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Electrochemistry and Spectroelectrochemistry of Iron Porphyrins in the Presence of Nitrite

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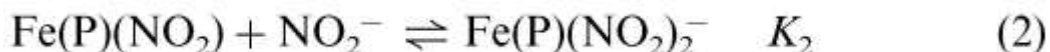
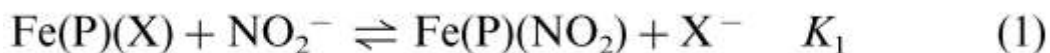
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Abstract: The reaction of nitrite with ferric and ferrous porphyrins was examined using visible, infrared and NMR spectroscopy. Solutions of either ferric or ferrous porphyrin were stable in the presence of nitrite, with only complexation reactions being observed. Under voltammetric conditions, though, a rapid reaction was observed between nitrite and iron porphyrins to form the nitrosyl complex, Fe(P)(NO) , where P = porphyrin. The products of the reduction of ferric porphyrins in the presence of nitrite were confirmed by visible spectroelectrochemistry to be Fe(P)(NO) and $[\text{Fe(P)}]_2\text{O}$. Visible, NMR and infrared spectroscopy were used to rule out the formation of Fe(P)(NO) by the iron catalyzed disproportionation of nitrite.

A reaction between iron porphyrins and nitrite only occurred by the presence of both oxidation states (ferric/ferrous). The kinetics of the reaction was monitored by visible spectroscopy, and the reaction was found to be first-order with respect to Fe(OEP)(Cl) and Fe(OEP). The products were the same as those observed in the spectroelectrochemical experiment. The rate was not strongly dependent upon the concentration of nitrite, indicating that the coordinated, not the free nitrite, was the reaction species. The observed kinetics was consistent with a mixed oxidation state nitrite bridged intermediate, which carried out the oxygen transfer reaction from nitrite to the iron porphyrin. The effect of nitrite coordination on the reaction rate was examined.

Introduction

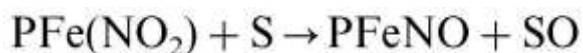
Over the past two decades, the reaction of nitrite with iron porphyrins and heme containing enzymes has been the subject of considerable study. Nitrite is a very versatile molecule which can be involved in a wide variety of reactions such as coordination, acid/base or oxygen transfer chemistry. Because of this reactivity, nitrite can be, in some cases, a necessary intermediate (in the nitrogen cycle) or, in others, a toxic material. While nitrite can react with a large number of transition metals, the primary focus of this work will involve iron porphyrins which are models for iron enzymes that react with nitrite. Nitrite can coordinate with both the ferric [1,2,3] and ferrous [4] porphyrins. Ferric porphyrins generally form bis-nitro low-spin complexes [1,3].



If $\text{X}^- = \text{halide}$, the mono-nitrite complex is only present over a narrow concentration range [1]. Weaker axial ligands such as NO_3^- or ClO_4^- can be readily displaced by nitrite, and both the mono- and bis- complexes have been observed.

There has been some controversy as to the stability of the nitrite-ferric porphyrin complexes. Finnegan et al. [5] found that ferric porphyrins slowly reacted with nitrite to lead to Fe(P)(NO) and $\text{Fe(P)(NO}_3\text{)}$. O'Shea et al. [6] observed that ferric nitrite complexes

were stable under an argon atmosphere, and could carry out a wide variety of oxygen transfer reactions if an appropriate substrate was present:



A later report attributed the instability of nitrite-ferric porphyrin complexes to the generation of ozone from trace dioxygen [7]. In addition to oxygen transfer reactions, nitrite may also be a nucleophile. Fanning and Keefer [8] found that nitrite will react readily with methylene chloride to form organonitro compounds.

In the assimilatory and dissimilatory nitrite reductases, nitrite is first reduced to NO. The NO molecule will dissociate in cytochrome cd1 nitrite reductases, but is reduced to ammonia in assimilatory nitrite reductases. The reaction of nitrite with metmyoglobin [9] and hemoglobin [10,11] has also been examined. For both proteins, the reaction product was a NO-coordinated protein.

In spite of these studies, the details of the reaction of nitrite with ferric and ferrous porphyrins are not clear. Many of the experiments by Finnegan et al. [5] were carried out in methylene chloride, creating some ambiguities as to whether the reactions were due to nitrite or organonitro compounds. Some of the differences may also be due equilibrium shifts caused by the presence or absence of halide ions (e.g., chloride as the axial ligand). Munro and Scheidt [12] have shown that the mono-nitrite complex is more reactive than the bis-nitro complex. The presence of this complex was minimized in the work of Castro et al. [13] because they utilized ferric porphyrins with chloride as the axial ligand (Fe(P)(Cl)). In order to investigate these issues, visible and infrared spectroelectrochemistry will be used in this work in order to characterize as completely as possible the intermediates that are formed in the reaction of nitrite with ferric and/or ferrous porphyrins.

Experimental

Chemicals.

Octaethylporphyrin iron(III) chloride (Fe(OEP)Cl), tetraphenylporphyrin iron(III) chloride (Fe(TPP)Cl), bis(triphenylphosphoranylidene)ammonium nitrite (PNPNO₂), sodium nitrite, bis(triphenylphosphoranylidene)ammonium chloride (PNPCI), dimethyl formamide, tetrahydrofuran (THF), and deuterated NMR solvents were obtained from Aldrich Chemical Co. Sodium nitrite (¹⁵N) was obtained from Isotec, and tetrabutylammonium perchlorate (TBAP) from G. F. Smith Chemical Co. Bis(triphenylphosphoranylidene)ammonium nitrite (¹⁵N) was obtained from the metathesis reaction of PNPCI and sodium nitrite-¹⁵N in distilled water. The product precipitated out of solution and was vacuum dried. Zinc amalgam was prepared by a literature procedure [14]. Ferrous-OEP was obtained by the reduction of Fe(OEP)(Cl) in THF by zinc amalgam.

Equipment.

Cyclic voltammograms were obtained with a Cypress CySy2Ra potentiostat. The reference electrode was a 0.1 M Ag/AgNO₃ electrode in acetonitrile. The working and auxiliary electrodes were platinum. An optically transparent thin-layer electrochemical (OTTLE) cell with a platinum gauze working electrode was used for the visible spectroelectrochemical studies [15]. The spectra were obtained with a Hewlett-Packard 8452 diode array spectrophotometer. The infrared spectra were obtained with a Mattson 4020 Galaxy FT-IR. The IR spectroelectrochemical cell was a modified Wilmad semi-permanent cell [16]. The Teflon spacer between two KBr windows was replaced by a polyethylene spacer in which the working, reference and auxiliary electrodes were melt-sealed. The working and auxiliary electrodes were fabricated from 100 mesh platinum gauze (Aldrich Chemical Co.), and a silver wire (0.05 mm diameter, Johnson Matthey) was used as a pseudo-reference electrode.

Procedures.

