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# Ferrate(VI) oxidation of aniline

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A detailed kinetic and thermodynamic study of ferrate(VI) oxidation of aniline (aminobenzene) has been carried out in isotopic solvents, $H_2O$ and $D_2O$, as a function of reductant concentration, solution pH, temperature and pressure by means of conventional stopped-flow and high-pressure stopped-flow spectrophotometric methods. Under pseudo first-order conditions with reductant in at least 10-fold excess over ferrate, these redox processes give rise to a simple exponential change of optical density. The temperature profile reveals relatively low activation enthalpies, and the activation entropies found for these processes are very negative. In addition, the significant negative activation volumes estimated from the pressure dependence of the rate constants indicate a substantial decrease in partial molar volume during the formation of the transition state, suggesting that highly structured transition states are formed in these reactions. An EPR result indicates a free radical reaction mechanism. The kinetic isotopic results for aniline systems measured in $H_2O$ and in $D_2O$ solvent indicate that the amino hydrogen/deuterium plays a role in the formation of the transition states.

## Introduction

Ferrate is of interest because of its role in biological reactions and industrial processes.[1–3] Since iron is ubiquitous in the environment and is largely tolerated in living systems, there is growing interest in the use of high-valent iron as an alternative to common oxidants, such as toxic chlorine, chromate, permanganate or ruthenate, in organic synthesis,[4] waste treatment,[5] and waste water treatment.[6–10] Sharma *et al.*[11–13] completed a series of studies on the use of Fe(VI) in treating sulfur-containing waste streams. High-valent iron has potential practical application in electrochemistry as well. The super-iron battery[14] is purported to have higher cathode capacity and a 50 percent energy advantage compared to conventional alkaline batteries.

Ferrate(VI) is a tetrahedral ion and is isostructural with chromate or permanganate.[15,16] So far, ferrate salts are the only high-oxidation-state complexes of iron which may be isolated as solids, and the potassium salt is indefinitely stable when kept dry. The ferrate anion ($FeO_4^{2-}$) decomposes spontaneously at a very rapid rate in neutral or acidic aqueous solution, but its stability increases with increasing solution pH.[17] Redox potentials for this strong oxidant are 2.20 V *vs.* NHE in an acidic medium and 0.72 V *vs.* NHE in alkaline solutions.[18]

High-pressure kinetic techniques have been particularly useful in the elucidation of reaction mechanism.[19–21] Such information supplies the intimate details of reaction mechanism including solvation–desolvation in the reaction process. In the same way that temperature-dependence investigations reveal the energetics along the reaction coordinate, pressure-dependence studies yield information on the volume profile of the process. By introducing one more experimental variable into the study, one can describe the reaction mechanism with greater confidence.

To our knowledge, volume profiles have not been established for ferrate chemistry. The volume of activation, $\Delta V^\ddagger$, is related to the difference between the partial molar volumes of initial and transition states. Associative mechanisms characteristically exhibit negative $\Delta V^\ddagger$ values and dissociative mechanisms positive $\Delta V^\ddagger$ values for reactions involving exchange of neutral ligands.[22,23] For redox reactions, intermolecular electron transfer is usually accompanied by a significantly negative activation volume.[24–26] Formation of highly charged complex species and bond-making also cause negative volumes of activation.[27]

Water soluble organic substances reduce potassium ferrate(VI) with very few exceptions.[28] Ferrate converts primary alcohols into aldehydes and secondary alcohols into ketones.[28–33] From the investigation of ferrate oxidation of hydrazine and monomethylhydrazine,[5] selenite,[34] and sulfur-containing compounds,[34–36] it appears that two-electron oxidation is a general feature of ferrate oxidations. However, Bielski, Thomas and Sharma[3,37] have observed Fe(VI) is reduced to Fe(V) by amino acids or $CO_2^-$ which indicates a one-electron oxidation mechanism. Sharma *et al.*[11–13] also report Fe(V) as a one-electron reduction intermediate when Fe(VI) reacts with hydrogen sulfide, cyanide or thiourea *via* radical reaction mechanisms. Johnson and Hornstein[4] have studied the ferrate oxidation kinetics of aniline and its *para*-substituted analogues. They found that the product of this reaction is highly dependent on the pH of the medium. It can be either a nitro-compound in 1 M $OH^-$ or an azo-product at pH 9. This selective transformation under relatively mild conditions has potential importance in synthetic chemistry. The present report focuses on extending the data to obtain more information on the essential characteristics of this reaction. Activation parameters, especially the activation volume determined for these redox processes, would be expected to shed more light on the reaction mechanism. In addition, a kinetic isotope effect and electron paramagnetic resonance (EPR) studies lend support to the reaction mechanism proposed in the present report.

