

# Reactivity of Superoxide toward Iron(II) Complexes with Pentadentate and Hexadentate Ligands Derived from Cyclononane

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The reactivity of superoxide toward two iron(II) complexes, one with the pentadentate ligand  $N,N'$ -di-2-picoly-4,7-diaza-1-oxacyclononane (DPC) and the other with the hexadentate ligand  $N,N',N''$ -tripicoly-1,4,7-triazacyclononane (TPC), has been examined using a range of electrochemical, spectroelectrochemical, and spectroscopic techniques. Repetitive cyclic voltammograms of both complexes indicate the formation of electrically conductive polymers on the electrode surface at negative potentials under aerobic conditions. Presumably, this electropolymerization is initiated by a hypervalent iron species obtained as a final product of the electroreduction of dioxygen in the presence of the complexes. Under nonaqueous conditions, both complexes react with superoxide giving pseudo-first-order rate constants:  $\text{Fe}(\text{DPC})^{2+}$ ,  $100 \pm 10 \text{ s}^{-1}$ , and  $\text{Fe}(\text{TPC})^{2+}$ ,  $335 \pm 30 \text{ s}^{-1}$ . The results of stopped-flow and potential-step spectroelectrochemical measurements were consistent with formation of an iron(III)–peroxo adduct as an intermediate in the reaction. The final product of the reaction of  $\text{Fe}(\text{TPC})^{2+}$  with superoxide appears to be the iron(III) complex as indicated by UV–visible and ESR spectroscopy, but for  $\text{Fe}(\text{DPC})^{2+}$  the product is a modified iron(III) complex that is ESR silent.

## Introduction

One of the quandaries of nature is that while many forms of life depend on the reduction of dioxygen during respiration, the intermediates in the net four-electron reduction of dioxygen to water are both highly reactive and destructive toward biological tissue.<sup>1</sup> Superoxide, the one-electron-reduction product of dioxygen has received much attention since, among other deleterious contributions, it has been implicated as a cause of tissue inflammation following injury, symptoms of ageing, and some cancers.<sup>2</sup> The effects could either arise from the reactivity of superoxide itself or from the hydroxyl radical intermediate derived from superoxide. In defence of a biological entity, the effects of superoxide are kept to a minimum by the action of the superoxide dismutase (SOD)<sup>3</sup> family of enzymes, variants of which are ubiquitous throughout living systems. This reactivity has been harnessed by phagocytes for the destruction of bacteria and other unwanted microorganisms.<sup>4</sup> There is much interest in developing synthetic transition metal complexes which are able to mimic the effects of these enzymes, as they would be expected to have considerable therapeutic potential.<sup>1(c),5</sup> Furthermore, superoxide has been found to be an active intermediate in the autoxidation of heme proteins, such as hemoglobin<sup>6</sup> and synthetic models.<sup>7</sup>

Consequently, there is considerable interest in understanding the reactivity of synthetic metal complexes with superoxide, for the development of SOD mimics, but also due to the interest in

expanding the chemistry of oxygen species with transition metal complexes. The chemistry of superoxide anion and the chemistry of oxygen species have recently been reviewed.<sup>8</sup>

Many iron complexes have been found to react with superoxide and to be active catalysts for its disproportionation.<sup>9</sup> Furthermore, in the presence of substrates, a number of iron complexes catalyze the oxidation of various organic functionalities by superoxide.<sup>10</sup> In contrast, the addition of superoxide to iron(III)–porphyrin complexes is known to yield the iron(III)–superoxide adduct  $\text{LFe}^{\text{III}}(\text{O}_2^-)$ , which is equivalent to the iron(II)–dioxygen adduct,<sup>11</sup> ultimately, the  $\mu$ -oxo dimer<sup>12</sup> may be formed. The formation of the dioxygen adduct by reaction between superoxide and the iron(III) compound has also been observed with hemoglobin.<sup>6d,13</sup> In general, it has been found that the nature of the reaction between

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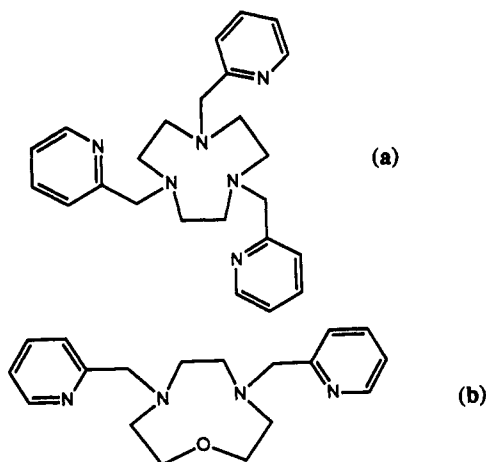


Figure 1. Planar representation of (a) TPC and (b) DPC ligands.

superoxide anion and transition metal complexes is dependent upon both the experimental conditions and, especially, the nature of the metal and the ligand of the complex. Thus it is of great interest to examine how changes in ligand structure affect the reactivity toward superoxide anion of otherwise similar metal complexes.

With this in mind, the reactivities of two iron(II) complexes with superoxide anion have been investigated. Both complexes (Figure 1) are based on substituted cyclononane ligands, the first complex [(*N,N'*-dipicolyl-4,7-diaza-1-oxacyclononane)iron(II); Fe(DPC)<sup>2+</sup>] incorporates a pentadentate ligand, whereas the second complex [(*N,N',N''*-tripicolyl-1,4,7-triazacyclononane)iron(II); Fe(TPC)<sup>2+</sup>] contains a hexadentate ligand. Comparison of the reactivities for the two complexes with superoxide anion provides insight into the influence of ligand structure in determining the behavior of the complexes with reduced dioxygen species. The reactivities of both iron(II) complexes with superoxide, generated *in situ* electrochemically and by reaction with solutions of potassium superoxide under aprotic conditions, have been investigated.

### Experimental Section

**Synthesis of Complexes.** The synthesis of the complexes FeTPC<sup>2+</sup> and FeDPC<sup>2+</sup> was accomplished as described previously.<sup>14</sup>

**Materials.** Solvents and reagents were the highest grade available and were found to be sufficiently pure for use as supplied. Where necessary, solvents were dried by prescribed techniques.<sup>15</sup> Saturated solutions of potassium superoxide in either anhydrous acetonitrile or DMSO were prepared as described by Riley and co-workers.<sup>16</sup> The UV-visible spectrum of the potassium superoxide in acetonitrile reveals several strong absorbance bands at 260 and 296 nm, which overlap with those of the hydrogen peroxide anion. The addition of a small quantity of water results in the rapid disappearance of a band centered at 296 nm, indicating that this band corresponds to superoxide, since superoxide is known to disproportionate rapidly in the presence of water.

**Physical Techniques.** UV-visible spectra were recorded on either a Varian 2300 spectrophotometer or a Hewlett-Packard 8452 diode array spectrophotometer, with a 9000 (300) Hewlett-Packard Chem Station computer. Both instruments incorporated flow-through temperature-regulated cell holders connected to a Neslab constant-temperature circulation system, giving a temperature precision of  $\pm 0.3$  °C.

Rapid kinetic experiments were performed on a Durrum Dionex stopped-flow spectrophotometer Model D-110, interfaced with a Northstar Horizon computer. The software for data acquisition and data processing was provided by On-line Instrument Systems Inc. Temperature control was maintained by circulating the water in the stopped-flow water bath through a Neslab RTE-8 temperature control unit.

All inert atmosphere manipulations were performed in a dry nitrogen filled Vacuum Atmospheres Corp. (VAC) glovebox, equipped with a gas circulation and oxygen removal system, either a VAC MO40-1 or HE-493 dry train. Oxygen concentrations were maintained below 1 ppm.