All the voltammetric solutions were deoxygenated by deaerating the solution for 15 min. with pre-purified dinitrogen. The dinitrogen was pre-saturated with the solvent in order to prevent evaporation. The spectroelectrochemical solutions were prepared in the glove box, and the data were obtained after the current had decayed to the background. The visible kinetics experiments were carried out using an anaerobic cell (Wilma Glass Co., WG-28-G). The iron porphyrin solution was placed in the cuvette, and the nitrite solution was placed in the side arm. The reaction was carried out in an argon atmosphere. After the starting spectrum was recorded, the solutions were mixed, and the spectra were obtained using a Hewlett-Packard 8452 diode array spectrophotometer in the kinetics mode. The solutions were prepared and the cell was filled in a glove box.

Results and Discussion

Stability of Ferric Porphyrin-Nitrite Complexes.

Nitrite in the presence of iron porphyrins has been notorious for the ease by which it can undergo redox reactions. In order to fully characterize its reactivity, it is critical that conditions under which redox chemistry can be avoided are identified and the spectral features of important iron porphyrin species are correctly identified. The stability of solutions of Fe(OEP)(X) (where X = NO₃, Cl) in the presence of nitrite was examined by visible, infrared and NMR spectroscopy. The chemical processes that occurred when nitrite (as the PNP⁺ salt) was mixed with Fe(OEP)(X) were identified by monitoring the spectral changes in an anaerobic cell, as described in the Experimental Section. At high concentrations of nitrite (≈ 10 mM), the spectrum of the Fe(OEP)(NO₂)₂⁻ was obtained immediately upon mixing. Over a period of 1000 s, no additional reactions were observed. When X = NO₃⁻, the spectrum of the mono-nitrite complex (Fe(OEP)(NO₂)) was obtained when the concentrations of nitrite and Fe(OEP)(NO₃) were 0.10 mM (Table 1). Under these conditions, the complex was slightly less stable, with a 4% absorbance change observed over a period of 1000 s. If the reaction was allowed to continue for 9 hr, the spectrum for the μ -oxo complex ([Fe(OEP)]₂O)

was observed. There was no evidence in the visible spectra for Fe(OEP)(NO), a product often formed by an oxygen transfer reaction.

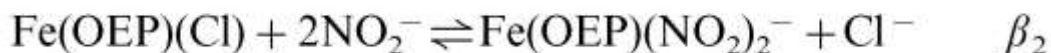
Further evidence for the stability of Fe(OEP)(X) in the presence of nitrite was obtained by infrared spectroscopy. Equimolar mixtures of Fe(OEP)(NO₃) or Fe(OEP)(Cl) (1.0 mM) and nitrite (1.0 mM) were examined in THF. Once again there was no evidence for the nitrosyl complex, even though it could have been observed under these concentration conditions. Unfortunately, the bands for the coordinated nitrite at this concentration of iron porphyrin could not be observed due to their lower molar absorptivity and/or the solvent bands below 1500 cm⁻¹.

The ¹H NMR spectra of 1 mM Fe(OEP)(NO₃) in the presence of 0, 1 and 10 mM nitrite in DMF-d₇ were also obtained. In the absence of nitrite, a high-spin ferric porphyrin spectrum was obtained with a resonance at 49.2 ppm, which is due to the methylene protons. Generally, two resonances are observed for the methylene protons for a five-coordinate complex, but a single methylene resonance has been observed for weak ligands such as perchlorate in the presence of a coordinating solvent (Fe(OEP)(ClO₄): δ = 35.5 [17,18]). When the concentrations of Fe(OEP)(NO₃) and NaNO₂ were both 1 mM, the high-spin spectrum disappeared and was replaced by a low-spin ferric porphyrin spectrum. If an oxygen transfer reaction occurred under the conditions of this experiment to form Fe(OEP)(NO) and Fe(OEP)(NO₃), the latter complex should be observed in the proton NMR [5]. In addition, the experiments were completed rapidly enough so that there was no evidence for the μ-oxo complex (CH₂: 6.04 and 5.08 ppm [19]), which was the long term decomposition product observed in our work by visible spectroscopy.

The stability of Fe(OEP)(Cl)/NO₂⁻ solutions is in agreement with the results of Castro et al. [7] who found that mixtures of Fe(P)(Cl) and nitrite were quite stable in the absence of dioxygen. The instability of stoichiometric ratios of Fe(P)(X) and nitrite (where X = easily displaceable anion) was similar to the work of Finnegan et al [5], where they observed a slow decomposition of the mono-nitrite complex. Unlike their work, though, we were unable to detect the disproportionation of nitrite to ferrous-NO and nitrate. This difference

may be due to formation of organonitro compounds in methylene chloride [8]. The kinetic studies in this work confirmed the report by Munro and Scheidt [12] that the mono-nitrite complex was more reactive than the bis-complex.

The changes in the visible spectra of Fe(OEP)(Cl) as a function of nitrite concentration are shown in Figure 1. In the absence of nitrite, the Soret band was observed at 374 nm, with additional bands at 532 and 629 nm. Upon addition of nitrite, the Soret band shifted to 389 nm, the 532 and 629 nm bands decreased, and a new band appeared at 586 nm (Table 1). Several isosbestic points are observed in the spectra, indicating the presence of only two species in equilibrium. The best fit was obtained for the addition of two nitrite ions to the complex, forming Fe(OEP)(NO₂)₂⁻. From the variation in the absorbance as a function of nitrite concentration, a β₂ value of 27±7 could be calculated.



There was no evidence in the visible spectra for the mono-nitrite complex, Fe(OEP)(NO₂), when 1.0 mM chloride was present in the solution. The spectrum of Fe(OEP)(NO₂)₂⁻ was identical whether one started with Fe(OEP)(Cl) or Fe(OEP)(NO₃).

Similar experiments were also carried out using Fe(TPP)(Cl), and were consistent with the formation of the bis-nitro complex, Fe(TPP)(NO₂)₂⁻. In the absence of nitrite, the Soret band was observed at 414 nm, with additional bands at 508, 649 and 691 nm. Upon addition of nitrite, the Soret band shifted to 422 nm and the 508 nm band shifted to 553 nm. The spectroscopic changes were quite comparable to the spectra reported by Nasri et al. [3] for Fe(TpivPP)(NO₂)₂⁻ (424 and 551 nm) in methylene chloride (Table 1).

The spectra of Fe(TPP)(NO₂) and Fe(TPP)(NO₂)₂⁻ can be obtained from analysis of the spectral changes as a function of nitrite concentration. The concentration of the mono-nitrite complex was enhanced in this set of data because no additional chloride ion was added (1 mM chloride was added to all the Fe(OEP)(Cl)/nitrite

solutions above). By using an iterative process, the values of K_1 and K_2 were varied, and the concentrations of $\text{Fe}(\text{TPP})(\text{Cl})$, $\text{Fe}(\text{TPP})(\text{NO}_2)$, $\text{Fe}(\text{TPP})(\text{NO}_2)_2^-$, and Cl^- were calculated. From these concentration values, the spectra of $\text{Fe}(\text{TPP})(\text{Cl})$, $\text{Fe}(\text{TPP})(\text{NO}_2)$ and $\text{Fe}(\text{TPP})(\text{NO}_2)_2^-$ can be calculated by a least-squares fit. The values of K_1 and K_2 were adjusted to minimize the errors. The spectral features are summarized in Table 1. The spectra of $\text{Fe}(\text{TPP})(\text{Cl})$ and $\text{Fe}(\text{TPP})(\text{NO}_2)$ in DMF are quite similar. In addition, there is substantial agreement between the spectrum obtained by our work and by Finnegan et al. [5]. A comparison of the calculated and experimental spectra for several concentrations are shown in Figure 2 for $K_1 = 2$ and $K_2 = 200$ ($\beta_2 = 400$).

