23]

MATERIALS AND METHODS

Materials

All solutions were prepared with water which had been distilled and passed through a Millipore ultrapurification system. Solution pH was adjusted with perchloric acid (GFS, distilled from Vycor) or NaOH (GFS, 99.99%). Phosphate and borate buffers were Baker reagents. Phenol was Amresco Ultrapure crystalline (>99.0%). Fenton reactions employed hydrogen peroxide (Baker, Ultrex, 30%) and ferrous sulfate (GFS Chemicals, 99.999%). Potassium ferrate (K_2FeO_4) was synthesized by the method of Thompson, *et. al.*[24] and was analyzed as 98.6% purity by atomic absorption spectroscopy. Concentrations were determined from its absorbance at 510 nm (ε = 1150 $M^{-1}cm^{-1}$).[25]

Methods

K_2FeO_4 and Fenton oxidations of phenol were carried out as follows. Reactant solutions were degassed with UHP nitrogen (MG Industries) before drawing them through a jet-mixer into a collection vessel. The reaction mixtures were maintained under N_2 and were quenched at various times, the shortest within 2 seconds, by concentrated H_2SO_4 (Aristar, 98%) which rapidly decomposed any excess of ferrate. Solutions were then adjusted to pH 2, frozen in a methylene chloride/dry-ice bath, and stored at −20°C for HPLC analysis. The products were separated on a 15 cm Beckman Ultrasphere column and detected with either a ESA Coulochem 5100A electrochemical detector or by UV detection. Authentic samples of p-hydroquinone, catechol, o-quinone, p-quinone and 2,2′–, 2,4′– and 4,4′-dihydroxybiphenols were used as calibrants.

Kinetics

The rate of reaction between ferrate(VI) and phenol was measured in an Applied Photophysics stopped-flow spectrometer in a 0.1 M ($NaClO_4$) ionic strength medium at pH 9 (5 mM phosphate/borate buffer) and 24 ± 1 °C. Pulse radiolysis experiments were performed on a 2 MeV Van de Graaff accelerator by premixing argon-bubbled ferrate(VI) and a phenol/2-propanol mixture. The mixture was pulse irradiated within 100 ms of mixing. The radiolysis of water[26] yields the following primary radicals G-values (radicals/molecules formed per 100 eV of absorbed energy)

$$H_2O \rightsquigarrow {}^{\bullet}OH\,(2.75),\ e_{aq}^{-}(2.65),\ H^{\bullet}(0.65), \qquad (I)$$

In this system the e_{aq}^- reduces ferrate(VI) to ferrate(V) directly, while the •OH radical reacts with the 2-propanol to give the reducing radical $(CH_3)_2COH$, which in turn reduces ferrate(VI) to ferrate(V); $(CH_3)_2COH + Fe^{VI} \rightarrow Fe^{V} + (CH_3)_2CO$.[17] The rate of ferrate(V) disappearance as a function of [phenol] was monitored at 380 nm ($\varepsilon_{max}(Fe^{V}) = 1000\ M^{-1}cm^{-1}$).[17] The spectra of transients were obtained by usual means.

Pulse radiolysis studies of the phenoxyl radical were also performed. Phenoxyl radicals were generated by oxidation of phenol with Br_2^- radicals in N_2O saturated solution.[21] These conditions produce the fast reactions: $e_{aq}^- + N_2O + H_2O \rightarrow N_2 + {\bullet}OH + OH^-$; ${\bullet}OH + 2\,Br^- \rightarrow Br_2^- + OH^-$. Bromine radicals oxidize phenol ($k = 6 \times 10^6 M^{-1}s^{-1}$) and hydroquinone ($k = 7 \times 10^7\ M^{-1}s^{-1}$) to phenoxyl or semiquinone radicals.[27] For comparative product analysis by HPLC, ^{60}Co radiolysis of phenol solution was performed in N_2O saturated buffers (5 mM phosphate/borate pH 9) at a dose rate of 7.3 μM/min of hydroxyl radical.