ESR spectra were recorded with a Varian E-112 spectrometer operating in the X-band. Samples were run as frozen glass samples in round quartz tubes at the boiling point of liquid nitrogen (77 K).

Fast atom bombardment mass spectra (FAB) were obtained with a Ribermag R10-10 mass spectrometer, using either nitrobenzyl alcohol (NBA) or a 3:1 mixture of dithiothreitol and dithioerythritol (alias magic bullet, MB) as matrices.

Electrochemical experiments were performed using a three-compartment cell. The working electrode was either a 3-mm-diameter glassy carbon electrode in Kel-F, (Bioanalytical Systems), a 1-mm glassy carbon electrode (Cypress Systems), or a polished glassy plate (Tokai Carbon Co., Ltd.) with a surface area of 1.05 cm<sup>2</sup>; the secondary electrode was a platinum wire separated by a glass frit from the working electrode compartment and the reference electrode was Ag/AgCl in the solvent of the experiment with supporting electrolyte (for reference electrode in a 1 M aqueous solution of KCl,  $E^\circ = 0.198$  V vs NHE; in a 0.1 M acetonitrile solution of Bu<sub>4</sub>NBF<sub>4</sub>,  $E^\circ = 0.09$  V vs NHE) separated from the main compartment by a capillary formed by sealing a platinum wire in glass. The experiments used a Princeton Applied Research (PAR) programmer, Model 175, and PAR potentiostat, Model 173, and the output was directly recorded on paper using a Houston Instruments Model 200 XY recorder. Aqueous solutions typically contained 1 M KCl as supporting electrolyte, and in nonaqueous solvents, the supporting electrolyte was 0.1 M tetrabutylammonium tetrafluoroborate (Southwestern Analytical Chemicals, Electrometric grade).

Spectroelectrochemical experiments (SEC) were performed using a cell containing closely spaced polished glassy carbon (Tokai Carbon Co. Ltd.) electrodes parallel to the optical beam, as described in more detail elsewhere.<sup>14a</sup>

### Results

**Electrochemistry.** As previously reported,<sup>14a</sup> cyclic voltammograms of Fe(DPC)<sup>2+</sup> in acetonitrile exhibit a reversible one-electron redox couple, at  $E_{1/2} = 0.71$  V vs NHE, with no other Faradaic processes observed in the absence of dioxygen over the potential range 2.0 to  $-1.7$  V.

Cyclic voltammograms of the dioxygen solution in the absence of the iron(II) complex showed only a reversible couple corresponding to the O<sub>2</sub>/O<sub>2</sub><sup>-</sup> redox couple at  $E_{1/2} = -0.81$  V vs NHE,  $\Delta E_p = 150$  mV (see Figure 2a), similar to that reported previously.<sup>8a,17</sup> The reversibility of the dioxygen/superoxide redox couple confirms the anhydrous nature of the solvents under the experimental conditions employed in this work.

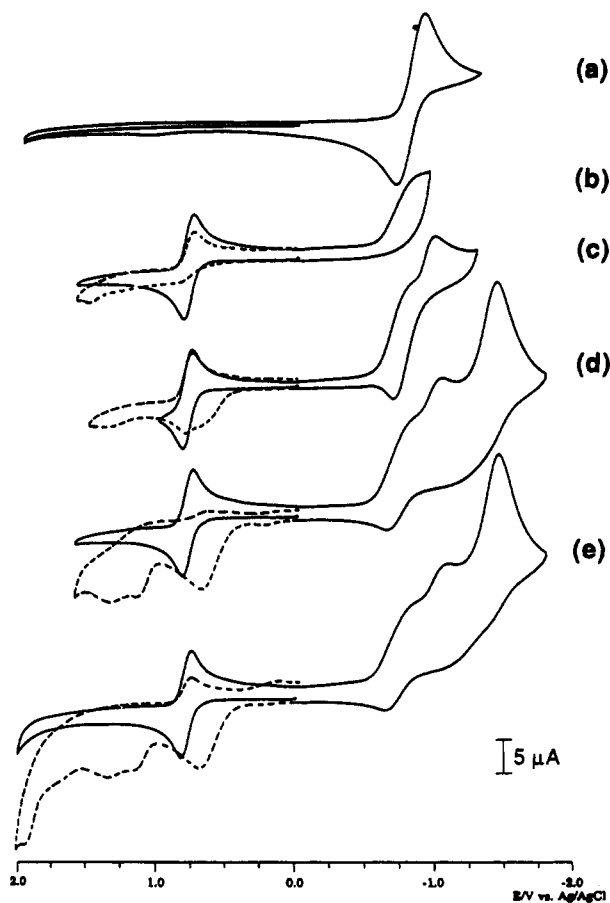
Cyclic voltammograms of the solutions of the Fe(DPC)<sup>2+</sup> in the presence of nearly a double excess of dioxygen are shown in Figure 2. It may be seen that, on the initial anodic sweep, the iron(III)/(II) redox couple remained unchanged by the presence of dioxygen, indicating that neither the iron(III) nor the iron(II) complexes react with dioxygen. In contrast, the reversible dioxygen reduction peak has been replaced by an totally irreversible reduction at a potential slightly more positive than the O<sub>2</sub>/O<sub>2</sub><sup>-</sup> redox couple,  $E_p = -0.74$  V. After sweeping anodically from a potential just negative of this dioxygen reduction process, oxidation of the iron(II) complex was severely inhibited, as shown in Figure 2b. This observation is consistent with reduction of dioxygen to superoxide, followed by reaction of superoxide with the iron(II) complex, resulting in a product which is insoluble and blocks the electrode surface. Extending the negative potential to  $-1.3$  V, an additional cathodic peak is observed at  $E_p = -1.05$  V, with an associated anodic peak at  $-0.71$  V (Figure 2c). This process may arise from simple reduction of dioxygen to superoxide, since this anodic peak is not observed when the iron(II) complex concentration is greater than that of dioxygen. At more negative potentials a third totally irreversible process is observed at  $-1.41$

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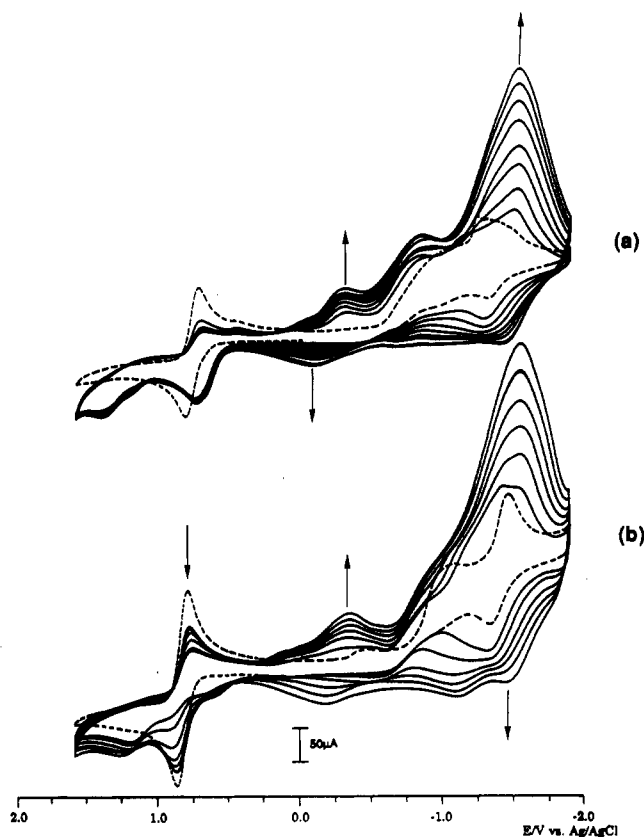
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**Figure 2.** Cyclic voltammograms of acetonitrile solutions containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> (a) saturated by air ( $\sim 2.0$  mM O<sub>2</sub>)<sup>8a</sup> or (b–e) containing 1.4 mM Fe(DPC)ClPF<sub>6</sub> and  $\sim 2.0$  mM O<sub>2</sub> and recorded over different scan ranges. Broken line indicates reverse scan. Scan sweep 0.2 V/s; temperature 25 °C.

