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## Ferrate(VI) Oxidation of Aqueous Phenol: Kinetics and Mechanism

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Kinetic and thermodynamic parameters for ferrate(VI) oxidation of phenol have been measured in isotopic solvents, H<sub>2</sub>O and D<sub>2</sub>O, using ambient and high-pressure stopped-flow UV–visible spectroscopy. An increase (fast stage) and then a decrease (slow stage) in absorbance at 400 nm are observed when potassium ferrate (K<sub>2</sub>FeO<sub>4</sub>) and aqueous phenol solutions are mixed rapidly. This suggests that small amounts of unstable intermediate 4,4'-biphenquinone are produced during this redox process. An electron paramagnetic resonance signal for the reaction mixture of ferrate and phenol trapped by spin-trap  $\alpha$ -(4-pyridyl-1-oxide)-*N*-*tert*-butylnitrone indicates a radical reaction pathway. Gas chromatographic/mass spectrometric measurements show *p*-benzoquinone is a major organic product, and the red ferric thiocyanate complex formed from addition of potassium thiocyanate to the spent reaction solution indicates that Fe(VI) is reduced to Fe(III). Activation enthalpy, entropy, and volume changes have been determined. There is a primary isotope effect for the formation of the intermediate (fast stage),  $k_{\text{fast}}(\text{H}_2\text{O})/k_{\text{fast}}(\text{D}_2\text{O}) = 2.4 \pm 0.6$ . Because the phenol hydroxylic hydrogen is deuterated in D<sub>2</sub>O, this isotope effect suggests that a hydrogen bond is formed in the transition state.

### Introduction

Iron is 'old economy', but in recent years some attention has been given to potassium ferrate (K<sub>2</sub>FeO<sub>4</sub>) and barium ferrate (BaFeO<sub>4</sub>). These two salts contain a hypervalent species of iron, Fe<sup>6+</sup>. Hypervalent iron is an important chemical species within the redox processes of such proteins as horseradish peroxidase and cytochrome P-450.<sup>1,2</sup> The recent announcement by Licht et al. of a 'super iron' battery based upon the ferrate salts has increased interest in and awareness of the Fe<sup>6+</sup> species.<sup>3–7</sup>

Evidence for the existence of such a hypervalent species of iron has long been known. Stahl, Eckerberg, and Becquerel all reported obtaining purplish-red powders in their mixtures of iron compounds.<sup>8–10</sup> However, it was Fremy who assigned the iron in those compounds to being in the +6 oxidation state as FeO<sub>3</sub>, although he was never able to isolate it.<sup>11</sup>

Although simple methods for the synthesis of K<sub>2</sub>FeO<sub>4</sub> have long been known,<sup>12–14</sup> relatively few investigations have been made of its reactivity until recently. Studies of FeO<sub>4</sub><sup>2–</sup> chemistry have shown that ferrate salts are a powerful oxidant of a wide variety of organic and biological compounds either in solution<sup>15–20</sup> or on solid supports.<sup>14,21</sup> Proposed mechanisms for the reactions of ferrate salts with numerous compounds involve one- and two-electron reductions of the Fe<sup>6+</sup> in the FeO<sub>4</sub><sup>2–</sup> and its conjugate acids followed by radical chain reactions of the reductants.<sup>22–28</sup>

In this study, the oxidation of phenol by FeO<sub>4</sub><sup>2–</sup> is examined and a mechanism is proposed that combines portions of the free radical mechanism proposed for the oxidation of hydrogen sulfide<sup>25</sup> and the oxidation of phenol by the oxochromium(IV) anion.<sup>29</sup> [Phenol is oxidized by the Fe(VI) to form the phenoxyl radical and Fe(V). Further steps in the mechanism lead to two products: quinone and biphenols. Biphenols are formed when the reaction proceeds through the biphenquinone intermediate reacting with excess phenol.]

The radical reactions were studied with spin traps and electron paramagnetic resonance (EPR) spectroscopy. EPR spectroscopy detects free radicals in small concentrations,<sup>30</sup> and spin traps react with the short-lived reductant radicals that would otherwise decay before the spectroscopy could be completed.<sup>31,32</sup> In addition to the EPR studies, the kinetic values of the oxidation of phenol by ferrate (including kinetic isotope effects) were obtained with a stopped-flow spectrophotometer including high-pressure studies to obtain the volumes of activation. Product analysis was performed using gas chromatography/mass spectrometry (GC/MS).