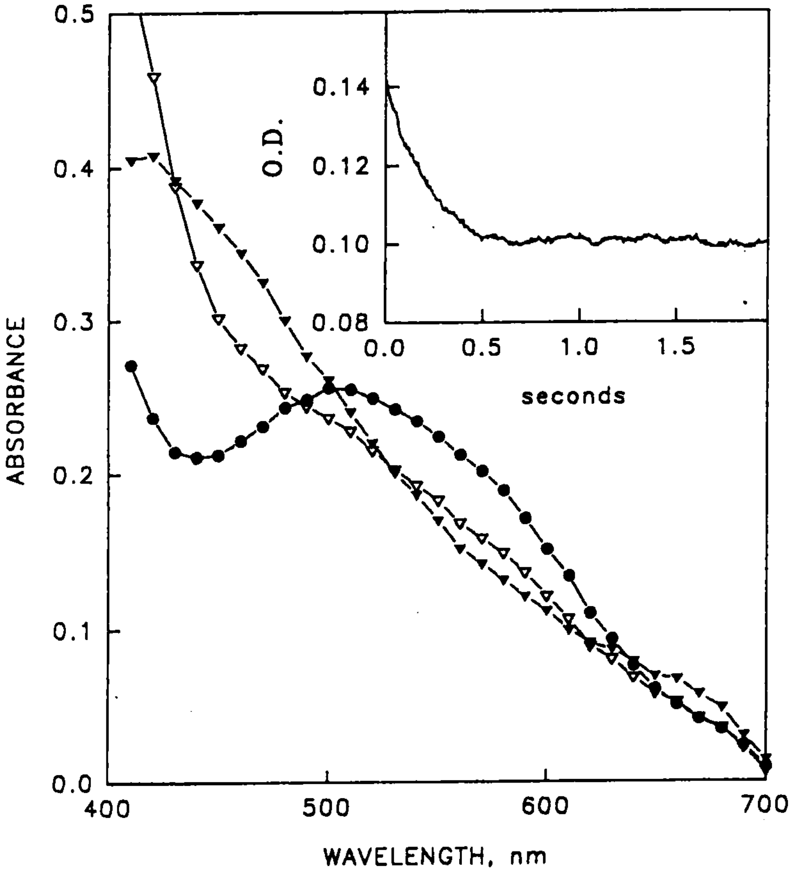


FIGURE 1. Kinetic absorption scans of the reduction of 200 μM ferrate(VI) by 0.05 M phenol at pH 9.0, 24°C. Shown are spectral scans: a) FeO_4^{2-} at time zero (●); b) Red transient (primarily Fe(III)-catechol complex) at time 0.4 seconds after mixing (▽); c) Final absorption of solution 2 seconds after mixing (▼). Inset: example of kinetic trace at 550 nm.

RESULTS AND DISCUSSION

Stopped-flow mixing of ferrate(VI) and phenol initiates a series of color changes. First, from the purple-red ferrate ion, a maroon-red species was formed. This color dissipated to a yellowish-brown in a few seconds before slowly fading. The corresponding transient spectra observed upon mixing 200 μM ferrate(VI) with 0.05M phenol at pH 9 are shown in Figure 1. The first-order phenol-dependent phase was monitored at 550 nm and a plot of observed rate constants are shown in Figure 2. The data are consistent with the rate law (II), where $k_I = 10^7 M^{-1}s^{-1}$:

$$-d[Fe^{VI}]/dt = k_I[Fe^{VI}][phenol] \qquad (II)$$

Repetition of these experiments in the pH range 5.5 to 10, showed no change in the observed rates of reaction, although the initial maroon colored product was longer lived at the higher pH.

The reacted phenol solutions were analyzed by HPLC as described under Methods. The results of product analyses from many runs are summarized in Table I. The fractions of measurable products obtained are based on three oxidizing equivalents of ferrate(VI) added and are approximately 25% of the expected value. However, long time elutions (several hrs) showed uncharacterizable polymers held back by the column, which most likely made up the remainder. Schuler *et al.*,[21,23] studied in great detail