V, as shown in Figure 2d,e. Presumably this peak corresponds to the further reduction of the product formed on reaction of superoxide and Fe(DPC)<sup>2+</sup>. Under conditions where the complex concentration exceeds that of the dioxygen, this reduction process has an initial sharp spike, indicative of a surface-bound reduction process. Associated with this latter wave, several new oxidative processes were observed on the subsequent anodic sweep at  $E_p = 0.70, 1.14, 1.35,$  and  $1.91$  V. Multiple sweeps over the potential range from 1.6 to  $-1.75$  V depicted in Figure 3a show a behavior that is consistent with the formation of an electrically conducting polymer on the electrode surface. Similar electrochemical response has been observed during electropolymerization of pyrrole, aniline, and thiophene.<sup>18</sup> The possibility that the buildup of current at very negative potentials might be due to the plating out of the metal is eliminated because of the absence of a typical sharp anodic peak. The graph of peak current vs number of scans is consistent with formation of a thin film, possibly a monolayer. For thick-film formation, the current should not change with the number of scans, but in this system the peak current reaches a plateau after  $\sim 16$  scans. Curiously, this electropolymerization is much more prevalent under conditions where the concentration of Fe(DPC)<sup>2+</sup> is in excess over that of the dioxygen. Under conditions when the dioxygen concentration is in excess, electropolymerization is still observed; however, the extent is greatly reduced.

It is probable that the new anodic peaks described above correspond to oxidation of either the iron(II) metal centers or the



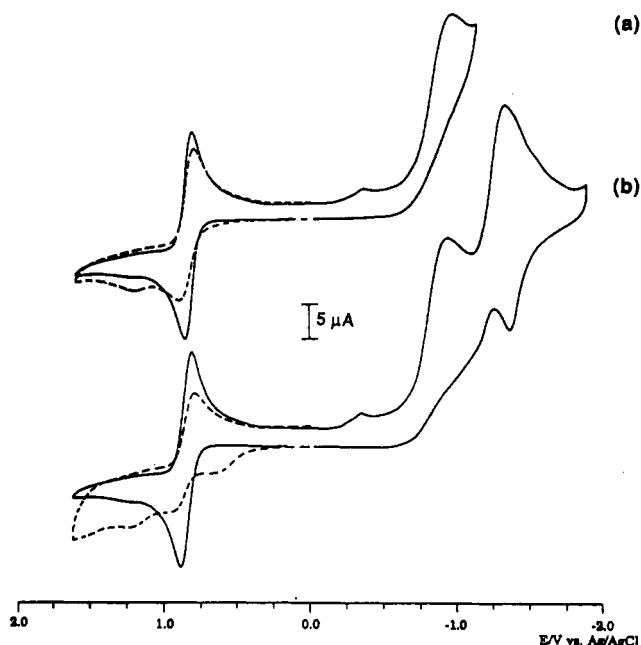
**Figure 3.** Repetitive cyclic voltammograms of acetonitrile solution of 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> saturated by air ( $\sim 2.0$  mM O<sub>2</sub>)<sup>8a</sup> (a) containing 5.4 mM Fe(DPC)ClPF<sub>6</sub> or (b) 8.3 mM Fe(TPC)(PF<sub>6</sub>)<sub>2</sub>. Broken line indicates first scan. Scan sweep, 0.2 V/s; temperature 25 °C.

peroxide species produced by the net reduction of dioxygen. Assignment of the oxidative processes is difficult, since the iron(II) complex has been chemically modified and the electrochemical properties of the electrode surface have been changed by the electropolymerization process. Similarly, the new quasi-reversible process at  $\sim -0.25$  V probably corresponds to an iron(III)/(II) couple within the polymer matrix, although the exact nature of this species remains unknown.

The cyclic voltammograms of Fe(TPC)<sup>2+</sup> in acetonitrile in the presence of dioxygen, shown in Figure 4, resemble those with Fe(DPC)<sup>2+</sup>, both for single sweeps and multiple sweeps. In contrast to Fe(DPC)<sup>2+</sup>, the reduction process of Fe(TPC)<sup>2+</sup> at  $\sim -1.45$  V has a more pronounced anodic process ( $E_p = -1.38$  V) associated with it on the reverse sweep. Moreover, the iron(III)/(II) redox couple of the complex ( $E_{1/2} = 0.74$  V vs NHE) is less inhibited. These contrasts may reflect minor differences in polymer morphology between the two complexes. Overall it appears that Fe(DPC)<sup>2+</sup> and Fe(TPC)<sup>2+</sup> undergo similar behavior in the presence of dioxygen under reducing conditions. Both complexes exhibit evidence for reaction of superoxide and formation of an electrically conducting polymer on the electrode surface upon further electroreduction (see Figure 3).

**Spectroelectrochemistry.** A series of spectroelectrochemical experiments were undertaken in order to gain better insight into the nature of the reactions described in the preceding section. The examination of the reduction of dioxygen in dry acetonitrile in a spectroelectrochemical cell, having glassy carbon electrodes parallel to the optical beam, revealed the formation of an absorbance band at  $\lambda_{\text{max}} = 246$  nm upon applying a potential sufficiently negative to reduce dioxygen. At more positive potentials this absorbance band disappeared. This result is consistent with the cyclic voltammetry and the known absorption spectrum of superoxide, ( $\lambda_{\text{max}} = 246$  nm); others have reported<sup>17</sup> that superoxide can be generated at the electrode and examined by spectroscopic techniques.

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**Figure 4.** Cyclic voltammograms of acetonitrile solution of 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> saturated by air (~2.0 mM O<sub>2</sub>)<sup>8a</sup> and containing 3.3 mM Fe-(TPC)(PF<sub>6</sub>)<sub>2</sub> over different scan ranges. Broken line indicates reverse scan. Scan sweep 0.2 V/s; temperature 25 °C.

As described previously,<sup>19</sup> upon electrooxidation of Fe(DPC)<sup>2+</sup>, two new overlapping bands, centered at 312 and 358 nm, developed and a small decrease was observed in the MLCT band, ( $\lambda_{\text{max}} = 396$  nm) at wavelengths greater than the isosbestic point at 385 nm. During this change, the absorbance for the ligand band at 260 nm increased by a factor of ~2. On return to potentials negative of the iron(III)/(II) redox couple, the spectra reverted to that of the original complex. At potentials more negative than that corresponding to the reduction of dioxygen and in the presence of the iron complex, spectral changes were observed that were not assignable to the known iron(II) or the iron(III) complexes, as shown in Figure 5. Spectroelectrochemical examination of the solution at the potential corresponding to the first dioxygen reduction wave,  $E_p = -0.75$  V vs Ag/AgCl, revealed that during this reduction process both the MLCT band and the ligand band decayed. Of signal importance, the observation that these two bands decay at the same rate indicates removal of the complex from solution rather than demetalation. These spectroscopic data are consistent with the cyclic voltammetric evidence for coating of the electrode during this reduction process. However, in the potential range corresponding to the second reduction wave ( $E_p = -1.30$  V), the absorbances of the MLCT and ligand bands increased again, indicating that the product of this reaction is soluble.

On the anodic sweep of the cyclic voltammogram, after the scan direction was reversed at  $-1.30$  V, the spectrum obtained at 0.0 V was similar to, but not identical to, that of the known iron(III) complex. At the potential of the new anodic peak ( $E_p = 0.75$  V), which appeared after the interaction of the complex with reduced dioxygen, the UV-visible spectral changes were consistent with the formation of the known iron(II) complex, but the intensities of the absorption bands were reduced from those of the original iron(III) solution. This result is consistent with some of the iron complex being consumed during the electropolymerization process.