A spin trap, POBN, was used in the present EPR study. The primary free radical produced in the ferrate reaction is so reactive and has such a low steady-state radical concentration that it cannot be observed directly by our conventional EPR

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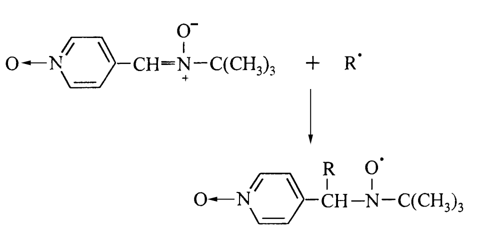
spectrometer. Spin trapping reactions involving POBN have the general form:[38]



(1)

This spin adduct is relatively stable but still paramagnetic and thus can be detected.

## Experimental

### Chemicals

Potassium ferrate ($K_2FeO_4$) was prepared by a procedure described by Audette and Quail,[39] in which potassium hypochlorite was used as the oxidizing agent and potassium hydroxide as the precipitation medium. The synthesized product was checked in the mid-IR and by UV-Vis spectrophotometric analysis at 510 nm ($\varepsilon = 1150\ M^{-1}\ cm^{-1}$, at pH 9.5).[37] Purity up to 90% was obtained. Read *et al.*[35] tested the thioxane oxidation by ferrate using ferrate with purities ranging from 40–90% and found the kinetic results were not affected by ferrate purity. The synthesized ferrate was kept in a vacuum desiccator to prevent slow decomposition caused by traces of water in air.

Aniline (99%) was purchased from Fisher Scientific. Deuterium oxide (99.9%) and *α*-(4-pyridyl-1-oxide)-*N*-*tert*-butylnitrone (POBN) (99%) were from Aldrich Chemicals. All other chemicals employed in this study were of analytical reagent grade and were used as received.

### Measurements

At ambient pressure the redox reactions were followed spectrophotometrically using a variable-temperature stopped-flow unit (Durrum-Gibson), combined with a photomutiplier tube (E 990–07, Hamamatsu Photonics K. K., Japan) assembly. Kinetic measurements at elevated pressure were carried out on a custom high-pressure stopped-flow system. The details of the detection system[40] and the high-pressure syringe system[41,42] have been described previously. Both stopped-flow spectrophotometers were interfaced with a computerized data collection system. At least 1000 points per kinetic trace were collected for analysis. All kinetic traces showed perfect first-order behavior over 10-half lives. Data fitting was done with custom-written software, through which results consistent with those calculated from the OLIS KINFIT set of programs (KINFIT version 3.0, Olis, Inc., Bogart, GA) were obtained. For all measurements, the temperature was controlled to ±0.1 °C.

The aqueous solutions were prepared by weight using 0.05 M sodium phosphate buffers in deionized water or $D_2O$ as solvent. The buffer solutions were filtered through Chelex 100 (Aldrich) to remove metal ions in the solutions, especially $Fe^{3+}$ ion.[43] All solutions were adjusted to pH 9–10 so that the decomposition of ferrate in aqueous solution was minimal.[33] In $D_2O$ solvent, the buffer pD values were calculated according to the pH meter reading using the following formula:[44–47] $pD = pH_{(\text{meter reading in } D_2O)} + 0.41$. The phosphate buffer also prevented precipitation of Fe(III) hydroxides. To remove dissolved oxygen, nitrogen gas was bubbled through all sample solutions. Single wavelength absorbance *versus* time traces were measured under pseudo first-order conditions with the reductant in at least 10-fold excess. The ferrate concentrations were about $5 \times 10^{-4}$ M. Each observed rate constant is based on an average of at least 5 independent rate measurements. Several rate constants at different temperatures ranging from 12–45 °C were obtained to evaluate the activation enthalpies and entropies for each rate-determining step. The volumes of activation were estimated from the rate constants at elevated pressures ranging from ambient pressure to 62 MPa at 25 °C.