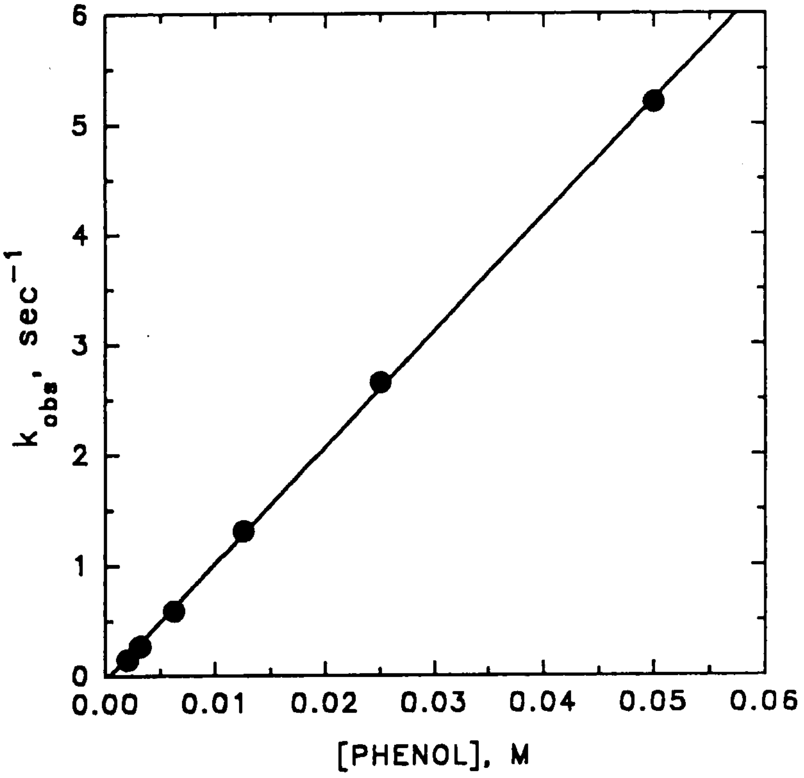
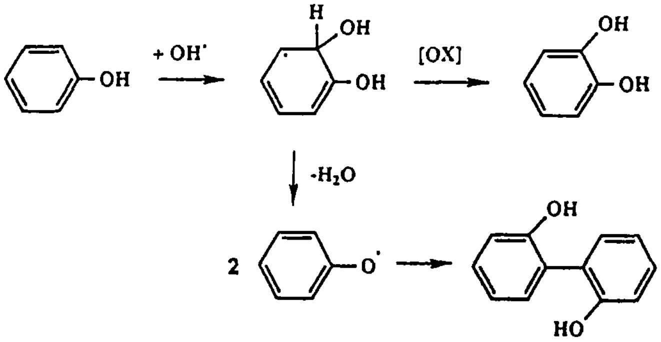


FIGURE 2. First order plot of observed rates of the reduction of ferrate(VI) as a function of [phenol] at pH 9.0 (buffer 5 mM phosphate/borate) containing 0.1 M $NaClO_4$. The temperature was ambient 24 ± 1°C.

the chemistry of the phenoxyl radical and its dimerization to the various dihydroxybiphenyl isomers; under optimal conditions these accounted for about 80% of the phenoxyl radicals generated while 10% yielded 2- and 4-phenoxyphenols. The authors also pointed out that repeated pulsing or exposure to ^{60}Co gamma rays significantly lowered the yields of dimers. Overall the complication is due to the high reactivity of phenoxyl radicals with biphenols, which leads to formation of tri- and polymeric compounds. Also shown in Table I are the results of HPLC analyses of phenol solutions which were gamma-irradiated under N_2O or exposed to Fenton reactions at pH 2.1 and 9.0. The products may be categorized as phenoxyl radical coupling products or as hydroxylated phenols. The primary difference in the results of oxidized/hydroxylated phenol by the three different systems is that a preponderance of the products resulting from oxidation by OH radical derive from coupling reactions of the phenoxyl radical.[28] Hydroxyl radicals react with aromatic systems via an electrophilic addition to produce hydroxyl adducts (Scheme I). These hydroxycyclohexadienyl radicals are converted to stable hydroxylated derivatives in the presence of an efficient oxidant[19,29-32] but, in the case of phenols, competitively lose water to form phenoxyl radicals. In deaerated solutions, their dimerization produces mainly biphenols (o,o′–; mm′–; p,p′–).

Scheme I



Formation of biphenols in the ferrate(VI) + phenol reaction clearly indicates a one-electron pathway in the oxidation of phenol where most of the determinable products are the para-hydroxylated derivatives, p-quinone and p-hydroquinone. From Table I it can be seen that the yields of ortho- and para-hydroxylation products and biphenols arising from ferrate(VI) oxidation are distinctly different from the other oxidizing

TABLE I.