These processes can be seen clearly in the inset of Figure 5, which shows the absorbance changes at 312 nm that occur when the potential is set to values sufficient, respectively, to oxidize the

complex to iron(III), reduce it again to iron(II), reduce dioxygen to superoxide, and oxidize superoxide to dioxygen again. Oxidation of the complex results in an increase in absorbance at 312 nm, as described above. When the potential is stepped to  $-1.3$  V, the absorbance change increases ~75% more than found for simple oxidation of the complex. When the potential is stepped back to 0 V, a potential at which free superoxide would be oxidized to dioxygen, the absorbance at 312 nm resembled that of Fe-(DPC)<sup>3+</sup> and decayed thereafter, as shown in the inset of Figure 5. It may be noted that, at  $E = 0.0$  V, the known iron(III) complex is expected to be electroreduced to the corresponding iron(II) complex; however, the spectroscopic data and the full spectrum of the product shown in Figure 5 (dotted line) suggested that another iron(III) species was present in solution which was stable in that potential range. It might be a hydroxy species, [Fe(DPC)OH]<sup>2+</sup> or a peroxy adduct [Fe(DPC)O<sub>2</sub>]<sup>+</sup> of the iron(III) complex. On stepping to 0.8 V, a potential sufficient to oxidize Fe(DPC)<sup>2+</sup>, the absorbance decreased to a value below that for the initial iron(III) complex, rather than increasing. This behavior, and also the slow decay of this absorbance at 0.0 V, as described above, may be due to the oxidation of small amounts of hydrogen peroxide, generated in the solution during the electroreduction of dioxygen, and/or hydrolysis of the final product. This result also indicates that some of the iron(II) complex has been lost from the solution, a result that is consistent with the electropolymerization process of the Fe(DPC)<sup>2+</sup>.

Concluding, it is suggested that the initial product formed between the iron(II) complex and superoxide is, formally, the iron(III)-peroxy adduct, [Fe(DPC)O<sub>2</sub>]<sup>+</sup>, rather than the hydroxy species, [Fe(DPC)OH]<sup>2+</sup>, since the latter is easily reduced into the iron(II)-hydroxy complex, at  $E = 0.0$  V, which does not exhibit any absorbance at 312 nm, as described earlier.<sup>14a,19</sup> This adduct is insoluble in acetonitrile, and its reduction on the electrode surface at potentials more negative than  $-1.3$  V initiates the polymerization. Therefore, this peroxy species is expected to be stable as the iron(III) complex at 0.0 V and to have a UV-visible spectrum analogous to that of the simple iron(III) complex. Further, in acetonitrile the [Fe(DPC)O<sub>2</sub>]<sup>+</sup> adduct undergoes slow hydrolysis, liberating hydrogen peroxide which, typically, is oxidized at potentials around  $E = 0.8$  V.<sup>20</sup>

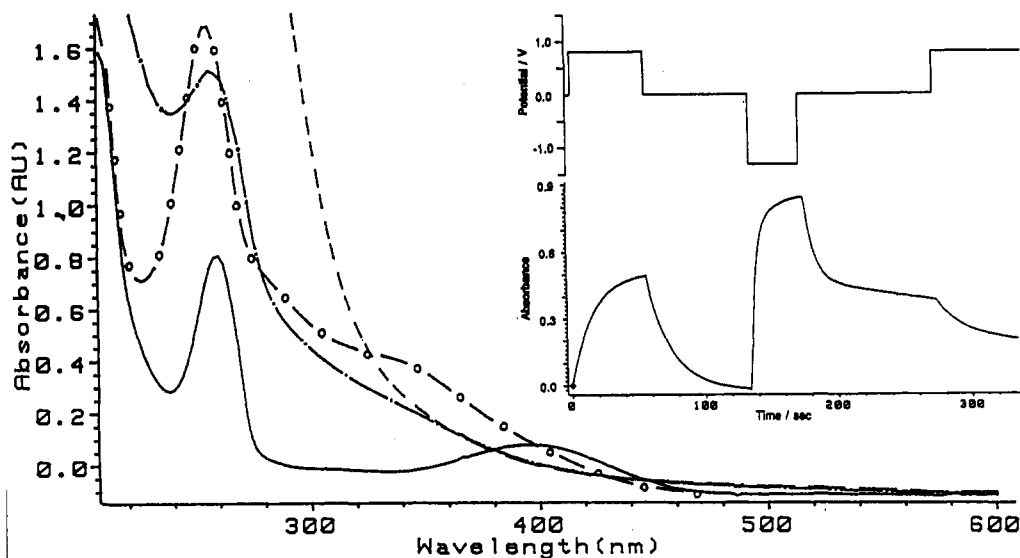
The UV-visible spectral changes occurring during analogous experiments with Fe(TPC)<sup>2+</sup> are shown in Figure 6. These data demonstrate that during the electrooxidation of the complex,<sup>19</sup> as well the electroreduction of dioxygen to superoxide in the presence of the complex, the absorbance at  $\lambda_{\text{max}} = 430$  nm decreases. Therefore, it is apparent that analogous processes are involved on reaction of Fe(TPC)<sup>2+</sup> with superoxide as were found for Fe(DPC)<sup>2+</sup>. In other words, at potentials negative of that required for dioxygen reduction, the spectroscopic changes arise from the oxidation of the iron(II) complex.

In further analogy to Fe(DPC)<sup>2+</sup>, after the potential step to  $-1.3$  V the absorbance at 434 nm decayed and a new band appeared at  $\lambda_{\text{max}} = 458$  nm with a shoulder at 420 nm; the new bands might be ascribed to an intermediate, presumably, a peroxy adduct of the iron(III) complex, [Fe(TPC)O<sub>2</sub>]<sup>+</sup>. This intermediate could form by replacement of the picolyl group at one of the coordination sites of the Fe(III) cation by the peroxy anion. A similar shift in the position of the MLCT band (from  $\lambda_{\text{max}} = 434$  to 462 nm in DMSO) was observed earlier, after substitution of the picolyl group in this complex by cyanide anion.<sup>19</sup> Stopped-flow measurements revealed that the species is very unstable and undergoes a fast subsequent hydrolysis, as will be shown later in the discussion of reaction kinetics.

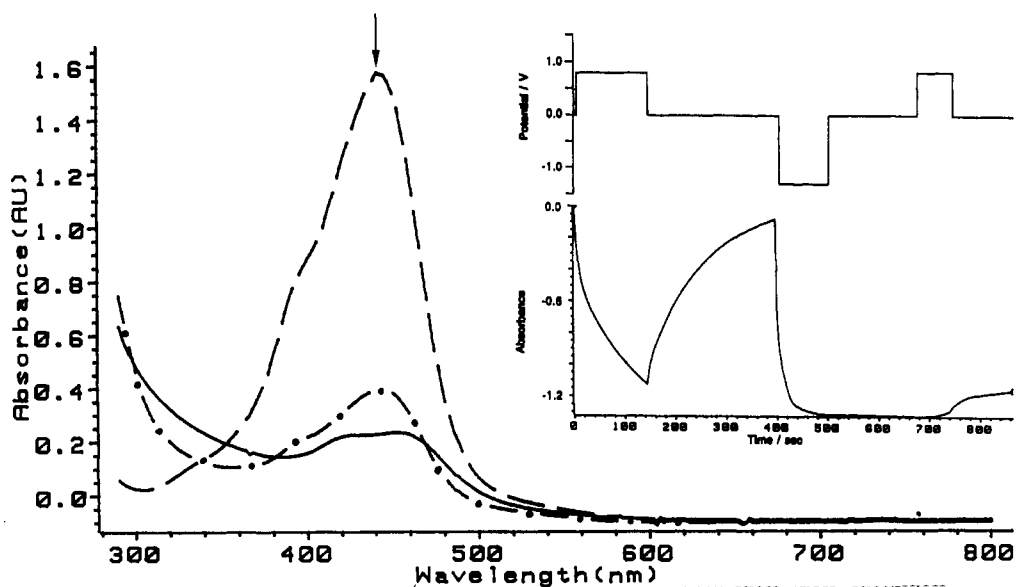
**Kinetics of the Redox Reactions.** The UV-visible spectral changes resulting from the reaction of Fe(DPC)<sup>2+</sup> with potassium superoxide in DMSO exhibited a rapid broad increase in absorbance at wavelengths between 310 and 380 nm (Figure 7);