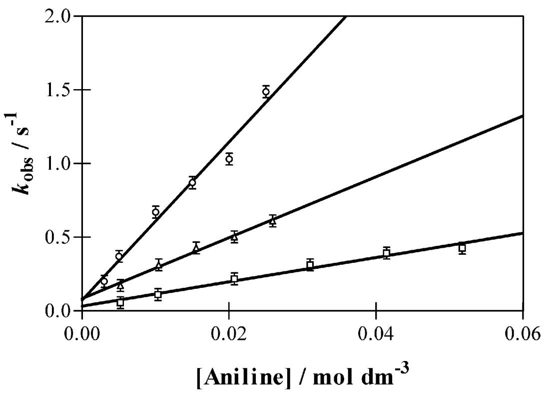


**Fig. 1** Typical plots of $k_{obs}$ *versus* the concentration of aniline at pH 8.99 (○), pH 9.53 (△), and pH 10.00 (□). Conditions: 25 °C, 0.05 M Na phosphate buffer, in $H_2O$.

pH values were determined with a Model 720A Benchtop pH meter (ORION) equipped with a Model 8102 Ross Combination pH electrode (ORION). A Bruker IFS 66/S FT-IR spectrometer was used to make the infrared measurements in this study.

X-Band electron paramagnetic resonance spectra were run with a Bruker 200D spectrometer upgraded with a 10 GHz solid state Gunn diode microwave source and a Bruker EMX data acquisition system. The EPR was outfitted with a $TM_{110}$ cylindrical cavity which allows for greater sensitivity with aqueous solutions. All the spectra discussed in this paper were obtained at 77 K using a liquid nitrogen dewar. A spin trap, POBN, was used in these experiments to obtain a relatively stable radical adduct from which an EPR signal can be seized. Therefore, the EPR spectra obtained are for the radical adduct species, not the radical itself.

## Results and discussion

### Rate law

The kinetic measurements for these redox reactions were made under pseudo first-order conditions. In thermostatted solutions, observed rate constants display a linear relationship with reductant concentration as presented in Fig. 1 for aniline in $H_2O$, at several pH values. The linear dependence indicates that the rate law is first-order with respect to the reductant. Therefore, for the oxidation of aniline by ferrate at a particular pH, we have the following rate law:

$$-d[\mathrm{Fe(VI)}]/dt = k_0[FeO_4^{2-}][\mathrm{Aniline}] \qquad (2)$$

One could add an additional term,[33] $k'[FeO_4^{2-}] + k''[FeO_4^{2-}]^2$, to account for the ferrate decomposition in aqueous medium. The decomposition reaction is at least three orders of magnitude slower[14] than the reaction between ferrate and aniline when the solution pH is in the 9–10 range and can be ignored for all practical purposes.

The second-order rate constants were measured in 0.05 M phosphate buffer at various solution pH (or pD) values. The measurements presented in Fig. 2 indicate a linear relationship in a plot of the second-order rate constants $k_0$ *versus* the hydrogen or deuterium ion concentration with a positive *y*-intercept, from which it is known that $k_0$ consists of a first-order acid dependent term along with a pH independent one. Thus $k_0$ in eqn. (2) can be expressed as $k_0 = k_3 + k_L[L^+]$, where L denotes H or D. Then, the overall rate law is presented as follows:

**Table 1** Rate constants and activation parameters for ferrate(VI) oxidation of aniline in $H_2O$ and in $D_2O$. The standard deviations were estimated from the experimental mean of four or more independent measurements

| | In $H_2O$ | In $D_2O$ |
|---|---|---|
| $k_L/10^{10}$ $M^{-2}$ $s^{-1}$ | 2.3 ± 0.3 | 3.9 ± 0.1 |
| $k_2/M^{-1}$ $s^{-1}$ | 365 ± 47 | 155 ± 5 |
| $\Delta H_2^‡$/kJ $mol^{-1}$ | 29.8 ± 1 | 33.7 ± 5 |
| $\Delta S_2^‡$/J $mol^{-1}$ $K^{-1}$ | −96 ± 1 | −92 ± 16 |
| $\Delta V_2^‡/cm^3$ $mol^{-1}$ | −28 ± 2 | −36 ± 3 |
| $k_3/M^{-1}$ $s^{-1}$ | 17 ± 3 | 9 ± 2 |
| $\Delta H_3^‡$/kJ $mol^{-1}$ | 24.3 ± 2 | 43.6 ± 1 |
| $\Delta S_3^‡$/J $mol^{-1}$ $K^{-1}$ | −141 ± 7 | −80 ± 3 |
| $\Delta V_3^‡/cm^3$ $mol^{-1}$ | −31 ± 3 | −25 ± 2 |