Typical Product %-Yields observed upon hydroxylation of Phenol by Fenton reactions, ferrate(VI) and OH radicals generated by ^{60}Co gamma-rays.

	pH	p-H_2Q	p-Q	o-H_2Q	o-Q	biphenols
Fenton*[a]	2.1	0.4	10	4	0.4	85
Fenton*[a]	9.0	3	32	26	3	36
Ferrate(VI)b	9.0	3	68	7	2	21
^{60}Co[c]	9.0	2	10	14	0	75

• Other products: Resorcinol < 2.5%, hydroxy p-quinone ≈ 8% of total.

[a] Fenton Reactions: $[Fe^{II}]$=0.11 mM, $[H_2O_2]$=0.9 mM, [phenol]=2.1 mM

[b] [Fe(VI)]=0.1 mM, [Phenol]=2.0 mM

[c] [Phenol]=2.1 mM; irradiated 7 min. at rate of 7.3 μM/min

systems. The Fenton system at low pH and ^{60}Co radiolysis yield primarily biphenols (≈ 80%). The ortho- and para-hydroxylation products are formed, within experimental error, in similar quantities. While the corresponding Fenton yields at pH 9 are approximately three times those observed at pH 2.0, the distribution of hydroxylated products is similar. As is apparent from Table I, the ferrate(VI) system preferentially hydroxylates phenol at the para-position. For this reason it is unlikely that hydroxylation by ferrate(VI) occurs via the dihydroxy-cyclohexadienyl radical pathway.

To account for the low overall yields, we examined the specific manner in which phenoxyl radicals affect the stoichiometry of the products formed by ferrate(VI) oxidation. Phenoxyl radicals decay bimolecularly ($2k = 2.2 \times 10^9\ M^{-1}s^{-1}$; this study) to biphenols which do not absorb above 350 nm. In steady-state ^{60}Co radiolysis experiments the concentration of biphenols accumulate with time to a maximum after which they decreased (results not shown). This suggests that simple biphenols were oxidized by phenoxyl radicals to a more complex product(s). Pulse radiolysis experiments confirmed this by showing that biphenols are readily oxidized by phenoxyl radicals to products which absorb at 400 nm (spectrum 4 in Figure 3). The inset shows the progressive increase in the average extinction coefficient at 400 nm due to increasing length of the polyphenol chains upon repetitive pulsing.

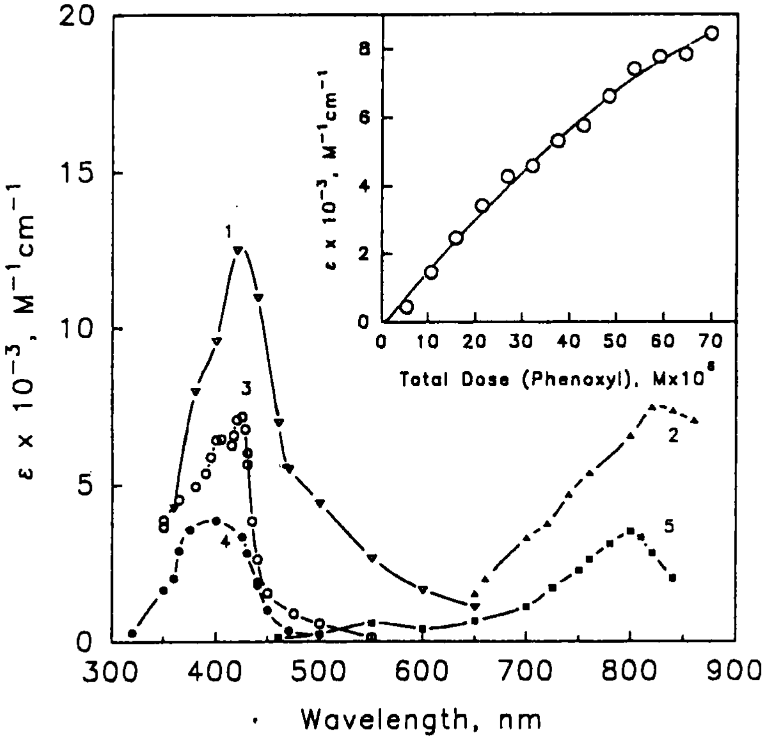


FIGURE 3. The spectra (1 and 2) of transients obtained upon pulse irradiation of solutions (pH 9) containing products formed from phenol oxidation by ferrate(VI). They are decaying at $k = 3 \times 10^3\ s^{-1}$ and $6 \times 10^3 s^{-1}$ respectively. Spectrum 3, of the para-semiquinone radical, was obtained by oxidation of p-hydroquinone by Br_2^-. Spectrum 4 is the stable spectrum of polyphenol products obtained after multiple pulsing (total dose accumulated 25μM of phenoxyl radicals). The increase in the extinction coefficient of the product at 400 nm as a function of the accumulated dose is shown in the inset. Spectrum 5 decays at the same rate as 2 and was obtained following the exhaustive oxidation of catechol by phenoxyl radicals.