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**Figure 5.** UV-visible spectra of 0.05 mM Fe(DPC)ClPF<sub>6</sub> in acetonitrile containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> and saturated by air (~2.0 mM O<sub>2</sub>)<sup>8a</sup> recorded during spectroelectrochemical experiments: (solid line) initial spectrum; (—○— line) after potential step to 0.8 V; (broken line) after potential step to -1.3 V, and (dotted line) after reverse potential step to 0.0 V with subsequent reduction of dioxygen. Spectra were recorded at 25 °C by using SEC thin-layer cell with GC working electrode.<sup>14a</sup> Inset shows absorbance-time trace at 312 nm recorded during the same SEC measurements following the potential steps whose time trace is shown in the upper part of the figure.



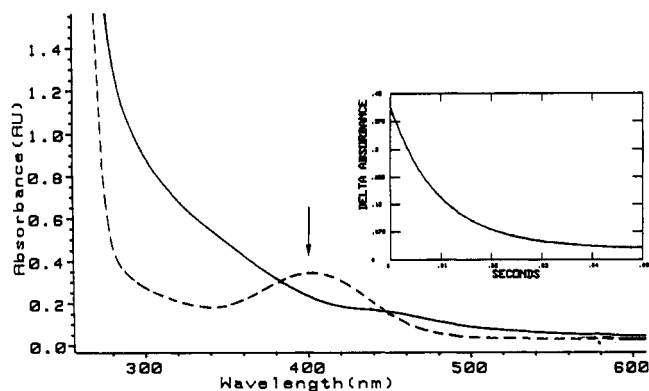
**Figure 6.** UV-visible spectra of 0.15 mM Fe(TPC)(PF<sub>6</sub>)<sub>2</sub> in acetonitrile containing 0.1 M Bu<sub>4</sub>NBF<sub>4</sub> and saturated by air (~2.0 mM O<sub>2</sub>)<sup>8a</sup> recorded during spectroelectrochemical experiments: (broken line) initial spectrum; (dotted line) after potential step to 0.8 V; (solid line) after potential step to -1.3 V. Spectra were recorded at 25 °C by using in SEC thin-layer cell with GC working electrode.<sup>14a</sup> Inset shows absorbance-time trace at 430 nm recorded during the same SEC measurements following the potential steps whose time trace is shown in the upper part of the figure.

the changes are similar to those observed during the electrooxidation of the iron(II) complex.<sup>19</sup>

The time scale of the reaction between superoxide and Fe(DPC)<sup>2+</sup> in DMSO is too short for the kinetics to be followed on the diode array UV-visible spectrophotometer, and therefore, the reaction between Fe(DPC)<sup>2+</sup> and potassium superoxide was monitored with a stopped-flow spectrophotometer. The experiments were performed in DMSO and acetonitrile. Typically, the superoxide concentration (DMSO saturated with KO<sub>2</sub>, ~2.0 mM;<sup>16</sup> MeCN saturated with KO<sub>2</sub>, ~1.8 mM<sup>21</sup>) was in excess over that of the iron(II) complex, (0.5 mM). The reaction was studied at wavelengths greater than 280 nm because of the absorbance of DMSO in the range. An observed decrease in the absorption at 400 nm reached completion within ~50 ms ( $k = 98 \pm 7 \text{ s}^{-1}$ , 27 °C), (see the inset of Figure 7). In acetonitrile, a similar decay in absorbance was observed at 400 nm ( $k = 60$

$\pm 5 \text{ s}^{-1}$ , 25 °C); however, at 450 nm ( $k = 81 \pm 5 \text{ s}^{-1}$ ) and at 320 nm ( $k = 110 \pm 20 \text{ s}^{-1}$ ) absorbance increases were recorded. Significantly, similar UV-visible spectral changes were observed earlier during electrogeneration of superoxide in the solution of the Fe(II) complex, indicating related mechanisms for the two systems. Attempts were not made to calculate the second-order rate constants, because of uncertainties in the superoxide concentration under the stopped-flow conditions, since the extent of water ingress has not been quantified.

These spectroscopic and kinetic results are consistent with the assignment of the net reaction as oxidation of Fe(DPC)<sup>2+</sup> to an iron(III) complex.<sup>19</sup> However, the increase at  $\lambda_{\text{max}} = 450 \text{ nm}$  indicates that the known Fe(DPC)<sup>3+</sup> complex cannot be the initial product of the reaction. Based on the spectroelectrochemical data obtained for the Fe(II) complex in aqueous solution,<sup>19</sup> the product appears more likely to be either the hydroxy species, [Fe(DPC)OH]<sup>2+</sup>, or the peroxy adduct, [Fe(DPC)O<sub>2</sub>]<sup>+</sup>.

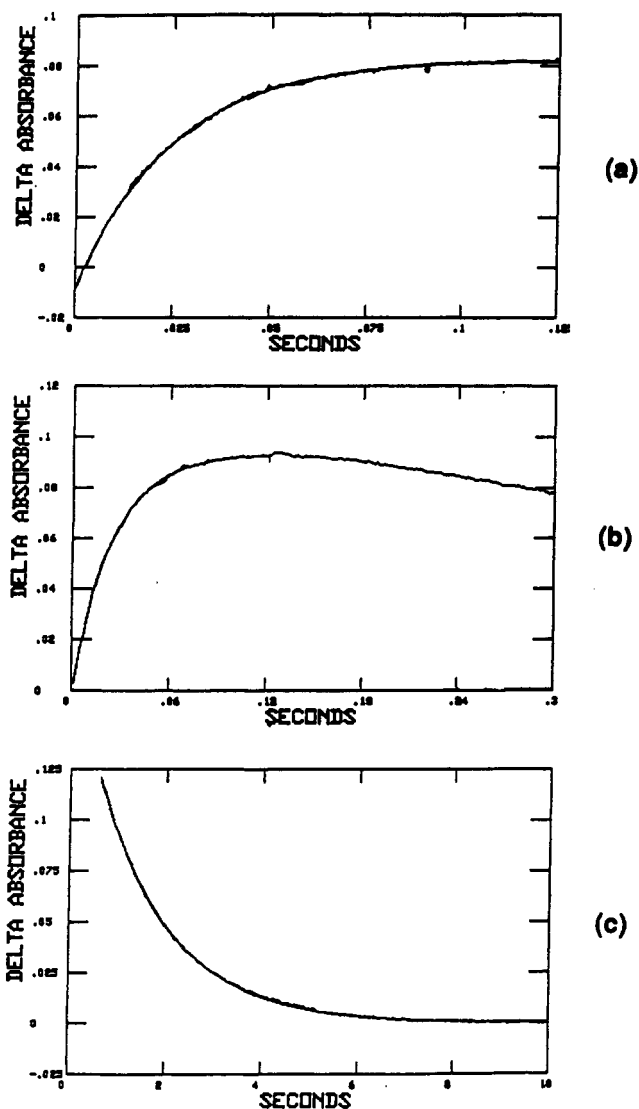


**Figure 7.** UV-visible spectral change following addition of DMSO saturated by  $\text{KO}_2$  (2 mM)<sup>16</sup> to a solution of 0.08 mM  $\text{Fe}(\text{DPC})\text{CIPF}_4$  in DMSO. Broken line indicates initial spectrum of the complex. Inset shows absorbance-time trace at 400 nm occurring on mixing solutions of the complex (0.54 mM) in DMSO with DMSO saturated by  $\text{KO}_2$  (2 mM)<sup>16</sup> at 25.5 °C measured by stopped flow.