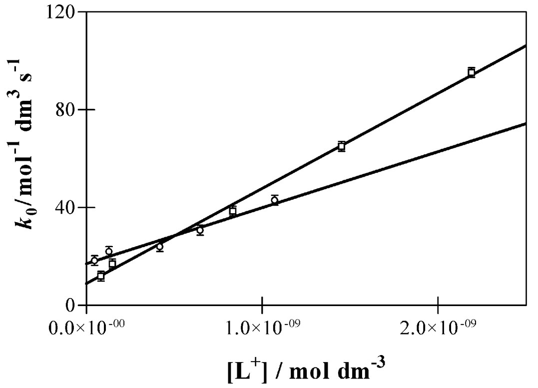


**Fig. 2** Observed rate constant as a function of $[H^+]$ (○, less steep line) or $[D^+]$ (□, more steep line) at 25 °C and atmospheric pressure.

$$-d[Fe(VI)]/dt = (k_3 + k_L[L^+])[FeO_4^{2-}][Aniline] \quad (3)$$

A similar rate law was reported for ferrate oxidation of hydrazine and monoethylhydrazine.[5] The values of $k_3$ and $k_L$ are listed in Table 1 for aniline oxidation in $H_2O$ and in $D_2O$.

Infrared spectroscopy was used to identify the organic product. The spent reaction mixtures were extracted with methylene chloride. The IR spectra showed azobenzene to be the end product. This is consistent with the results of Johnson and Hornstein[4] who used GC/FID to analyze the end products. The final oxidation state of iron was determined visually using potassium thiocyanate (KSCN). No red complex appeared when KSCN was added to the spent reaction mixture indicating that Fe(VI) was reduced to Fe(II) also in agreement with Johnson and Hornstein.[4]

On the basis of the above information, the following overall reaction is thought to occur in these experiments:

$$LFeO_4^- + FeO_4^{2-} + 4C_6H_5\text{–}NL_2 \rightleftharpoons 2Fe^{2+} + 2C_6H_5N{=}NC_6H_5 + 7OL^- + L_2O \quad (4)$$

where aniline is expressed as $C_6H_5$–$NL_2$ since the amino hydrogen atoms of aniline are replaced by deuterium when $D_2O$ is used as solvent.[48]

## Temperature dependence

The activation enthalpy and entropy can be calculated from the expression:

$$k_i = (\kappa T/h)\exp(-\Delta G_i^‡/RT) \quad (5)$$

where $\kappa$ is Boltzmann's constant, $T$ is the temperature in Kelvin, $h$ is Planck's constant, $R$ is the gas constant, and $\Delta G_i^‡$ is the activation free energy, expressed as $\Delta G_i^‡ = \Delta H_i^‡ - T\Delta S_i^‡$, where $\Delta H_i^‡$ is the activation enthalpy and $\Delta S_i^‡$ is the activation entropy. The activation energy plots for the oxidation of aniline by ferrate are shown in Fig. 3. The rate constants shown in Fig. 3 have been calculated taking into account the temperature dependence of the solution pH (or pD) that results due to the temperature dependence of the acid dissociation constant of the phosphate buffer.[49] The calculated activation parameters are presented in Table 1.

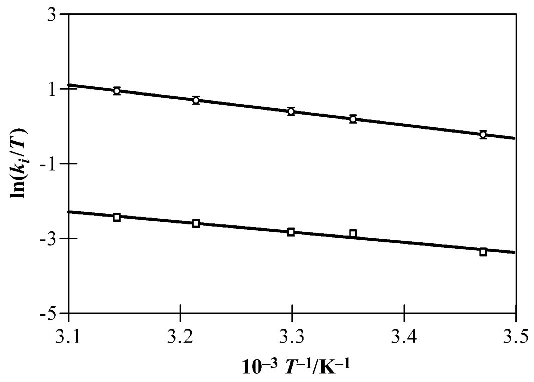


**Fig. 3** Eyring plots for ferrate(VI) oxidation of aniline for $k_2$ (○, upper line) and $k_3$ (□, lower line). Conditions: 0.05 M Na phosphate buffer, in $H_2O$.