### Experimental Section

**Chemicals.** Potassium ferrate with a purity up to 90% was synthesized by the hypochlorite oxidation of ferric hydroxide based on a method reported by Audette and Quail.<sup>13</sup> The product was assayed by mid-IR and UV–visible spectroscopy.<sup>33,34</sup> A vacuum desiccator prevented the synthesized ferrate from undergoing slow decomposition caused by traces of water in air.

Phenol (99%) was purchased from Fisher Scientific. Deuterium oxide (99.9%),  $\alpha$ -(4-pyridyl-1-oxide)-*N*-*tert*-butylnitrone (POBN) (99%), and *o*-, *m*-, *p*-cresol were from Aldrich Chemicals. All other chemicals used in this study were of analytical reagent grade and were not subjected to further purification.

**Measurements.** All atmospheric pressure kinetic experiments were performed using a variable-temperature stopped-flow spectrophotometer (Durrum-Gibson), combined with a photomultiplier tube (E990–07, Hamamatsu Photonics K. K., Japan) assembly. The pressure-dependent experiments were conducted with a laboratory-made high-pressure stopped-flow system described elsewhere.<sup>35–37</sup> *n*-Heptane was the pressure-transmitting medium. Kinetic traces were recorded by a computerized data collection system, and calculation of the observed rate constants was done with the OLIS KINFIT set of programs.

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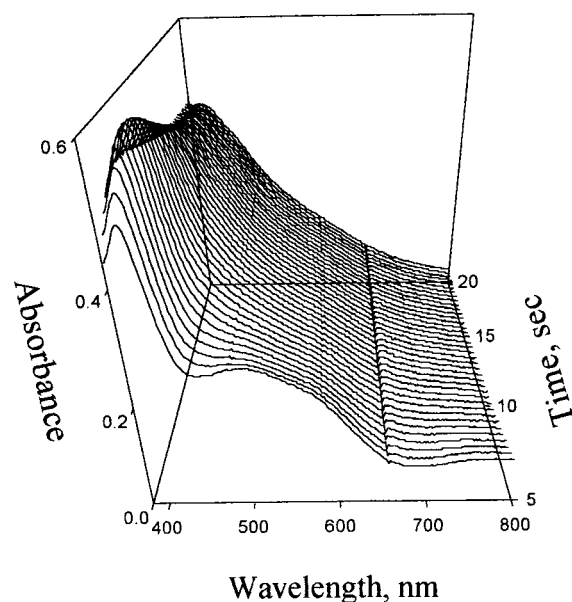
Sample liquids for kinetic measurements were thermostated within  $\pm 0.1$  °C. Sample solutions were transferred with the aid of gastight syringes. Transient signals were monitored for at least 10 half-lives at a wavelength (400 nm) corresponding to the absorption maximum of a reaction intermediate. Solutions were buffered at pH 9.85 to diminish interference from the decomposition of ferrate in aqueous solution as much as possible.

The aqueous solutions were prepared using deionized water or D<sub>2</sub>O. Solutions of 0.05 M sodium phosphate buffer with the required pH were prepared by mixing appropriate quantities of Na<sub>2</sub>HPO<sub>4</sub>·7H<sub>2</sub>O and NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O. The buffer solutions were filtered using Chelex 100 (Aldrich) to remove metal ions in the solution, especially Fe<sup>3+</sup> ion.<sup>38</sup> Phosphate also 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).

Reports<sup>3,6</sup> indicate that Ni<sup>2+</sup> and Co<sup>2+</sup> catalyze the decomposition of FeO<sub>4</sub><sup>2-</sup>, and it may be possible that either or both of these ions catalyze the reaction between phenol and ferrate. A subset of experiments was repeated in the presence of added Ni<sup>2+</sup> or Co<sup>2+</sup> near the solubility limit of the respective hydroxide salts. The rate constants for the oxidation of phenol by ferrate are independent of the concentration of Ni<sup>2+</sup> and Co<sup>2+</sup>. We verified that the decomposition of ferrate is catalyzed by Ni<sup>2+</sup> and Co<sup>2+</sup>, but this reaction, under our experimental conditions, has a half-life on the order of hours. The reaction between ferrate and phenol has a half-life on the order of seconds. The only influence of this decomposition reaction is a nonzero intercept that occurs in a plot of the concentration of phenol versus observed rate constant. The decomposition does not influence the reaction between ferrate and phenol. All of the ferrate solutions were prepared and used as quickly as possible so that the concentration of the ferrate was known at the beginning of each kinetic determination.