The stability of $\text{Fe}^{\text{II}}(\text{OEP})$ in the presence of nitrite was also examined using the same anaerobic cell procedure. The $\text{Fe}^{\text{II}}(\text{OEP})$ and nitrite solutions (as the PNP^+ salt) were mixed, and the spectral changes were monitored using a diode array spectrophotometer. No spectral changes were observed upon mixing. This indicates either that nitrite does not complex with $\text{Fe}^{\text{II}}(\text{OEP})$ or that the complex has the same high-spin spectrum as $\text{Fe}^{\text{II}}(\text{OEP})$. In any case, no redox reaction was observed. It is important to note that extreme care must be used to prevent leakage of dioxygen into the cell. This leakage was probably the cause of the small decrease in the Soret band (less than 5%) after 1000 s. If any dioxygen were to leak in, a redox reaction, which will be discussed below, was observed. The experiment was repeated with the picket-fence porphyrin ($\text{Fe}^{\text{II}}(\text{TpivPP})$), and the spectrum for the previously characterized low-spin ferrous-nitrite complex was obtained [4].

The results of the visible and other spectroscopic studies clearly indicate that *both* the ferric and ferrous oxidations states of iron porphyrins are stable in the presence of nitrite. The only reactions that were observed were complexation reactions between iron and nitrite. If any complexation occurs between $\text{Fe}^{\text{II}}(\text{OEP})$ and nitrite, the product is a high-spin complex, rather than the low-spin complex observed with the picket-fence porphyrin.

Cyclic Voltammetry.

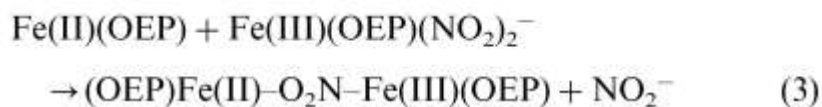
The cyclic voltammetry of Fe(OEP)(Cl) was examined in the presence of nitrite in DMF and THF, and was consistent with previous results (see Figure 3 of Ref. 1). In the absence of nitrite, two reduction waves were observed for Fe(OEP)(Cl) in both solvents between +0.3 and -1.9 V vs Ag/AgNO₃, with peak potentials at -0.88 V (Wave Ia) and -1.76 V (Wave II). When nitrite was added, a new wave was observed at -1.51 V (Wave Ib), and the first wave shifted slightly to -0.84 V. The new wave (Wave Ib) occurred at the same potential as Fe(OEP)(NO). Wave II was essentially unchanged. While the potential of Wave II was unchanged, more than one redox process may be occurring because the E_p value for [Fe(OEP)]₂O is essentially the same as the second wave of Fe(OEP)Cl. In addition to shifting slightly in potential, the cathodic current for Wave Ia decreased substantially when nitrite was added. All the voltammetric studies were carried out under conditions where it has been shown that no significant decomposition of the ferric species would occur.

The voltammetric data clearly indicate that a reaction is occurring between iron porphyrin and nitrite, as had been reported by previously [1,5,7,20]. The voltammetric evidence strongly suggests the formation of Fe(OEP)(NO). These results appear to contradict the visible and infrared evidence that both ferric and ferrous porphyrins are stable towards redox reactions in the presence of nitrite. In order to investigate this apparent contradiction, visible spectroelectrochemistry and further kinetic experiments were carried out.

Visible Spectroelectrochemistry.

The reduction of Fe(OEP)(Cl) in DMF or THF in the absence of nitrite gave rise to a typical Fe^{II}(OEP) spectrum (Soret band at 410 nm) at Wave I and Fe^I(OEP)- spectrum at Wave II (Figure 3). When the solution was electrolyzed at Wave Ia in the presence of nitrite, the Fe^{II}(OEP) Soret band was significantly attenuated, and only appeared as a small shoulder (Figure 4, Curve A). In addition, a new band at 557 nm, which was due to Fe(OEP)(NO), appeared. Using the known spectra for the ferrous and ferric porphyrins, the composition of the

product solution at Wave Ia was calculated: 0.20 mM Fe(OEP), 0.10 mM Fe(OEP)(NO), 0.10 mM [Fe(OEP)]₂O and no Fe(OEP)(Cl). The calculated spectra for the final product is shown in Figure 4 (Curve B). It is important to note that the nitrosyl and the μ -oxo complex, formed by the reaction of nitrite of iron porphyrins, were generated in a 1:1 mole ratio. In addition, there was a significant amount of Fe(OEP) remaining, even though excess nitrite was present. This last result was consistent with the visible spectroscopic studies. These results indicate that both iron oxidation states must be present for the reaction to occur, suggesting a mixed oxidation state bridged intermediate:



(the oxidation states of the cleavage products are presented for illustrative purposes; other oxidation states can be written). The details of the coordination of the bridged intermediate can only be speculated on at this time; other coordination states could also be written.

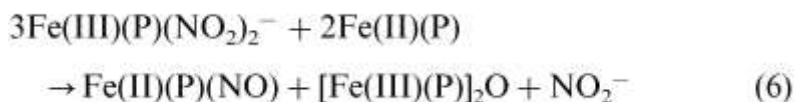
When the potential was shifted to Wave Ib, the Soret band for Fe^{II}(OEP) increased due to reduction of [Fe(OEP)]₂O. Authentic μ -oxo complex yielded the same spectroelectrochemical changes. In addition to the reduction of the μ -oxo complex, a new band appeared at 538 nm (Figure 5), which is due to Fe(OEP)(NO)⁻. Further reduction at Wave II (Figure 5) gave rise to a new band at 685 nm (Fe^I(OEP)⁻), and the 538 nm band of Fe(OEP)(NO)⁻ was unchanged. The Soret bands for Fe(OEP)(NO)⁻ and Fe^I(OEP)⁻ are quite similar, hence only one Soret band was observed in Figure 5. Because of the overlap of Wave Ib and Wave II, reduction of the μ -oxo complex will occur along with Fe(OEP)(NO).

Infrared Spectroelectrochemistry.