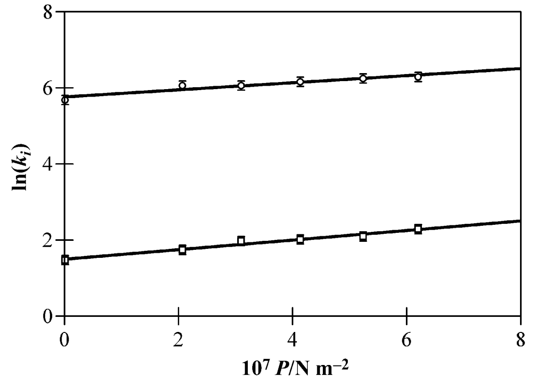


**Fig. 4** Pressure dependence to determine the activation volume of the reactions of ferrate(VI) oxidation of aniline for $k_2$ (○, upper line) and $k_3$ (□, lower line). Conditions: 25 °C, 0.05 M Na phosphate buffer, in $H_2O$.

## Pressure dependence

The pressure dependence of two rate constants is shown in Fig. 4. The plots exhibit significant pressure dependence. Volumes of activation have been calculated from the slope of these plots based on the following equation,[19–21]

$$\ln(k_i) = -\Delta V_i^‡ P/RT + \ln(k_{i0}) \quad (6)$$

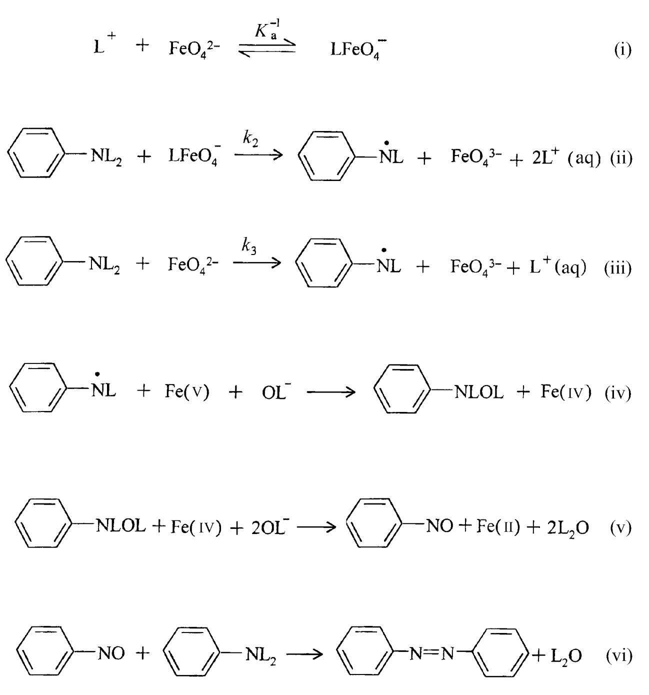
where $k_{i0}$ denotes the rate constants extrapolated to zero pressure, and $R$ and $T$ have their usual meanings. As both the acid dissociation constant of the phosphate buffer and the $HFeO_4^-$ species are pressure dependent, the calculations performed to obtain values for $k_2$ and $k_3$ have taken this into account. The $\Delta\bar{V}$ values used were −26.0 $cm^3$ $mol^{-1}$ for the second acid dissociation of phosphoric acid[20] and −23.6 $cm^3$ $mol^{-1}$ for the acid dissociation of $HFeO_4^-$. As the $\Delta\bar{V}$ for the acid dissociation of $HFeO_4^-$ is not known, it has been estimated to be the same as that for $HCrO_4^-$.[50] Volumes of activation for each step are listed in Table 1. The negative $\Delta V_i^‡$ along with the negative value of the activation entropy indicate the transition states have significantly lower partial molar volumes than the reactants, implying associative reaction mechanisms. These values suggest a bond-making process and intermolecular electron transfer.

## Kinetic isotope effects

Measurements for ferrate oxidation of aniline using $D_2O$ as solvent have been made to determine the kinetic isotope effects. The rate constants and activation parameters in $D_2O$ are exhibited in Table 1. The kinetic isotope effect is defined as the ratio of measured parameters caused by an isotopic exchange and is used as lighter-over-heavier isotope.[51] When $D_2O$ is the solvent, a decrease in both rate constants was observed, *i.e.* $k_2(H_2O)/k_2(D_2O) = 2.4 \pm 0.3$ and $k_3(H_2O)/k_3(D_2O) = 1.9 \pm 0.3$. Combined with the negative values of activation entropy and activation volume these results suggest that the amino hydrogen/deuterium atoms of aniline play a role in the bond-making process.

### Mechanistic interpretation

A plausible general mechanism for ferrate oxidation of aniline, consistent with the above kinetic information and reaction products, is shown in Scheme 1.