Nitrogen was bubbled through all solutions to remove dissolved oxygen. Experiments were conducted under pseudo-first-order conditions with phenol concentrations kept in excess. The ferrate concentrations were on the order of 10<sup>-4</sup> M. When D<sub>2</sub>O was the solvent, the buffer pD values were calculated<sup>39-42</sup> as pD = pH<sub>meter reading in D<sub>2</sub>O</sub> + 0.41. The observed rate constants were the average of five experimental runs for each phenol concentration. Temperature-dependent runs from 7.5 to 45 °C yielded activation enthalpies and activation entropies for the formation and decay processes of the intermediate. Volumes of activation were estimated from rate constants obtained at pressures ranging from ambient up to 62 MPa at 25 °C.

The final oxidation state of iron was identified visually and spectrophotometrically with use of potassium thiocyanate (KSCN).<sup>43-45</sup> A blood-red complex appearing when KSCN was added to the spent reaction mixture, which had an absorption peak at 480 nm, indicated Fe<sup>3+</sup> was the reaction product. Authentic samples of the reaction product of Fe(NO<sub>3</sub>)<sub>3</sub> and KSCN were used for comparison. GC/MS was used to determine organic products. The components of the reaction mixture were separated by a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 30-meter DB-5 capillary column, then detected and analyzed with a Hewlett-Packard Mass Selective Detector (MSD) model 5971A. The instrument was equipped with a Hewlett-Packard 6890 Series injector. For GC/MS measurements, the spent reaction mixtures were extracted with methylene chloride. The results indicate that *p*-benzoquinone is the end product in agreement with results published by Rush



**Figure 1.** Successive spectral changes at 0.4-s intervals during the oxidation of phenol (10.38 mM) by FeO<sub>4</sub><sup>2-</sup> (0.6 mM) at pH 9.85. Conditions: 25 °C, 0.05 mol dm<sup>-3</sup> Na phosphate buffer, in H<sub>2</sub>O.

et al.<sup>15</sup> *p*-Benzoquinone is also the major product of phenol oxidation by the pentaquaioxochromium(IV) ion.<sup>29</sup>

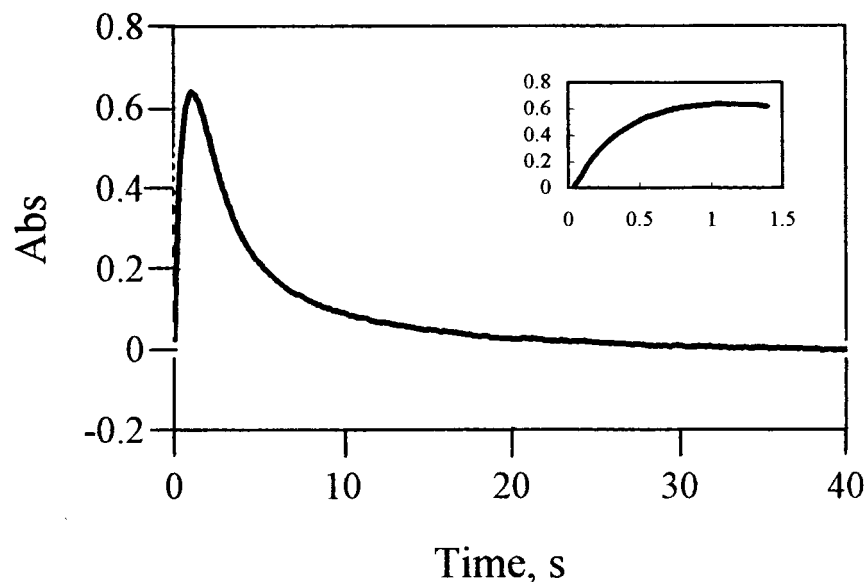
The EPR spectra were obtained using a Bruker 200D X-band electron paramagnetic resonance spectrometer. In the upgraded instrument, the klystron has been replaced by a 10-GHz solid-state Gunn diode microwave source, and the console has been replaced by a Bruker EMX data acquisition system with a PC computer workstation (Pentium 200). The EPR is outfitted with a TM<sub>110</sub> cylindrical cavity, which allows for greater sensitivity with aqueous solutions. All the spectra discussed in this article were obtained at 77 K using a liquid-nitrogen Dewar. Although use of liquid nitrogen cooling decreases the sensitivity of the instrument, it was necessary to quench the reactions to obtain EPR spectra of the relatively short-lived spin adducts. The spin-trap POBN was used in these experiments.