$$HO\text{–}(C_6H_4)_2\text{–}OH + C_6H_5O^\bullet \rightarrow HO\text{–}(C_6H_4)_2\text{–}O^\bullet + C_6H_5OH \qquad (2)$$

$$2\ HO\text{–}(C_6H_4)_2\text{–}O^\bullet \rightarrow \text{tetraphenols/oxidation products} \qquad (3)$$

When the system was modified by oxidizing a small part of the phenol with ferrate(VI) prior to pulsing, the absorption spectra 1 and 2 in Figure 3 were obtained (≈ 1 msec after the pulse). Both represent radicals which are derived from the major products of phenol oxidation by ferrate(VI). Spectrum 1 has not been characterized, but is most likely a complex semiquinone. The spectrum of the simple para-semiquinone radical (spectrum 3) is shown for comparison. Both spectrum 1 and 2 are products which are not detected by HPLC and hence are most likely polymers. Electrochemical experiments have shown that catechol in particular is likely to produce ether-bridged polymers under oxidizing conditions.[31] We confirmed this by exhaustive pulse radiolytic oxidation of catechol by phenoxyl radicals. An absorption at 800 nm (Spectrum 5, Figure 3), that disappears at a rate of $3 \times 10^3 s^{-1}$, was observed and increased in intensity with each successive electron pulse. The nature of the species responsible is unclear but it is polymeric and is consistent with the low yields of simple products obtained from HPLC sampling.

The low yields of catechol and orthoquinone in HPLC product analysis is partly due to the instability of these species in the presence of iron(III) at higher pH. The ortho hydroxylation products were detected only in solutions which had been immediately acid-quenched. In contrast, the oxidation of p-hydroquinone by ferrate(VI) is fast ($k \approx 2 \times 10^5 M^{-1}s^{-1}$; this study) and gives virtually quantitative yields of the quinone.

The analysis of products is consistent with a sequential $1\text{–}e^-/2\text{-}e^-$ reduction of ferrate(VI) which leads to iron(III). The initiating and rate-determining step is most likely reaction (4) since in the absence of a proton catalyzed path, the rate of an inner-sphere process is most likely limited by the slow rate of oxygen-ligand exchange on the FeO_4^{2-} ion ($k_{exch} = 1.6 \times 10^{-3} s^{-1}$).[15]

$$FeO_4^{2-}/HFeO_4^- + C_6H_5OH \rightarrow Fe^V/HFe^V + C_6H_5O^\bullet \qquad (4)$$

$$2\ C_6H_5O^\bullet \rightarrow \text{dihydroxybiphenyl isomers} \qquad (5)$$

Protonation of ferrate(VI), $pKa(HFeO_4^-/FeO_4^{2-}) = 7.8$,[16] was shown in earlier studies to strongly affect the rates of reaction with organic substrates.[11,13] We examined the oxidation of phenol by ferrate(VI) in the pH range 5–10 and found the rate constant unaffected.

Reaction of Ferrate(V) with Phenol

Ferrate(V) was produced by the reaction of 2-propyl radicals and the hydrated electron with ferrate(VI) in the presence of phenol as described earlier. At pH 9 ferrate(V) exists in a monoprotonated form ($HFeO_4^{2-}$), which decays to Fe(III) and H_2O_2 bimolecularly ($k \approx 10^7 M^{-1}s^{-1}$).[17] This characteristic of $HFeO_4^{2-}$ might imply a much greater susceptibility to inner sphere processes than is exhibited by the FeO_4^{2-} ion. We observed sequential first order processes (Figure 4, Inset) leading to the spectral intermediates shown in Figure 5. In the first process, ferrate(V) is reduced by phenol to a ferric complex which absorbs broadly near 500 nm (Figure 5). The spectral features of this intermediate are very similar to that of the iron(III)-catechol complex as shown in the