It has previously been shown in this work that solutions of Fe(OEP)(Cl) and nitrite do not lead to the formation of Fe(OEP)(NO) at potential significantly positive of Wave Ia. Electrolysis of Fe(OEP)(Cl) in the presence of nitrite at a potential between Wave Ia and Ib led to the appearance of a band for Fe(OEP)(NO) in the infrared spectrum at 1672 cm⁻¹. When ¹⁵NO₂⁻ was used, the band shifted to 1641 cm⁻¹, which was identical to the band observed for Fe(OEP)(¹⁵NO). The band for the μ-oxo complex at 870 cm⁻¹ could not be observed due to solvent absorption.

Reaction Kinetics.

Due to diffusion processes, the voltammetric or spectroelectrochemical reduction of Fe(OEP)(X) will lead to solutions that contain both oxidation (ferric/ferrous) states. In order to investigate the reaction of nitrite with iron porphyrins under these conditions, the kinetics of the reaction of nitrite with mixed oxidation state solutions were examined. When both oxidation states were present, an immediate reaction was observed when nitrite was added (Figure 6). Using the known spectra of Fe(OEP)(Cl) (in 5 mM nitrite), Fe(OEP), Fe(OEP)(NO) and [Fe(OEP)]₂O, it was possible to calculate the concentration of each species as a function of time. The changes in concentration of reactants and products obeyed the following reaction:



From the concentration of reactants as a function of time, it is possible to determine the rate law and the rate constant for the reaction.

If Reaction 3 is the rate determining step, the rate law should be first-order in Fe(OEP)(NO₂)₂⁻ and Fe(OEP), and the following equation can be written:

$$\text{rate} = k[\text{Fe(III)(OEP)(NO}_2)_2^-][\text{Fe(II)(OEP)}] \quad (7)$$

Using cumulative formation constant, β₂, and the mass balance equation, Eq. 7 can be written in terms of the total concentration of

the ferric porphyrin, $[\text{Fe}^{\text{III}}(\text{OEP})]$ (sum of all the coordination forms of the ferric porphyrin: $\text{Fe}^{\text{III}}(\text{OEP})(\text{Cl})$, $\text{Fe}^{\text{III}}(\text{OEP})(\text{NO}_2)$, $\text{Fe}^{\text{III}}(\text{OEP})(\text{NO}_2)_2^-$):

$$[\text{Fe}(\text{III})(\text{OEP})\text{NO}_2]_2^- \\ = [\text{Fe}(\text{III})(\text{OEP})] \frac{\beta_2[\text{NO}_2^-]^2}{\beta_2[\text{NO}_2^-]^2 + [\text{Cl}^-]} = \alpha_2'[\text{Fe}(\text{III})(\text{OEP})] \quad (8)$$

If $[\text{NO}_2^-] \gg [\text{Fe}^{\text{III}}(\text{OEP})]$, then the fraction of the ferric porphyrin species in the bis-nitro form will be constant for a given concentration of nitrite (experiment). In addition, when the ferric porphyrin concentration is about 0.1 mM, over 90% of the ferric porphyrin is in the bis-nitro form for concentrations of nitrite greater than 5 mM. Eq. 7 can then be rewritten as:

$$\text{rate} = k'[\text{Fe}(\text{III})(\text{OEP})][\text{Fe}(\text{II})(\text{OEP})] \quad (9)$$

where $k' = k \alpha_2'$. The following relationship can be written between $[\text{Fe}^{\text{III}}(\text{OEP})]$ and $[\text{Fe}^{\text{II}}(\text{OEP})]$, based on the stoichiometry of the reaction:

$$[\text{Fe}(\text{III})(\text{OEP})] = M_{\text{Fe}} + 0.5[\text{Fe}(\text{II})(\text{OEP})]$$

where $M_{\text{Fe}} = M_{\text{Fe}^{\text{III}}(\text{OEP}),i} - 0.5 M_{\text{Fe}^{\text{II}}(\text{OEP}),i}$, and $M_{\text{Fe}^{\text{III}}(\text{OEP}),i}$ and $M_{\text{Fe}^{\text{II}}(\text{OEP}),i}$ are the initial concentration of the ferric and ferrous porphyrin, respectively. Combining these equations, we can write:

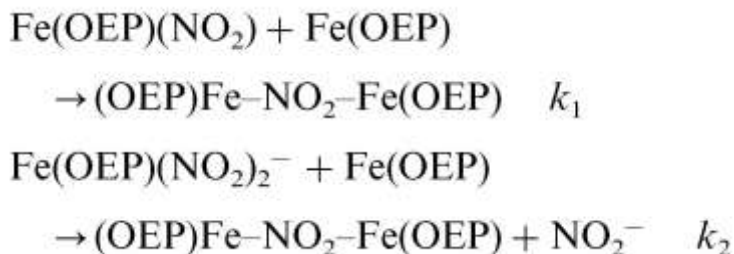
$$\text{rate} = - \frac{d[\text{Fe}(\text{II})(\text{OEP})]}{2 dt} \\ = k'(M_{\text{Fe}} + 0.5[\text{Fe}(\text{II})(\text{OEP})])[\text{Fe}(\text{II})(\text{OEP})]$$

Integration of this equation yields:

$$\begin{aligned}
 & M_{\text{Fe(III)(OEP),i}} \\
 & \neq 0.5 M_{\text{Fe(II)(OEP),i}} \ln \frac{[\text{Fe(III)(OEP)}]}{[\text{Fe(II)(OEP)}]} \\
 & = \ln \frac{M_{\text{Fe(III)(OEP),i}}}{M_{\text{Fe(II)(OEP),i}}} + 2k' M_{\text{Fe}} t \\
 & M_{\text{Fe(III)(OEP),i}} \\
 & = 0.5 M_{\text{Fe(II)(OEP),i}} \frac{1}{[\text{Fe(II)(OEP)}]} \\
 & = \frac{1}{M_{\text{Fe(II)(OEP),i}}} + 2k' t
 \end{aligned}$$

A plot of left hand side of the equations as a function of t should yield a straight line with a slope equal to $2k' M_{\text{Fe}}$ (or $2k'$). The data for various concentrations of iron porphyrin and nitrite are shown in Figure 7. The rate constants are summarized in Table 2. The agreement between the experimental data and the theoretical rate law confirms the assumption that the reaction is first order in both $\text{Fe}^{\text{III}}(\text{OEP})(\text{NO}_2)_2^-$ and $\text{Fe}^{\text{II}}(\text{OEP})$.