## Results

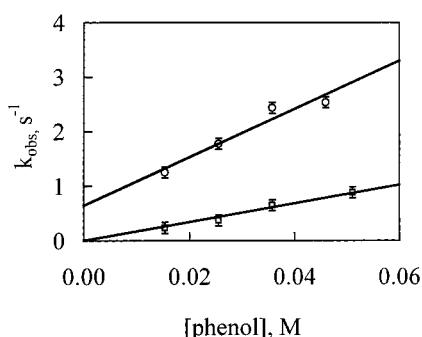
**Rate Law.** The mixing of aqueous phenol and ferrate(VI) leads to a series of solution color changes. The solution starts out purple, rapidly turns yellowish brown, and then slowly faded to colorless. The transient spectra arising from mixing phenol with K<sub>2</sub>FeO<sub>4</sub> are shown in Figure 1. The yellowish-brown intermediate has a maximum absorption at 400 nm. This absorption is typical for 4,4'-biphenquinone,<sup>34</sup> which is formed by the coupling of phenoxyl radicals followed by oxidation. The reaction products, *p*-benzoquinone and 4,4'-biphenquinone, are formed in rapid post-rate-controlling steps (vide infra). The kinetic measurements for these redox reactions were made under pseudo-first-order conditions with phenol present in 10-fold or greater excess over ferrate. Traces of the transmission of light versus reaction time are shown in Figure 2. The sequential first-order rate constants were evaluated by fitting the kinetic trace to a biexponential function:

$$A_t - A_\infty = \alpha \exp(-k_{\text{fast}}t) + \beta \exp(-k_{\text{slow}}t) \quad (1)$$

where  $A_t$  is the absorption value at 400 nm at time  $t$ ,  $A_\infty$  is an average of the last 10 absorption values of the kinetic trace, and  $\alpha$  and  $\beta$  are coefficients related to the molar absorption coefficient of the intermediate and the concentration of FeO<sub>4</sub><sup>2-</sup>



**Figure 2.** Absorbance change versus time at 400 nm for the redox process between phenol and  $\text{FeO}_4^{2-}$ . The inset shows the buildup of the intermediate in the first 1.5 s. Conditions: 25 °C, 0.05 mol  $\text{dm}^{-3}$  Na phosphate buffer, in  $\text{H}_2\text{O}$ .



**Figure 3.** Typical plots of  $k_{\text{obs}}$  versus the concentration of phenol at pH 9.85 for the fast stage (O) and the slow stage (□). Conditions: 25 °C, 0.05 mol  $\text{dm}^{-3}$  Na phosphate buffer, in  $\text{H}_2\text{O}$ .

ion.<sup>29</sup> In thermostated solutions, observed rate constants for both the fast stage and the slow stage display a linear relationship with phenol concentration as presented in Figure 3 for phenol in  $\text{H}_2\text{O}$ , at pH 9.85. The linear dependence is consistent with a rate law that is first-order with respect to phenol in the formation and the decay processes of the intermediate. The nonzero intercept for the first stage arises from decomposition of ferrate in aqueous solution. Measurements were also done in solutions buffered at pH 8.75. For both stages, no change in the rate constants was observed in the pH 8.75–9.85 range within experimental error, which is consistent with the report of Rush et al.<sup>15</sup> Therefore, for the oxidation of phenol by ferrate, the following rate law is observed:

$$\frac{d[\text{intermediate}]}{dt} = \{k_{\text{fast}}[\text{FeO}_4^{2-}][\text{phenol}] + C\} - k_{\text{slow}}[\text{intermediate}][\text{phenol}] \quad (2)$$

Similar measurements were performed in  $\text{D}_2\text{O}$  solvent, and the isotopic results are listed in Table 1. In this report, phenol is expressed as  $\text{C}_6\text{H}_5\text{-OL}$ . Because the phenol concentration is much smaller than that of the solvent in this report, when  $\text{D}_2\text{O}$  is used as solvent, the hydroxy hydrogen atoms of phenol rapidly exchange with deuterium,<sup>46</sup> and phenol is deuterated to  $\text{C}_6\text{H}_5\text{-OD}$  in  $\text{D}_2\text{O}$ .