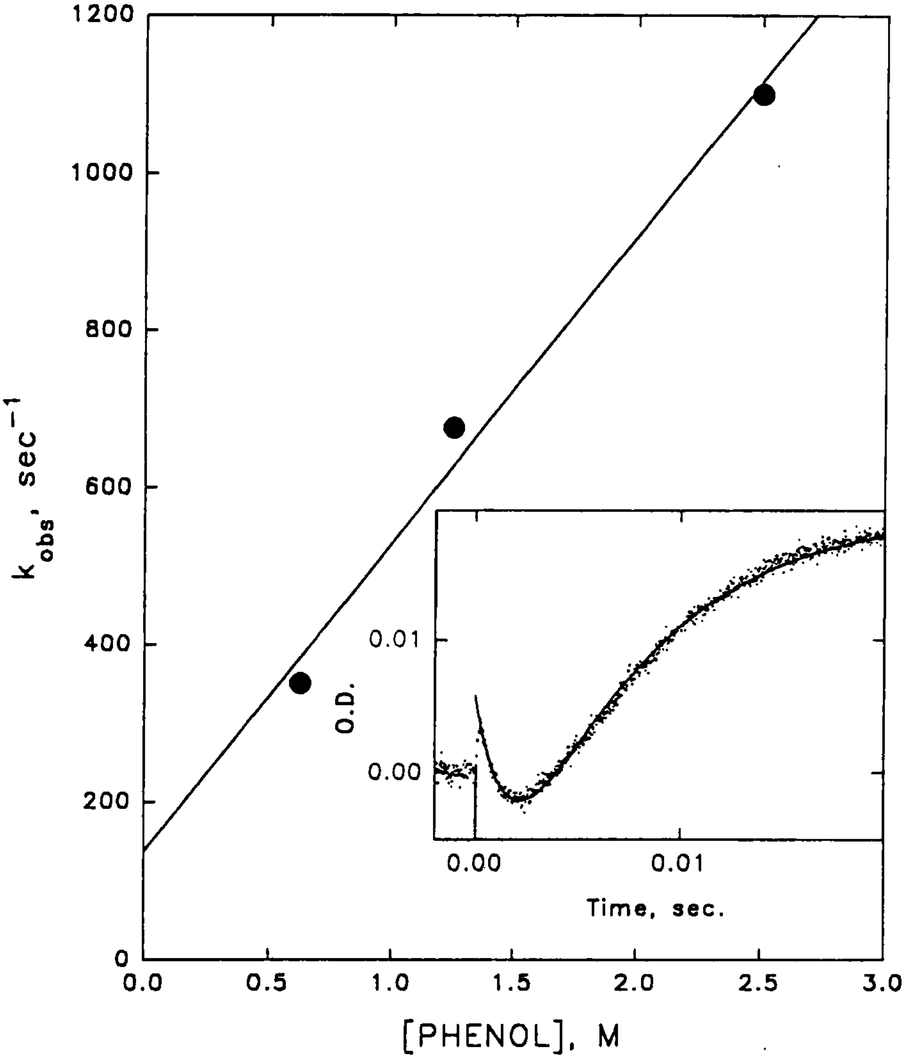


FIGURE 4. The observed first rate constants as a function of [Phenol] for reduction of ferrate(V) at pH 9.0, 25°C. The formation of ferrate(V) is complete within μ-seconds (not shown) while its reaction with phenol (first 2 ms in inset; 412nm and 2.5 mM phenol) is dependent on the phenol concentration as illustrated. The slope corresponds to a rate constant k (Ferrate(V) + Phenol) = $(3.8 \pm 0.4) \times 10^5$ $M^{-1}s^{-1}$.

Inset of Figure 5. The spectrum of ferric mono-catecholate was obtained by reacting the semiquinone radicals of catechol with ferrous ions:

$$Fe^{2+} + \text{ortho-}C_6H_4O_2^{-\cdot} \rightarrow Fe^{III}(\text{catecholate}) \qquad (6)$$

No interaction between para-semiquinone radicals and iron(II) was found. Based on the spectral similarity between the ferric-catechol complex and the ferrate(V) reduction product, and the extinction coefficient at 550 nm of (4000 ± 200) $M^{-1}cm^{-1}$,