In order to examine these possibilities and to test the stability of the initial product, the stopped-flow experiments were conducted over different time ranges (50, 100, and 300, ms and 10 s). Two reaction time regimes are revealed at 320 nm, as shown in Figure 8, and only one at 450 and 400 nm in the course of the first 10 s. As described above, the first reaction was associated with increases in absorbance at 320 and 450 nm and a decay at 400 nm and the second reaction resulted in an absorbance decrease at 320 nm ( $k = 0.65 \pm 0.15 \text{ s}^{-1}$ ) and no absorbance change at 400 and 450 nm. The latter reaction was  $\sim 170$  times slower and reached completion within  $\sim 10$  s.

It is apparent that the absorbance increase in the first reaction is associated with the formation of an Fe(III) species, but several possibilities might be suggested for the second reaction: (1) If the preceding electron transfer between these reactants follows an outer-sphere mechanism, the second reaction could be hydrolysis of the Fe(III) complex; (2) if the redox reaction follows an inner-sphere mechanism, or a concerted electron-transfer-substitution reaction, the second rate process could be hydrolysis of an intermediate peroxy adduct; and (3) if the local pH change is great enough, the reaction might be demetalation of the Fe(III) complex. The first explanation appeared to be unlikely because the reaction was performed in nonaqueous solution; moreover, dissociation of a proton from the aqua Fe(III) species requires a pH greater than 9.2,<sup>19</sup> which is not likely in these media. Also, the third explanation seems implausible since a demetalation of the Fe(III) complex cannot account for the absorbance increase at 450 nm, and in this wavelength range the free ligand and free Fe(III) cation are spectroscopically inactive. Moreover, control experiments were undertaken, involving the reaction of the iron(II) complexes ( $\sim 0.4$  mM) with a large excess of hydrogen peroxide (16 mM) in DMSO. No reaction was observed on the time scale of the superoxide experiments; however, an oxidation process was observed on longer time scales ( $k = 2.5 \pm 0.2 \text{ s}^{-1}$ , 26 °C, 400 nm) consistent with the known reactivity of these complexes with hydrogen peroxide.<sup>19</sup>

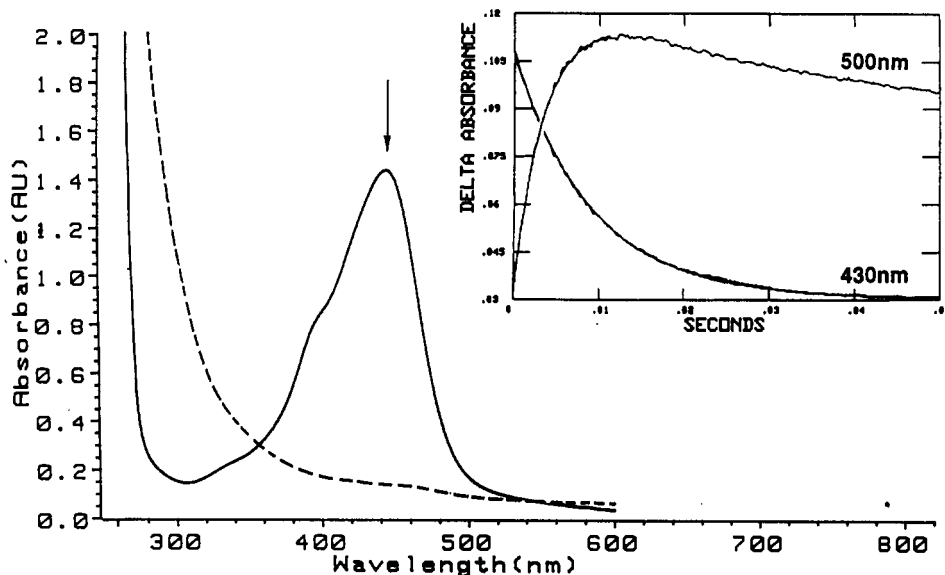
Similar to  $\text{Fe}(\text{DPC})^{2+}$ ,  $\text{Fe}(\text{TPC})^{2+}$  reacts very rapidly with potassium superoxide in dry DMSO and may be followed by the decay of the absorption band at 434 nm. Moreover, there was an increase in absorbance below the approximate isosbestic point ( $\sim 320$  nm; Figure 9). Clearly the spectral changes upon reaction of the iron(II) complex with superoxide are very similar to those obtained by electrooxidation of the iron(II) complex, indicating that the reaction of superoxide with  $\text{Fe}(\text{TPC})^{2+}$  results in oxidation of the complex to an iron(III) species. In order to examine these changes in more detail, the reaction between superoxide and  $\text{Fe}(\text{TPC})^{2+}$  was studied by stopped flow in DMSO and acetonitrile. The results indicated that two reactions occur on the second and subsecond time scales and that both reactions could be satis-



**Figure 8.** Changes in absorbance at 320 nm occurring on mixing solutions of 0.46 mM  $\text{Fe}(\text{DPC})\text{CIPF}_4$  in acetonitrile with acetonitrile saturated by  $\text{KO}_2$  at 25.5 °C, measured by stopped flow over different time ranges: (a) within the first 0.12 s; (b) within the first 0.3 s; (c) within the first 10 s.

factorily fitted to the pseudo-first-order rate law. The spectral changes occurring during the first reaction involved a decay in the  $\text{Fe}(\text{TPC})^{2+}$  MLCT band at 430 nm ( $k = 100 \pm 10 \text{ s}^{-1}$ , 25 °C) and an increase in absorbance at 320 and 500 nm ( $k = 335 \pm 30 \text{ s}^{-1}$ , 25 °C), as shown in Figure 9. The second kinetic process was  $\sim 100$  times slower and was observed as a decay in both new bands at 320 and 500 nm with the same rate of  $\sim 1.8 \pm 0.3 \text{ s}^{-1}$  at 25 °C. The slower reaction reached completion within 5 s. No reactions were observed over these time scales for control experiments involving the iron(II) complex and hydrogen peroxide (0.1 M, 25 °C).

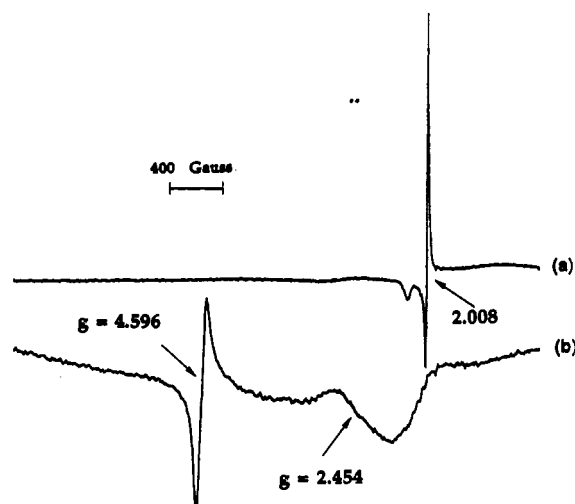
These rate processes and spectral changes are consistent with formation of the same kind of intermediate that was observed during the spectroelectrochemical experiments with the complex and indicate that the reaction between superoxide and  $\text{Fe}(\text{TPC})^{2+}$  is not limited to outer-sphere electron transfer. The absorbance increase at 320 nm indicates that the iron(II) complex has been oxidized, and the absorbance increase at 500 nm and the decay at 430 nm are reminiscent of the spectrum of the proposed peroxy adduct,  $[\text{Fe}(\text{TPC})\text{O}_2]^+$ .<sup>14a</sup> These results clearly indicate that the coordination environment about the iron has been markedly changed upon reaction of  $\text{Fe}(\text{TPC})^{2+}$  with superoxide anion. It is interesting to note the close parallels in the reaction patterns with superoxide for the two complexes.