From Table 2, we can see that the observed rate constant, k' , was not strongly dependent upon the concentration of nitrite. This indicates that it is the coordinated nitrite, not the free nitrite in solution, that reacts with the ferric/ferrous porphyrins. From the value of β_2 , the fraction of the ferric porphyrin in the bis-nitrite form (α_2') can be calculated, and the results are summarized in Table 2. While the value of k' does decrease with the concentration of nitrite, the dependence is much weaker than expected based in the equilibrium concentration of $\text{Fe}(\text{OEP})(\text{NO}_2)_2^-$. Munro and Scheidt [12] have shown that the mono-nitrite complex was particularly reactive. Even though its equilibrium concentration is not significant under our conditions (which makes it possible to deconvolute the experimental spectra by ignoring the presence of the mono-nitro complex), it may be an important pathway if its rate constant (k_1) is larger than the one for the bisnitrite complex (k_2). The observed rate constant is therefore the combination of the two reactions:



Including both pathways for the formation of the bridged complex, and assuming that the rate of ligand exchange is faster than the redox reaction, the observed rate constant is equal to:

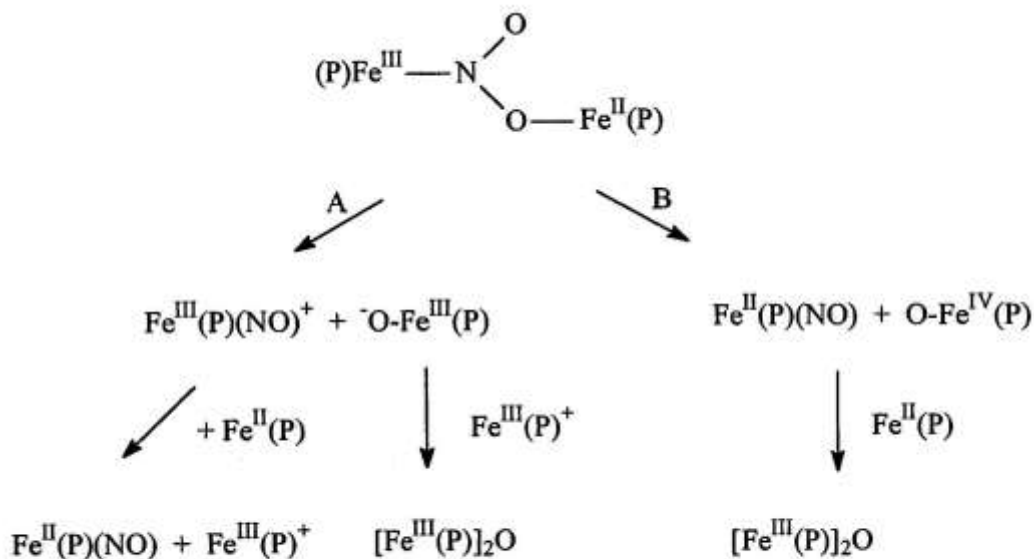
$$k' = \alpha_1' k_1 + \alpha_2' k_2$$

where α_1' is the fraction of the ferric porphyrin in the mono-nitro complex:

$$\begin{aligned} & [\text{Fe(III)(OEP)(NO}_2\text{)}] \\ & = M_{\text{Fe(III)(OEP)}} \frac{K_1[\text{NO}_2^-]}{[\text{Cl}^-] + K_1[\text{NO}_2^-] + \beta[\text{NO}_2^-]^2} \\ & = \alpha_1' M_{\text{Fe(III)(OEP)}} \end{aligned}$$

and α_2' has been previously defined in Eq. 7 (because the concentration of the mono-nitrite complex is always small, K_1 can be ignored in the calculation of α_2' , and the cumulative formation constant, β_2 used instead). Without K_1 , it is not possible to exactly calculate α_1' . The value of K_1 , though, can be estimated to be 0.012 from the known value of K_2 (2200) in DMF [1], because $\beta_2 = K_1 K_2$. With these values of the equilibrium constant, the rate constant as a function of nitrite concentration was calculated for $k_1 = 30 \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 6 \text{ M}^{-1}\text{s}^{-1}$ (Table 2). It is not clear why the mono-nitrite complex is more reactive than the bis-nitrite complex. When this experiment was repeated using the picket-fence porphyrin, no reaction was observed over the same time frame. While one side of the porphyrin is still exposed in this complex, the ferrous species is complexed with nitrite under these conditions, which would significantly reduce its ability to form a bridged mixed-oxidation state intermediate.

The results for the kinetics and spectroscopic studies can be summarized by the scheme below. Two pathways are outlined for the formation of the products:



Scheme 1.

The kinetic evidence, shown above, favors the bridged intermediate. Indirect evidence favors Pathway B. The formation of $\text{Fe}^{\text{II}}(\text{P})(\text{NO})$ in high yield would be expected by this pathway. The product formed in Pathway A, $\text{Fe}^{\text{III}}(\text{P})(\text{NO})^+$, would rapidly dissociate to form $\text{Fe}^{\text{III}}(\text{P})^+ + \text{NO}$, reducing the yield of the nitrosyl complex relative to the μ -oxo complex, due to the escape of NO. In addition, Pathway A would give rise to charged intermediates in a low dielectric solvent such as THF. This should be less favorable than the neutral intermediates in Pathway B.

Conclusions

Nitrite is quite stable in the presence of either ferric or ferrous porphyrins. The only reactions observed were complexation reactions. The stability of these complexes is quite dependent upon the complete exclusion of dioxygen. When there is a mixture of oxidation states, the solution has the right combination of Lewis acids and bases to coordinate nitrite, and facilitate the oxygen transfer reaction. The

details of the cleavage process still needs experimental confirmation, but the most likely process is the transfer of oxygen from the ferric coordinated nitrite to the ferrous species (Pathway B). Proton NMR evidence showed that the ferric species was coordinated with nitrite to form a strong low-spin complex for either the mono- or bis-nitro species, while the ferrous complex is weak in the absence of additional interactions provided by the picket-fence porphyrin. Cleavage by Pathway B would also readily form the observed products in high yield. Steric hinderance and/or ferrous coordination (as in the picket-fence porphyrins), both of which would make the bridged intermediate less favorable, was shown to significantly reduced the rate of the redox reaction of nitrite with iron porphyrins. Further studies investigating the importance of these factors are in progress.

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Table 1
Electronic spectra of nitrite complexes of iron porphyrins

Species	Solvent	Band maxima/nm ($\epsilon/\text{mM}^{-1}\text{cm}^{-1}$)	Reference
Fe(TPP)(Cl)	DMF	414 (9.5), 508 (11), 570 (4.0), 691 (2.7)	this work
	DMF	380 (49.7), 416 (9.5), 508 (12), 572 (3.87), 690	[17]
Fe(TPP)(NO ₂)	CH ₂ Cl ₂	417 (120), 508 (9.6), 570sh, 650 (2.4), 687 (2.4)	[5]
	DMF	413 (98), 506 (10.7), 568 (4.8), 607s, 690 (2.7)	this work
Fe(TpivPP)(NO ₂)	CH ₂ Cl ₂	412, 506, 579	[3]
Fe(TpivPP)(NO ₂) ₂ ⁻	CH ₂ Cl ₂	424, 551, 651	[3]
	DMF	425, 552	[3]
Fe(TPP)(NO ₂) ₂ ⁻	DMF	422 (141), 553 (9.6), 608sh, 690sh	[1], this work
	CH ₂ Cl ₂	424, 546, 576sh, 602sh	[1], this work
Fe(OEP)(Cl)	THF	374 (95.3), 504 (12.5), 532 (13.4), 629 (8.17)	this work
	CH ₂ Cl ₂	378 (99.6), 504 (8.7), 534 (9), 578 (2.6), 634 (4.5)	[20]
Fe(OEP)(NO ₂)	THF	392 (174.5), 494 (14.0), 613 (7.45)	this work
Fe(OEP)(NO ₂) ₂ ⁻	THF	394 (102), 534 (11), 588sh, 620 (6.8)	this work
	DMF	391, 541, 564s, 588s	this work
Fe(OEP)(NO ₂) ₂ ⁻	THF	389 (96), 558 (11.9), 586 (10.7)	this work
	DMF	381, 502, 535, 588s, 627	this work