**Temperature Dependence.** The activation enthalpy and entropy are estimated based on the expression of the transition state theory:

**TABLE 1: Rate Constants at 25 °C and Activation Parameters with Standard Deviation for Ferrate(VI) Oxidation of Phenol in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$ <sup>a</sup>**

	in $\text{H}_2\text{O}$	in $\text{D}_2\text{O}$
$k_{\text{fast}}$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$44 \pm 8$	$18 \pm 3$
$\Delta H_{\text{fast}}^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$35.7 \pm 4$	$56.3 \pm 19$
$\Delta S_{\text{fast}}^\ddagger$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$-94 \pm 12$	$-32 \pm 6$
$\Delta V_{\text{fast}}^\ddagger$ ( $10^{-6} \text{m}^3 \text{mol}^{-1}$ )	$-18 \pm 1$	$-17 \pm 1$
$K_{\text{slow}}$ ( $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$ )	$17 \pm 1$	$14 \pm 1$
$\Delta H_{\text{slow}}^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$44.2 \pm 11$	$30 \pm 1$
$\Delta S_{\text{slow}}^\ddagger$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$-73 \pm 33$	$-123 \pm 3$
$\Delta V_{\text{slow}}^\ddagger$ ( $10^{-6} \text{m}^3 \text{mol}^{-1}$ )	$-33 \pm 5$	$-26 \pm 5$

<sup>a</sup> The standard deviations were estimated from the experimental mean of four or more independent measurements.

$$k_i = (\kappa T/h) \exp(-\Delta G_i^\ddagger/RT) \quad (3)$$

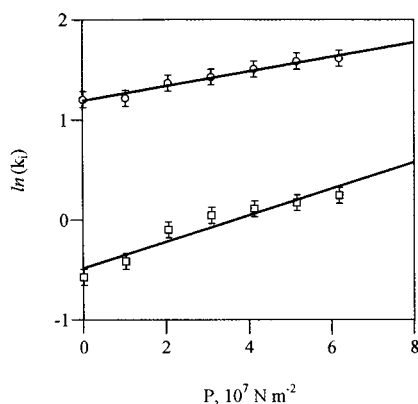
where  $\kappa$  is Boltzmann's constant,  $T$  is absolute temperature,  $h$  is Planck's constant,  $R$  is the gas constant, and  $\Delta G_i^\ddagger$  is the activation free energy, given by the activation enthalpy,  $\Delta H_i^\ddagger$ , and activation entropy,  $\Delta S_i^\ddagger$ , as  $\Delta G_i^\ddagger = \Delta H_i^\ddagger - T\Delta S_i^\ddagger$ . Kinetic measurements at several temperatures yielded activation energy plots for the formation and disappearance of the intermediate during the oxidation process of phenol by ferrate in  $\text{H}_2\text{O}$  and in  $\text{D}_2\text{O}$ , respectively. The activation parameters obtained are shown in Table 1.

**Pressure Dependence.** Rate constants for ferrate oxidation of phenol have been measured as a function of pressure at 25 °C. Plots of  $\ln(k_{\text{obs,fast}})$  or  $\ln(k_{\text{obs,slow}})$  versus pressure are shown in Figure 4, where  $k_{\text{obs,fast}}$  and  $k_{\text{obs,slow}}$  are observed rate constants for fast and slow steps, respectively. Volumes of activation have been evaluated by fitting eq 4 to these data,

$$\ln(k_i) = -\Delta V_i^\ddagger P/RT + \ln(k_{i0}) \quad (4)$$

where  $k_{i0}$  denotes the rate constants extrapolated to zero pressure. Significant pressure dependence of the rate constants was observed. Volumes of activation for each step are listed in Table 1.

**Kinetic Isotope Effects.** Kinetic measurements for ferrate oxidation of phenol using  $\text{D}_2\text{O}$  as solvent gave rise to the rate constants and activation parameters in  $\text{D}_2\text{O}$  exhibited in Table 1. The kinetic isotope effect is by convention the ratio of the



**Figure 4.** Pressure dependence to determine the activation volume change for the fast stage (O) and the slow stage (□). Conditions: 25 °C, 0.05 mol dm<sup>-3</sup> Na phosphate buffer, in H<sub>2</sub>O.