**Figure 9.** UV-visible spectral changes following addition of DMSO saturated by  $\text{KO}_2$  (2 mM) to a solution of 0.16 mM  $\text{Fe}(\text{TPC})(\text{PF}_6)_2$  in DMSO. Solid line indicates initial spectrum of the complex. Inset shows absorbance–time trace at 430 and 500 nm occurring on mixing solutions of the complex (0.51 mM) in DMSO with DMSO saturated by  $\text{KO}_2$  (2 mM) at 25.5 °C measured by stopped flow.

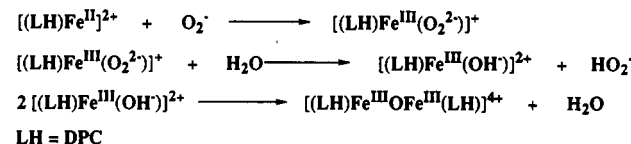
**Mass Spectra and ESR Spectroscopy.** In order to confirm the structures of the final products formed during the reactions of both iron(II) complexes with superoxide, mass spectroscopy (FAB) and ESR studies were performed on their reaction mixtures. The FAB spectrum of a DMSO solution of  $\text{Fe}(\text{DPC})^{2+}$  (2.5 mM), recorded ~5 min after mixing with a saturated DMSO solution of potassium superoxide (2 mM) at room temperature, exhibited only one major peak at 403 mass units, corresponding to  $\text{Fe}(\text{DPC})\text{Cl}^+$  and a cluster with DMSO at 481 mass units. From this observation it appears that the iron complex and the ligand remain intact following reaction with superoxide. In contrast, the FAB mass spectrum of the product of reaction of superoxide and (~3 mM)  $\text{Fe}(\text{TPC})^{2+}$  under similar conditions exhibited molecular peaks at 458 and 403 mass units, consistent with the presence of both  $\text{Fe}(\text{TPC})^+$  and free ligand.  $\text{Fe}(\text{TPC})^{2+}$  undergoes a demetalation reaction, either with superoxide or under the conditions of the FAB experiment. It is of note that there was no evidence for ligand oxidation in the mass spectrum.

ESR measurements (DMSO, 77 K) showed that the addition of a saturated DMSO solution of potassium superoxide to a dry DMSO solution (2 mM) of  $\text{Fe}(\text{DPC})^{2+}$  at room temperature resulted in no spectral changes over the time range from 15 s to 5 min. This demonstrates that the final product of the reaction is ESR silent and confirms the conclusion from stopped-flow and SEC results that it could not be the known  $\text{Fe}(\text{DPC})^{3+}$  species. As previously reported,<sup>14a</sup> the  $\text{Fe}(\text{III})$  complex exhibits resonances at  $g = 9.324$ , 8.291, and 5.776, typical of high-spin iron(III) complexes with rhombic distortion. The final product of the reaction may be a  $\mu$ -oxo dimer,  $[\{\text{Fe}(\text{DPC})\}_2\text{O}]^{4+}$ , since compounds of this type are generally regarded to be ESR silent at temperatures greater than 77 K.<sup>22</sup> For example, similar ESR properties were found for the analogous dimers derived from tetraphenylporphyrins,  $(\text{FeTTP})_2\text{O}$ .<sup>22a</sup> On the other hand, preliminary ESR results of  $(\text{Fetsalen})_2\text{O}$ <sup>22c</sup> and  $(\text{FePc})_2\text{O}$ <sup>22d</sup> were reported to show resonance signals at  $g = 2.028$  and  $g \sim 6$ . Presumably, the  $\mu$ -oxo dimer  $[\{\text{Fe}(\text{DPC})\}_2\text{O}]^{4+}$  would result from the hydrolysis of the peroxy adduct,  $[\text{Fe}(\text{DPC})\text{O}_2]^+$ , with a subsequent dimerization of the hydroxy species,  $[\text{Fe}(\text{DPC})\text{OH}]^{2+}$ , according to Scheme I. However, we have no direct evidence for



**Figure 10.** ESR spectra of DMSO solution (a) containing 2 mM of  $\text{KO}_2$  and (b) the same as (a) but 5 min after addition of DMSO solution of 1.4 mM  $\text{Fe}(\text{TPC})(\text{PF}_6)_2$ . Spectra were recorded at 77 K;  $\nu^\circ = 9.16$  GHz.

#### Scheme I



that mechanism. The product present ~15 s after mixing superoxide with  $\text{Fe}(\text{TPC})^{2+}$  was also ESR silent (DMSO, 77 K); however, after ~5 min at room temperature, resonances were observed at  $g = 4.596$  and 2.454 as shown in Figure 10. A control ESR experiment using the binary compound  $\text{FeCl}_3$  in DMSO (2 mM) failed to exhibit any such signal, suggesting that the resonance did not derive from the demetalated complex. For comparison, the iron(III) species generated by electrolysis of  $\text{Fe}(\text{TPC})^{2+}$  and examined by *in-situ* ESR spectroelectrochemical experiments also revealed resonances at  $g = 4.568$  and 2.080.<sup>19</sup> This result suggests that the iron(II) complex of TPC can be oxidized by superoxide to the  $\text{Fe}(\text{III})$  species. However, the ESR data indicate a difference in the coordination sphere of  $\text{Fe}(\text{III})$  cation between the  $\text{Fe}(\text{III})$  complex of TPC generated electrochemically and obtained after the reaction with superoxide. In

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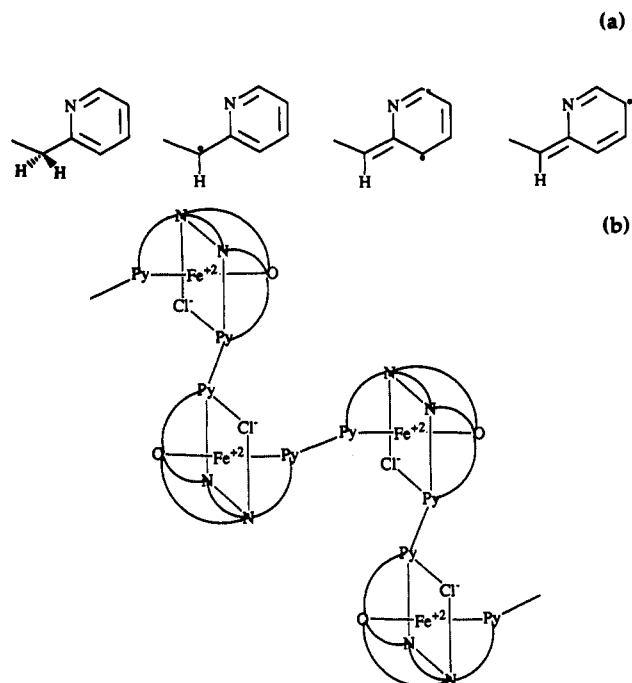


Figure 11. (a) Resonance structures of picolyl radical. (b) Schematic drawing of the hypothetical polymer of  $\text{Fe}(\text{DPC})_2^{2+}$ .

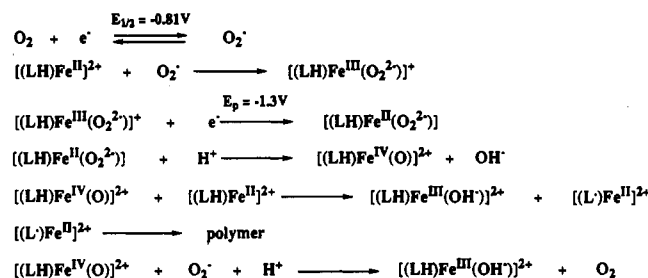
contrast to  $\text{Fe}(\text{DPC})_2^{2+}$ , dimerization of the complex may be inhibited by the steric hindrance and competitive coordination of the third picolyl group.