Table 2
Kinetics of the reaction of Fe(OEP)(Cl) with nitrite in THF

[NO ₂ ⁻]/mM	$M_{\text{Fe(OEP)(Cl)}}$ /mM	$M_{\text{Fe(OEP)(NO}_2)_2^-}$ /mM	Intercept		$k_{\text{obs}}/\text{M}^{-1}\text{s}^{-1}$	α_2	$k_{\text{obs}}/\text{M}^{-1}\text{s}^{-1}$ ^a
			Experiment	Calculated			
0.050	0.050	0.050	0	0.0	3.2	0.936	3.1
0.50	0.050	0.050	0	0.0	6.2	0.91	7.1
5.0	0.050	0.050	0	0.0	7.5	0.94	7.6
5.0	0.050	0.025	0.69	0.71	8.0	0.94	7.6
5.0	0.025	0.050	1.0	1.0	5.3	0.94	7.6

^a $K_1 = 0.013$, $K_2 = 2000$, $k_1 = 30 \text{ M}^{-1} \text{ s}^{-1}$ and $k_2 = 6 \text{ M}^{-1} \text{ s}^{-1}$.

Figure Captions

Figure 1. Visible spectra of 0.050 mM Fe(OEP)(Cl) in 0.10 M TBAP. Solvent: THF. Dotted line: 0 mM (PNP)NO₂. Thick solid line: 10 mM (PNP)NO₂ with 0 mM (PNP)Cl. Thin solid lines: intermediate concentrations of 2.0, 4.0, 6.0 and 10. mM (PNP)NO₂ with 1 mM (PNP)Cl.

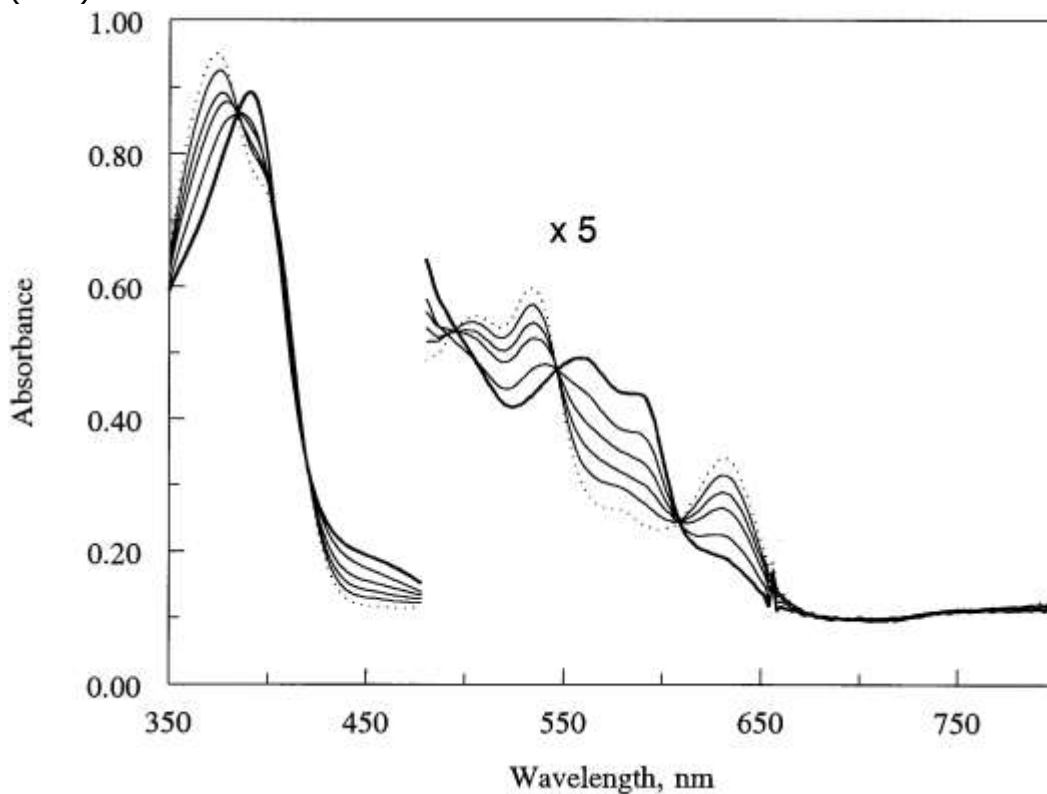


Figure 2. Visible spectra of 0.10 mM Fe(TPP)(Cl) in 0.10 mM TBAP. Solvent: DMF. A) 0.0 mM nitrite; B) 0.50 mM nitrite; C) 10 mM nitrite. Dotted lines are the calculated spectra for $K_1 = 2$ and $K_2 = 200$. Solid lines are the experimental spectra.