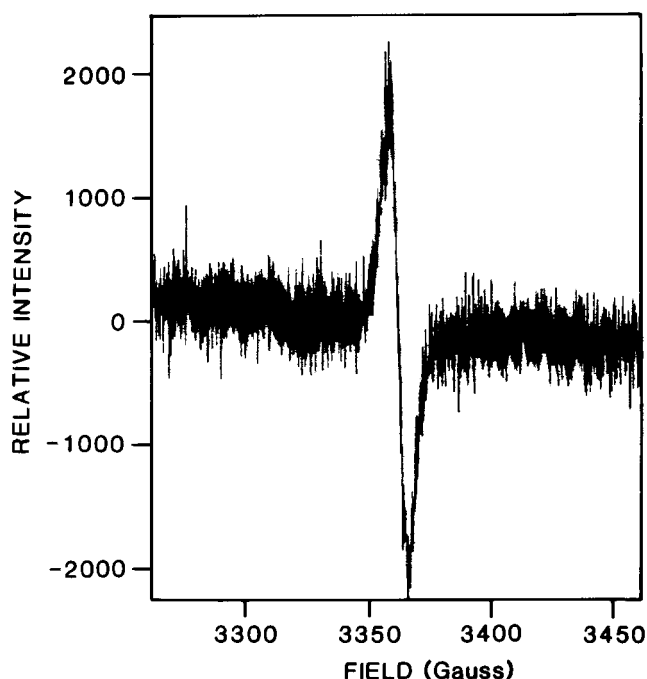
rate constant for the lighter-over-heavier isotope.<sup>47</sup> The switch from H<sub>2</sub>O to D<sub>2</sub>O solvent causes a decrease in  $k_{\text{fast}}$ , that is,  $k_{\text{fast}}^{\text{H}_2\text{O}}/k_{\text{fast}}^{\text{D}_2\text{O}} = 2.4 \pm 0.6$ . The corresponding kinetic isotope effect for the slower reaction is  $k_{\text{slow}}^{\text{H}_2\text{O}}/k_{\text{slow}}^{\text{D}_2\text{O}} = 1.2 \pm 0.1$ .

EPR spectra were obtained for this reaction. The reaction is too fast for the radicals to be detected without the aid of a spin trap. Therefore, POBN, the spin trap, was used to form a spin adduct that could be detected by EPR. POBN is water-soluble with an octanol–water partition coefficient of 0.09, and this molecule is diamagnetic and has no EPR signal of its own. The spin-trap adduct signal forms when the electron is transferred from the radical to the spin trap. A quenched 50 mM solution of POBN exhibits a very weak signal at  $g = 2.007$  because of a paramagnetic contaminant within the POBN. The quenched reaction of 50 mM phenol with 1 mM ferrate in the presence of 50 mM POBN yields an isotropic EPR signal that is significantly stronger than the contaminant signal (Figure 5). Because POBN is a diamagnetic species, a radical is produced within the reaction mixture and is trapped by the POBN, although lack of resolution prevented detection of the triplet signal. EPR spectra of the reaction components separately yielded nothing but noise for phenol and ferrate in the region of interest. Combinations of the reactants gave more interesting, but still negative results. Phenol and ferrate produce a minor EPR signal, but again, not much more than the noise. Ferrate and POBN yield a similar result: a minor triplet not much larger than the noise. Only when all three (phenol, ferrate, and POBN) are present do we obtain a significant EPR signal with a respectable signal-to-noise ratio. Unfortunately, the resolution of the signal is such that no detailed information about the radical adduct can be obtained from it. All that can be said from these data is that at some point within the first 10 s of the reaction, a radical species is produced and trapped by the POBN.

## Discussion

A plausible general mechanism for ferrate oxidation of phenol, consistent with the kinetic information and reaction products, follows. The proposed mechanism for the oxidation of phenol by the ferrate(VI) anion involves the formation of the phenoxyl radical in the first step. The phenoxyl radical then goes on to form the quinone and biphenols as products.