**Scheme 1**

The equations in Scheme 1 are not balanced, since the unstable Fe(IV) complex has not been characterized, though it has been observed in pulse radiolysis studies.[37,52] Steps (ii) and (iii) are thought to be the rate-determining steps. According to this scheme, $k_L$ is a composite of $k_2$ and $K_a$:

$$k_L = k_2 K_a^{-1} \qquad (7)$$

$K_a$ is the dissociation constant of $LFeO_4^-$. For $HFeO_4^-$, its $pK_a$ is 7.8.[53] The relationship between $K_a$ in $H_2O$ and that in $D_2O$ is estimated as:[44]

$$pK_a(\text{in } D_2O) \approx 1.02pK_a(\text{in } H_2O) + 0.42 \qquad (8)$$

Thus the $pK_a$ for $DFeO_4^-$ in $D_2O$ is calculated to be 8.4. These $K_a$ values were employed for the determination of $k_2$ from $k_L$ using eqn. (7). These $k_2$ values are listed in Table 1. Note that $k_2$ for step (ii) is one order of magnitude greater than $k_3$ for step (iii) both in $H_2O$ and in $D_2O$. This can be attributed to the enhanced reactivity of $LFeO_4^-$ as compared to $FeO_4^{2-}$.[29,33]

The negative activation entropy, activation volume values and the kinetic isotope effects are consistent with a transition complex of the form shown below.

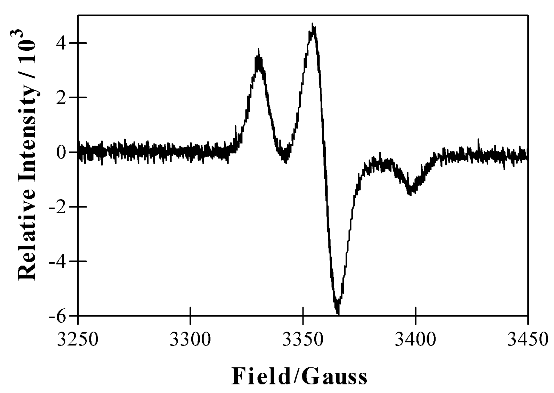
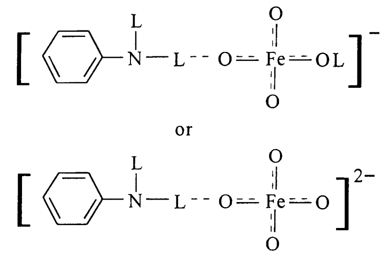


**Fig. 5** EPR spectrum for a reaction mixture of $K_2FeO_4$ (1 mM) and aniline (50 mM), trapped by POBN (50 mM) and quenched in liquid nitrogen. Experiments were carried out with an X-band EPR (10 GHz) microwave frequency operating with 100 kHz magnetic field modulation. Spectrometer conditions were: modulation amplitude 10 G; microwave power 0.625 mW; time constant 1.280 ms; scan range 3150.00–3450.00 G; receiver gain $5.02 \times 10^4$.



This sort of compressed transition state can only result from a predominantly bond-making process, *i.e.* an associative mechanism.

The proposed mechanism for the oxidation of aniline by the ferrate(VI) anion involves a formation of the anilino radical. The anilino radical then goes on to form a phenylhydroxylamine. In investigating this proposed radical mechanism, EPR spectra were sought of the anilino radical.

For effective spin trapping, spin trap concentrations often must be high ($10^{-2}$ to $10^{-1}$ M). POBN is quite water soluble and 50 mM POBN aqueous solution can be prepared. This molecule is diamagnetic with no EPR signal of its own. The spin-trap adduct signal forms when the electron is transferred from the radical to the spin-trap as shown in eqn. (1). The quenched reaction of 50 mM aniline with 1 mM ferrate in the presence of 50 mM POBN yields a triplet EPR signal (Fig. 5) at $g_1 = 1.994$, $g_2 = 2.012$ and $g_3 = 2.027$. Since POBN is a diamagnetic species, this means that a radical is produced within the reaction mixture and is trapped by the POBN. EPR spectra for each reaction component and combination of two of these three components (aniline, ferrate and POBN) yielded nothing other than noise in the region of interest. Therefore, it can be concluded that within the first 10 seconds of the reaction, a radical species is produced and trapped by the POBN. Because this signal only occurs when aniline is present, we attribute it to the anilino radical. Though the structure of the EPR signal is similar to that for the mixed-valence Fe(II)–Fe(III) species,[54] the observed $g_2$ and $g_3$ values for this signal are too large (>2.000) to be attributed to the Fe(II)–Fe(III) mixed-valent species.

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