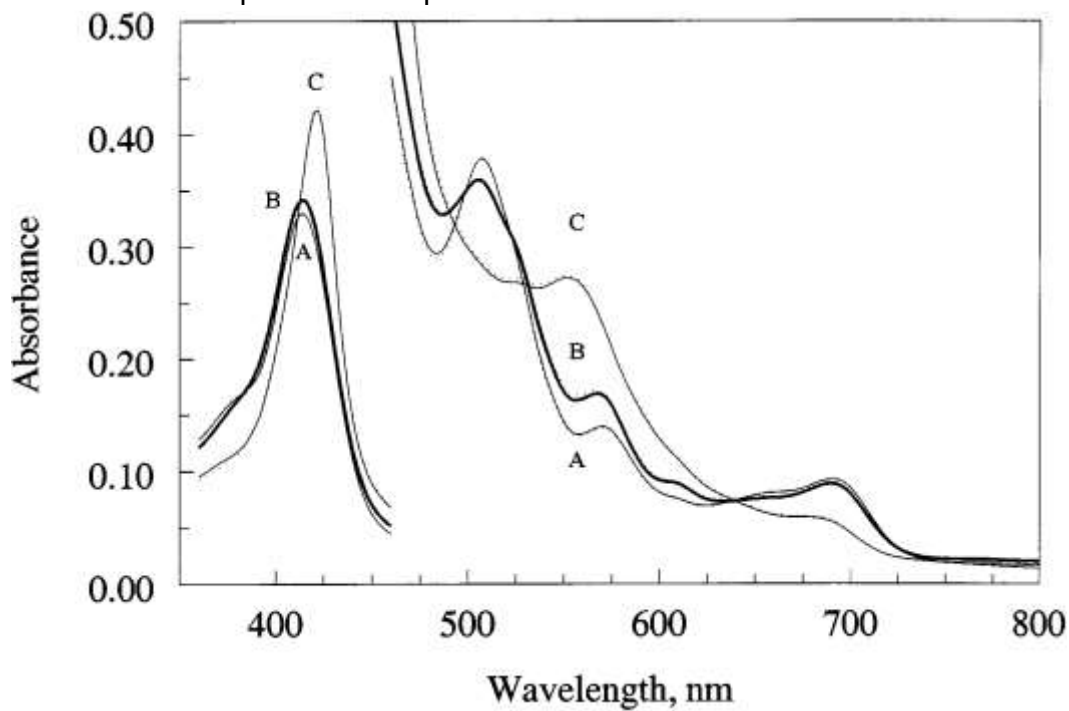


Figure 3. Thin-layer visible spectroelectrochemistry of 0.50 mM Fe(OEP)(Cl). Thin solid line: initial spectrum; thick solid line: spectrum at Wave Ia; dashed line: spectrum at Wave II. Solvent: DMF; Supporting electrolyte: 0.10 M TBAP; Working electrode: Platinum gauze.

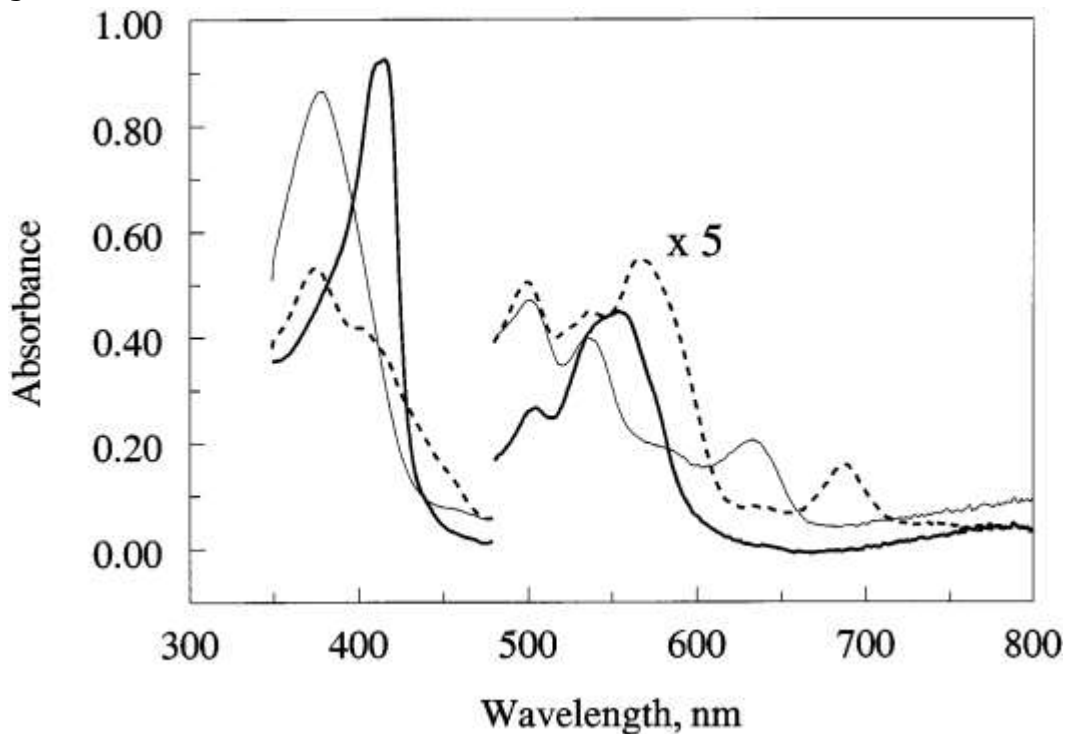


Figure 4. Thin-layer visible spectroelectrochemistry of 0.50 mM Fe(OEP)(Cl) in the presence of 5.0 mM (PNP)NO₂. Curves A. Potential is scanned through Wave Ia. Dotted line: Initial spectrum; thin solid lines intermediate spectra; thick solid line: spectrum at Wave Ia. Curve B. Calculated spectrum based on [Fe(OEP)] = 0.20 mM; [Fe(OEP)(NO)] = 0.10 mM; [(Fe(OEP)₂)O] = 0.10 mM. Solvent: DMF; Supporting electrolyte: 0.10 M TBAP; Working electrode: Platinum gauze.

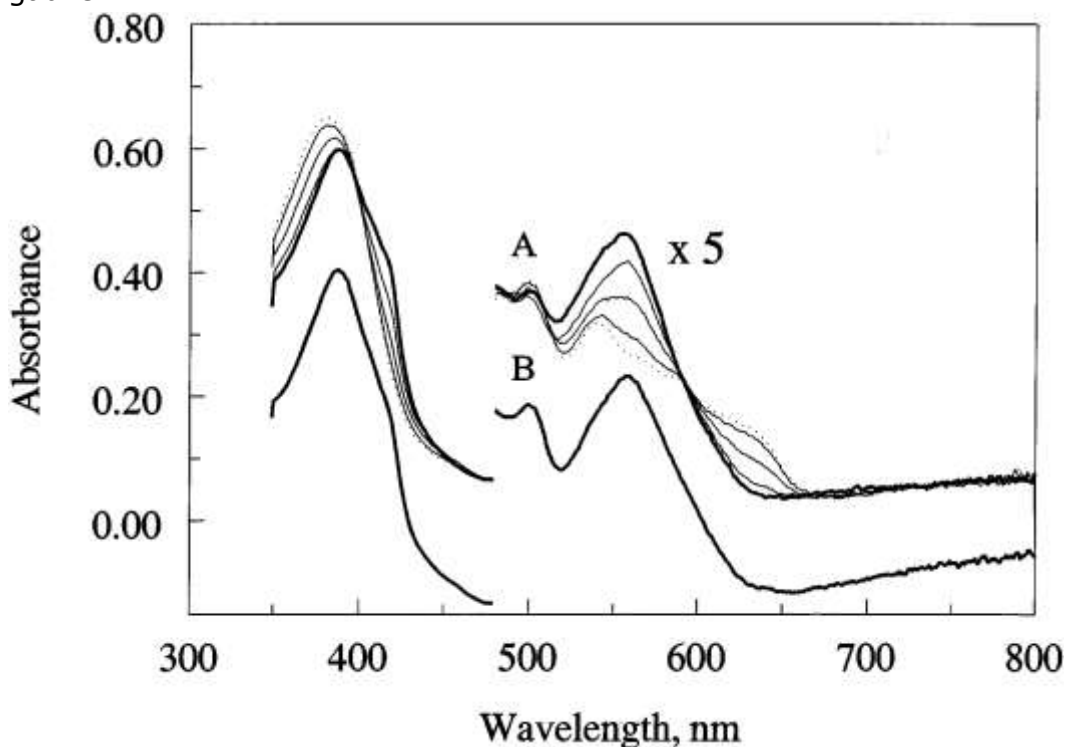


Figure 5. Thin-layer visible spectroelectrochemistry of 0.50 mM Fe(OEP)(Cl) in the presence of 5.0 mM (PNP)NO₂. Dotted line: spectrum at Wave Ia; thin solid line: spectra at potentials between Wave Ia and Wave Ib; thick solid line: spectrum at Wave Ib; dashed line: spectrum at Wave II. Solvent: DMF; Supporting electrolyte: 0.10 M TBAP; Working electrode: Platinum gauze.