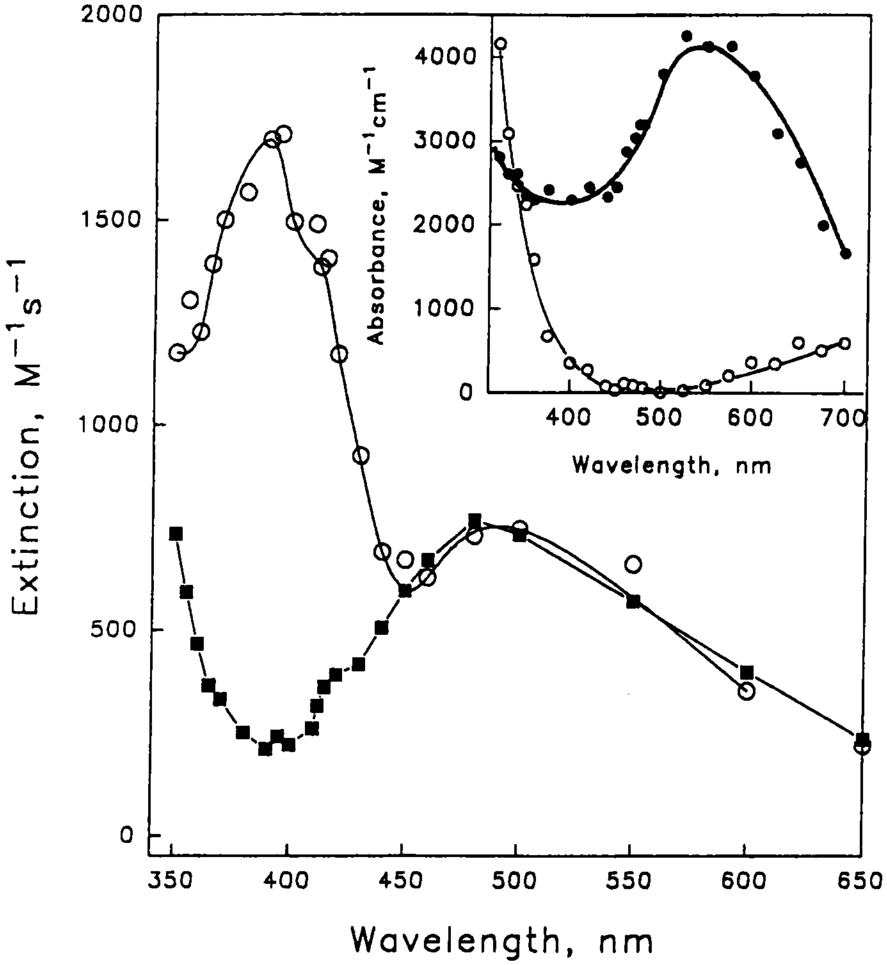
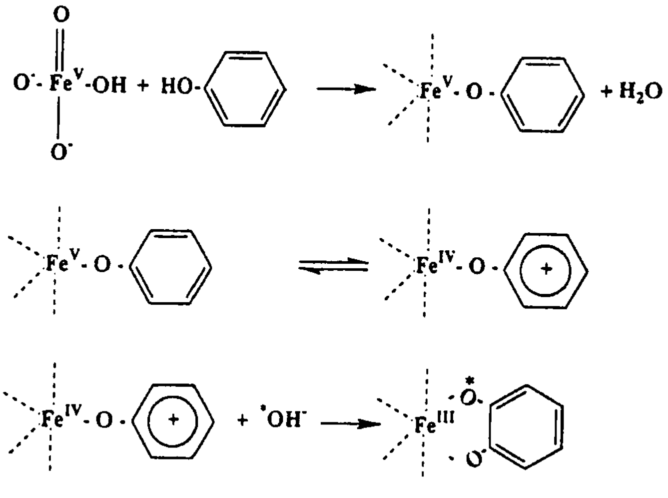


FIGURE 5. The absorbances of the products of ferrate(V) reduction by phenol calculated at ~ 3 msec (■) and 30 msec (O) following reaction with phenol (see kinetic trace, inset Figure 4). The inset in Figure 5 shows (O) the absorption spectrum of o-semiquinone and (●) the spectrum of iron(III)-catechol complex obtained on reacting the semiquinone radicals with ferrous ion at pH 9.