The observed<sup>15</sup> color changes during the mixing of phenol and  $\text{FeO}_4^{2-}$  correspond nicely with the results of the present research and support the mechanism given in Scheme 1. The reaction is initiated by the phenol uniting with  $\text{FeO}_4^{2-}$  to form the phenoxyl radical and  $\text{FeO}_4^{3-}$ . At this point, three separate



**Figure 5.** EPR spectrum for reaction mixture of  $\text{K}_2\text{FeO}_4$  (1 mM) and phenol (50 mM), trapped by POBN (50 mM) and quenched in liquid nitrogen. Experiments were performed with an x-band EPR (10 GHz) microwave frequency operating with 100-kHz magnetic field modulation. Spectrometer conditions were: modulation amplitude, 10 G; microwave power, 0.628 mW; time constant, 1.280 ms; scan range, 3162.01 ~ 3462.01 G; receiver gain,  $5.02 \times 10^4$ .

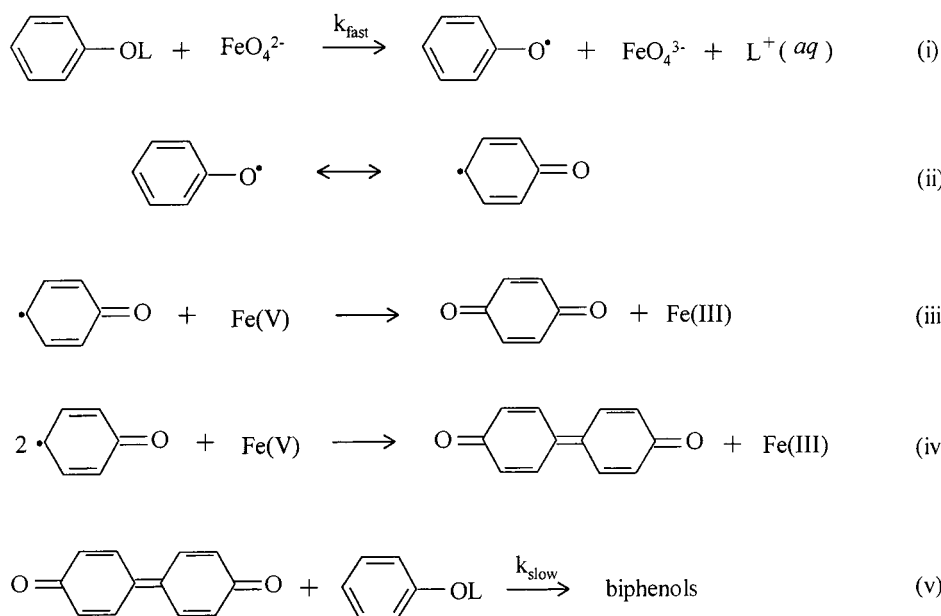
product pathways develop. Along the first pathway, the phenoxyl radical undergoes a 2-electron oxidation with the Fe(V) species to form *p*-benzoquinone. The second pathway results in the formation of the observed intermediate 4,4'-biphenolquinone. Again, this is a 2-electron process and results in the formation of an Fe(III) species.<sup>34</sup> The ferric ion is readily detected by complexation with  $\text{SCN}^-$  to form a blood-red solution. The third product is one that has not been seen spectroscopically. However, given the self-reactivity of the phenoxyl radical and evidence from other researchers,<sup>15</sup> it is postulated that polyphe-nols are reaction products. This is especially likely given the large excess of phenol in the reaction mixture.

The kinetic values of this reaction were determined by observing the formation and decomposition of the intermediate, 4,4'-biphenolquinone, at 400 nm. Although the Fe(V) species has a maximum absorption at 390 nm, Fe(V) and Fe(IV) react 2–3 orders of magnitude faster than Fe(VI) in aqueous solutions.<sup>15</sup> That being the case, any Fe(V) and Fe(IV) present have reacted long before our spectrophotometer would detect them. By monitoring the absorbance at 400 nm, a two-term rate law is obtained as eq 2. The first term in eq 2 represents the rate of formation of the phenoxyl radical as detected in the formation of the 4,4'-biphenolquinone. The intercept C included in this term accounts for the ferrate decomposition. The second term gives the rate at which the intermediate decomposes to biphenols. The kinetic data support this by yielding a first-order dependence on the phenol concentration. The reactions were also run at different pH values and showed no pH dependence. Again, this is consistent with the proposed mechanism, our kinetic results and similar experimental results obtained by Rush and co-workers.<sup>15</sup>