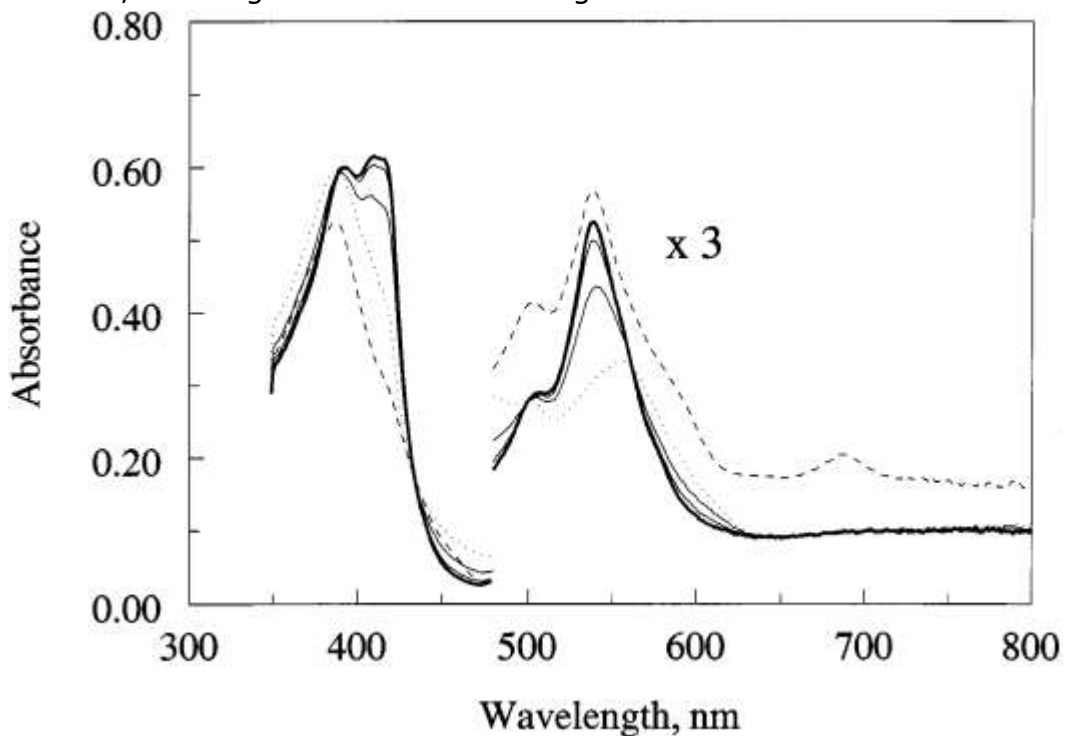


Figure 6. A. Visible spectra obtained after the mixing Fe(OEP)/Fe(OEP)(Cl) with nitrite. $[\text{Fe(OEP)(Cl)}] = [\text{Fe(OEP)}] = 0.050 \text{ mM}$; $[\text{NO}_2^-] = 10 \text{ mM}$; Solvent = THF. Dotted solid line: 0 s; thin solid lines: 200, 400, 600 and 800 s. Thick solid line: 1000 s.

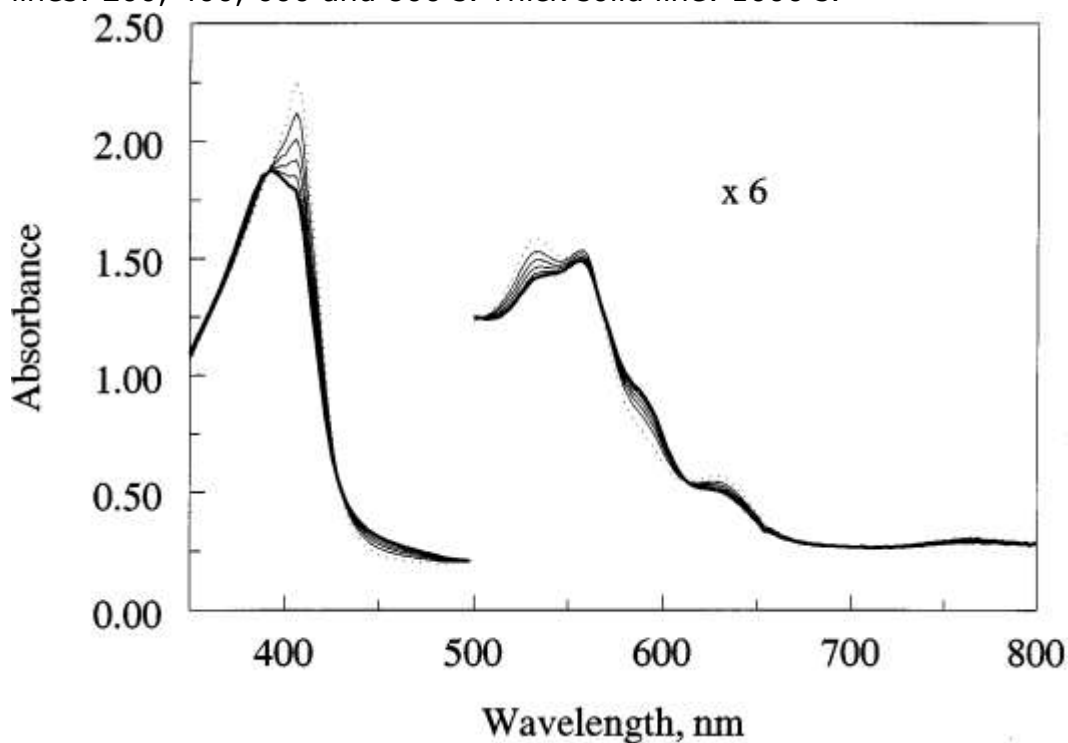


Figure 7. Variation in the concentration of Fe(OEP)(Cl)/Fe(OEP) as a function of time. Solid symbols: left y-scale. Open symbols: right y-scale. Open symbols: [Fe(OEP)(Cl)] = [Fe(OEP)] = 0.050 mM; (◆) [NO₂⁻] = 0.050 mM; (◻) [NO₂⁻] = 0.50 mM; (∇) [NO₂⁻] = 5.0 mM. Solid symbols: (●) [Fe(OEP)(Cl)] = 0.050 mM; [Fe(OEP)] = 0.025 mM; [NO₂⁻] = 5.0 mM; (▲) [Fe(OEP)(Cl)] = 0.025 mM; [Fe(OEP)] = 0.050 mM; [NO₂⁻] = 5.0 mM.