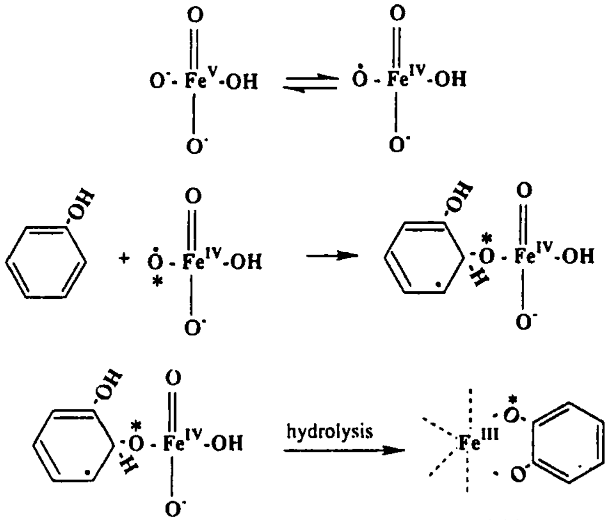
approximately 20% of phenol is oxidized to catechol by ferrate(V); a smaller amount was detected by HPLC. The remainder (~ 80%) is converted to the p-hydroquinone which does not form a distinctively absorbing iron(III) complex, but has been determined by HPLC.

The initial reduction of ferrate(V) to the Fe(III)-catechol complex (See Figure 4, Inset) is followed by a slower ($k = 150\ s^{-1}$) formation of a transient that has an absorption band at 400 nm. This may be due to a secondary oxidation of product(s) by ferrate(VI). Two schemes by which the coordinated Fe(III)-catechol complex may be formed are: 1) Inner sphere substitution of phenol by ferrate(V) followed by oxidation reactions (Scheme 2) and 2) Electrophilic attack on the aromatic ring by ferrate(V), (Scheme 3):

Scheme 2: Inner-Sphere Substitution



Scheme 3: Electrophilic Addition



Both schemes show only the product of the ortho substitution which leads to Fe(III)-catechol complex formation. The para-product is formed by analogous pathways in each case. The asterisk (*) on the oxygen indicates that the hydroxyl group derives from solvent hydroxide ion in Scheme 2 and oxy-ligand of Fe(V) in Scheme 3. The rate-determining step in Scheme 2 is substitution of a hydroxide ligand on Fe(V) by phenoxide, followed by addition of hydroxide ion to a proposed Fe(IV)-(phenoxonium$^+$) intermediate. The rate determining step in Scheme 3 is an electrophilic attack of $HFeO_4^{2-}$ on the aromatic ring to produce an intermediate form which is analogous to the hydroxycyclohexadienyl intermediate formed by OH radical attack in Scheme 1. The hydroxycyclohexadienyl transient decomposes by an intramolecular redox reaction to a Fe(III)-catecholate complex if the attack by $HFeO_4^-$ occurs at an ortho position and to Fe(III) and p-hydroquinone if the attack is at the para position.

CONCLUSIONS

The principal hydroxylating agent in the oxidation of phenol by the ferrate(VI) ion is a ferrate(V) species which produces both catechol (detected spectrally) and p-hydroquinone/quinone (detected by HPLC). The hydroxylating mechanism involves either an inner-sphere oxidation of a phenolate ligand by ferrate(V) or an electrophilic addition of Fe^V=O moiety to the ring. The reaction is overall a concerted two-electron oxidation. At present, the mechanisms cannot be unambiguously resolved, but the d^3 (e.g. Cr(III) or Fe(V)) electronic configuration in metal complexes is typically slow in undergoing ligand substitutions. The very fast reaction between ferrate(V) and phenol is thus unexpected if it requires replacement of a water or hydroxide ligand attached to the iron center as we have suggested in (Scheme 2).

The parent FeO_4^{2-} ion is, by contrast, three orders of magnitude less reactive than ferrate(V) at pH 9 and oxidizes phenol by a one-electron transfer. Spectral analysis indicates that ≈ 20% of catechol is formed. A similar small ratio (13%) was found in the inner-sphere oxidation of phenol by a Ru^{IV}oxo complex although oxidation was proposed to occur via formation of an intermediate phenoxyl radical.[32] It is interesting to note here that the ortho product is the least favored species even when the formation of a stable ferric chelate system would seem to favor it. The structure of aqueous ferrate(V) is not known but in all likelihood it has a Fe^V=O bond in an overall octahedral structure. In summary, the results suggest that the present ferryl system serves as a simple model for the various iron-containing enzyme systems that hydroxylate and oxidize biological substrates, and which involve Fe(IV) and Fe(V) oxidation states during their catalytic cycle.

Acknowledgments

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