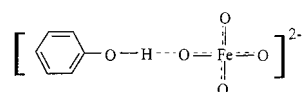
The proposed rate law is further supported by kinetic isotope and high-pressure studies. The initial step is the fast oxidation of phenol by ferrate. When phenol is placed in D<sub>2</sub>O, a rapid



## SCHEME 1



equilibration occurs resulting in the formation of  $\text{C}_6\text{H}_5\text{-OD}$ . When reacted with ferrate, a significant isotope effect is seen with  $k_{\text{fast}}(\text{H}_2\text{O})/k_{\text{fast}}(\text{D}_2\text{O}) = 2.4 \pm 0.6$ . This isotope effect indicates that the proton (or deuteron as the case may be) plays an active role in the transition-state species for this fast, initial step. Similar effects were measured for ferrate oxidation of propanol and mandelic acid,<sup>48</sup> and for phenol oxidation by the oxochromium(IV) anion.<sup>29</sup> The volume of activation and entropy of activation are both negative for this step as well. This indicates that the reaction mixture is becoming more organized as it goes from reactant to transition state or that the reaction proceeds through an associative type of mechanism and may involve hydrogen bond formation in the activated complex accompanied by intermolecular electron transfer. Given these data, the following transition-state species is proposed for the initial step of the mechanism:



The most direct evidence supporting the initial step of the mechanism is the EPR results. A spin trap, POBN, was used to react with the radical and form a spin adduct. As mentioned previously, the spectra obtained after trapping and quenching the reaction show an isotropic signal at  $g = 2.010$ . One would expect a triplet or distorted triplet that looks like an orthorhombic signal from a POBN spin-adduct species. The isotropic signal arises from a lack of resolution in the spectra due to anisotropic line broadening. This limits our ability to obtain detailed information from the spectra. However, it does not obscure the most important fact: a spin adduct has formed. The reaction does produce a radical species which is trapped by the POBN. Because this signal only occurs when phenol is present, we attribute it to the phenoxyl radical adduct.

Turning now to the 4,4'-biphenylquinone intermediate, this intermediate has a  $\lambda_{\text{max}}$  of 418 nm in acidic medium.<sup>29</sup>  $k_{\text{slow}}$  is the rate constant for the decomposition of this long-lived intermediate. This decomposition proceeds in the presence of excess phenol to form biphenol products.<sup>49,50</sup> There is no significant kinetic isotope effect for this step of the reaction when  $\text{C}_6\text{H}_5\text{-OD}$  is used as the reactant. As in the initial step of

the reaction, the volume of activation for  $k_{\text{slow}}$  is negative. This indicates that the reaction may go by way of an associative mechanism.

Further experiments were conducted to shed more light upon this aspect of the mechanism. The oxidation of *o*-, *m*-, and *p*-cresol by ferrate(VI) was examined. This experiment provides evidence regarding the nature of the phenoxyl radical involved in this reaction. It is believed that the *p*-phenoxyl radical is the most stable radical in this solution for the following reasons. When *p*-cresol is oxidized by ferrate(VI), no intermediate forms. The only resonance states available to the radical are at the *oxo* and *ortho* sites of the ring. Again, no intermediate is detected when *m*-cresol is oxidized by ferrate(VI). Although the *p*-phenoxyl radical is now possible, the presence of the methyl groups at the meta position sterically hinder formation of the intermediate. However, when *o*-cresol is oxidized by ferrate(VI), the intermediate grows and decays as it does in the unsubstituted phenol. The methyl groups occupying the *ortho* position on the ring prevent formation of the *ortho* radical, but are far enough away so as to not interfere with the active *para*-position.

Another experiment involved the oxidation of biphenol by ferrate(VI). In this experiment, the peak at 400 nm decayed much slower than in previous experiments. However, upon addition of phenol to the reaction mixture, the 4,4'-biphenylquinone vanished in a matter of seconds. As the proposed mechanism in Scheme 1 indicates, the decomposition process is driven by the presence of excess phenol.

Because an excess of phenol is used in the reaction, it is believed that the major product of this reaction is the formation of various polyphenols. The phenoxyl radical is very reactive, being very self-reactive and capable of either donating or accepting an electron. Phenol and 2,6-disubstituted phenols undergo oxidative coupling involving the loss of water to form polyphenylene ethers.<sup>51</sup> Rush and co-workers report the formation of polyphenols in their pulse-radiolysis studies of the reaction of phenol and ferrate(VI).<sup>15</sup>

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