The ESR and FAB results confirm that both Fe(II) complexes react with superoxide very quickly because the signal typical of the oxygen radical disappeared almost immediately after mixing these reagents (Figure 10), and ESR-active intermediates were not detected. In the case of  $\text{Fe}(\text{DPC})_2^{2+}$ , a stable  $\mu$ -oxo dimer  $[\{\text{Fe}(\text{DPC})_2\}_2\text{O}]^{4+}$ , was probably obtained, but for the  $\text{Fe}(\text{TPC})_2^{2+}$ , the corresponding known Fe(III) complex was detected as a final product of the reaction. The difference probably results from the greater steric hindrance and competitive coordination of the third picolyl group in the case of  $\text{Fe}(\text{TPC})_2^{2+}$ .

## Discussion

Cyclic voltammetry and associated spectroelectrochemical studies have revealed complex reactions of both  $\text{Fe}(\text{DPC})_2^{2+}$  and  $\text{Fe}(\text{TPC})_2^{2+}$  complexes with superoxide in acetonitrile. For both complexes, an initial reaction between the iron(II) complex and superoxide results in formation of an insoluble product on the electrode surface. At more negative potentials, a second reduction process leads to formation of an electrically conductive polymer on the electrode surface. Since, in the absence of dioxygen, the iron(II) complex is electrochemically inert over this potential range, we can assume that the polymer is derived from the reaction product between the iron complex and a reduced dioxygen species. A likely scenario for polymer formation involves initial hydrogen abstraction from the ligand (presumably, from the picolyl methylenes; see Figure 11) by a radical species derived from the reduction of dioxygen. The increased prevalence of polymer formation in the presence of excess iron(II) complex indicates that either polymer formation is retarded by excess dioxygen/superoxide or, alternatively, the polymer formation process is facilitated by excess iron(II). A partial mechanism may be suggested based on the above evidence, where LH denotes the TPC or DPC ligand (see Scheme II). The first two equations depict reduction of dioxygen to superoxide and its subsequent reaction with the iron(II) complex. The product  $\text{LFe}(\text{II})(\text{O}_2)^+$  may be considered as either an iron(II)-superoxo adduct or an iron(III)-peroxo species. This species is postulated to be the insoluble material found to coat the electrode surface. Reduction

## Scheme II



of this material would result in formation of the iron(II)-peroxo species  $\text{LFe}^{\text{II}}(\text{O}_2^{2-})$ , which is likely to be unstable, by analogy to iron(II)/hydrogen peroxide chemistry.<sup>23</sup> Decomposition in the presence of trace levels of moisture is likely to result in the formation of the formally iron(IV) ferryl species and hydroxide anion. The ferryl may react with the ligand by a hydrogen abstraction process; alternatively, the ferryl species may be removed from the system by reduction by superoxide, which will be present if dioxygen is in excess. The products of the hydrogen abstraction reaction would be the iron(III)-hydroxo complex and a ligand radical. This ligand radical may provide the pathway to formation of the polymer on the electrode surface (see Figure 11), by a mechanism analogous to that for the formation of polypyrrole, polyaniline, and polythiophene following electrooxidation of the appropriate monomers.<sup>18,24</sup> The recent electrochemical literature has included a number of papers examining formation of polymer coatings on electrode surfaces which contain metals or metal cations. These have typically been prepared by incorporation of the metal complexes into the polymer by entrapment during the polymerization process, and the studies have been motivated by the assumption that the presence of the metal complexes will significantly affect the electrochemical and electrocatalytic properties of these modified electrodes.<sup>25</sup> There are a few examples of formation of metal ion containing polymers by polymerization using the metal complexes or their ligands as monomers.<sup>26</sup>

The stopped-flow results support the electrochemical data indicating the rapid reaction between the iron(II) complexes and superoxide. In parallel to the electrochemical experiments, the two complexes were observed to behave in a similar manner, displaying comparable spectral changes at similar rates. The similarity of the rates seems to indicate closely related rate-

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determining processes for the two systems. This contrasts strongly with the oxidation of these complexes by hydrogen peroxide. In aqueous solution,  $\text{Fe}(\text{DPC})^{2+}$  was found to react much more rapidly than  $\text{Fe}(\text{TPC})^{2+}$ , possibly because of the ready availability of a coordination site in that medium. In contrast, in acetonitrile, both complexes reacted slowly with hydrogen peroxide (minutes), a result that is consistent with dissociation of a ligand, possibly the picolyl group, as the rate-determining step.<sup>19</sup>

On the bases of UV-visible and ESR spectral changes, the reactions of the complexes with superoxide appear to involve metal oxidation. The products of this reaction in DMSO were distinct from the simple known iron(III) complexes, and the UV-visible spectrum of both complexes resembled that of  $\text{Fe}(\text{DPC})(\text{OH})^+$ . This observation indicates that reaction of the iron(II) complexes results in a change in the coordination environment about the iron. The short time scale of reaction for this complex argues against a mechanism involving dissociation of a picolyl group in the rate-determining step since reaction of the same complex with hydrogen peroxide is believed to proceed by a picolyl dissociation mechanism and has been found to much slower (minutes).<sup>19</sup> Furthermore, under the anhydrous conditions employed, outer-sphere reduction of superoxide to form free peroxide ( $\text{O}_2^{2-}$ ) is implausible due to the unfavorable thermodynamics of free peroxide formation.<sup>27</sup> Production of a seven-coordinated iron(II) complex is also not considered highly likely.<sup>28</sup> Therefore a mechanism involving prior coordination of superoxide would appear dubious.

A possible explanation that would satisfy the experimental observations entails the concerted electron transfer between superoxide and the iron(II) complex and nucleophilic attack of the evolving peroxide ion on the iron(II) complex to form a

transient seven-coordinate iron(III) species. The two processes must operate concurrently and rapidly to overcome the thermodynamic limitations of the formation of free peroxide anion. Such a reaction pathway may be facilitated by ion pair formation in solvents of modest polarity. Peroxide dianion would be a very powerful nucleophile capable of displacing one of the picolyl groups in the case of  $\text{Fe}(\text{TPC})^{2+}$  and/or chloride anion in the case of  $\text{Fe}(\text{DPC})^{2+}$  to form the postulated intermediate six-coordinate iron(III) complex.

In conclusion, the reactivity of superoxide with iron(II) complexes with a pentadentate and a hexadentate ligand has been compared in the nonaqueous media acetonitrile and DMSO. By choosing compounds with very similar iron(III)/(II) redox potentials, the differences in behavior may be correlated with the geometry of the iron(II) complexes. It was found that superoxide undergoes rapid multistep reactions with both complexes, resulting in net oxidation to the iron(III) form, without apparent ligand modification. An iron(III)-peroxy adduct is proposed as an intermediate in the reaction, based on kinetic and electrochemical results. Despite the differences in ligand structure and in donor sites about the two iron(II) complexes, both  $\text{Fe}(\text{DPC})^{2+}$  and  $\text{Fe}(\text{TPC})^{2+}$  appear to react with superoxide in a nonaqueous environment according to the same mechanism. This reaction probably involves substitution of one of the picolyl groups in the complexes by peroxy anion by a concerted electron-transfer-nucleophilic substitution reaction with superoxide. Cyclic voltammograms at more negative potentials exhibit electropolymerization, a feature typically associated with ligand oxidation. This process is probably initiated by a ferryl species obtained during electroreduction of the iron(III)-peroxy adduct.

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