The tungsten imido complex **5** was employed for model studies on eq 3. Alcoholysis of **5** (eq 8) is known.[7] Heating a 1:1 mixture

$$\underset{\mathbf{5}}{(t\text{-BuNH})_2W(N\text{-}t\text{-Bu})_2} + 2ROH \rightarrow (RO)_2W(N\text{-}t\text{-Bu})_2 + 2\text{-}t\text{-BuNH}_2 \quad (8)$$

of **5** with linalool (toluene, reflux) afforded, after hydrolysis, the rearranged (geranyl and neryl) amines in 90% yield (Table II). Similar results were obtained with other allylic alcohols. It is noteworthy that allyl alcohol-1,1-d_2 afforded a mixture of 22% 1,1- and 78% 3,3-dideuterated allyl-*tert*-butylamines.[12] This observation, along with the results for the isomeric octenols (Table II), suggests that the reaction does not proceed exclusively by a concerted electrocyclic rearrangement of the type implied by eq 3. A competing pathway, perhaps involving an allyl/metalate ion pair, must additionally be involved.

In conclusion, homogeneous analogues of the two C–N bond-forming processes proposed by Grasselli in the ammoxidation of propylene have been observed by us under mild conditions. While these observations constitute neither a necessary nor a sufficient condition for the mechanism of the heterogeneous process to be correct, they lend support to the Grasselli proposals while also opening the way to detailed mechanistic studies of such elemental steps.

Registry No. **2a**, 71851-94-0; **2b**, 71851-95-1; **3**, 6852-58-0; $PhCH_2\cdot$, 2154-56-5; $CH_2{=}CHCH_3$, 115-07-1; PhC(O)OOC(O)Ph, 94-36-0; $(Me_3SiO)_2CrO(N\text{-}t\text{-Bu})$, 83619-58-3.

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[13] Contribution No. 3615.

Articles

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Chemistry of the Pentacyano(4-nitroimidazolato)ferrate(II) Ion: Unusual Oxidation States of Iron

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Complexes involving 4-nitroimidazole as a ligand have been little studied. They are of potential interest because of the rather facile reduction of this compound to a radical anion, which raises the possibility of studying metal-complexed radicals or complexes of metals in unusually low oxidation states. An Fe(II) complex containing this ligand associated with the pentacyanoferrate moiety has been synthesized, and its spectroscopic properties are reported. They demonstrate that the 4-nitroimidazolato ion is a strong field ligand. The kinetics of ligand-exchange reactions of this compound have been studied. The rates of association and of dissociation are comparable to those reported for similar pentacyanoferrate(II) complexes. The Fe(II) complex can be oxidized to a thermodynamically less stable Fe(III) compound. More interestingly it can be reduced by sodium dithionite. Stopped-flow spectrophotometry shows that there are two reduction steps, both involving the SO_2^- radical. Both steps are pH dependent and involve simultaneous one-electron reduction and protonation of the complex. ESR spectroscopy establishes that the first reduction product is a pentacoordinate Fe(I) complex. Protonation has occurred on the imidazole ring. Proton NMR of the final product shows a resonance around 20 ppm to high field of Me_4Si, strongly suggesting that the second reduction step is accompanied by protonation on the metal to give a hydridoiron(II) compound. The analogy with the catalytically active isoelectronic pentacyanocobaltate(II) and hydridopentacyanocobaltate(III) ions is noted.

Introduction

Some years ago it was reported that 4-nitroimidazole forms a thermodynamically very stable and kinetically inert complex with metmyoglobin.[1] Of the wide variety of complexes of metmyoglobin known, this complex is second only to that formed with the cyanide ion in terms of the magnitude of the formation constant (8800 M^{-1}) and its slow rate of dissociation ($k = 0.04$ s^{-1}). pH measurements indicated that the complex contained the 4-nitroimidazolato ion rather than the neutral 4-nitroimidazole molecule. These results suggest that the 4-nitroimidazolato ion might form stable complexes with a variety of transition-metal ions.

4-Nitroimidazole and its derivatives show a number of properties that suggest that these metal complexes may be of interest. They have pharmaceutical applications as radiosensitizers and as drugs.[2,3] In the presence of radiation, 4-nitroimidazole is reduced to radical anions, the structures of which have been studied as a function of pH by ESR.[4] It has been suggested that these radical anions are responsible for the radiosensitizer properties. Kinetic studies of the reduction of the myoglobin derivative by dithionite indicated that the electron was transmitted through the 4-nitroimidazole π system and that a radical ligand existed as a transient intermediate. It occurred to us that if the radical ligand were associated with a metal ion less easily reduced than Fe(III), more stable radical complexes might result. We have been interested in such complexes for some years.[5,6] Alternatively the good π-accepting properties of the 4-nitoimidazole ligand might serve to stabilize unusually low oxidation states of metal ions. The question also arises as to how the oxidation/reduction properties of the imidazole ring are linked to the acid/base properties. The potential importance of such linkage in imidazole chemistry to processes such as oxidative phosphorylation has been discussed

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by Wang.[7] We have therefore undertaken a project to synthesize and investigate the oxidation/reduction chemistry of representative transition-metal complexes containing the 4-nitroimidazole ligand (abbreviated 4-NIM).

There has been a recent report of one such complex, pentaammine(4-nitroimidazolato)cobalt(III) chloride.[8] This compound was prepared by the facile nitration of the unsubstituted imidazole compound. Its molecular structure was determined by X-ray crystallography. The pK_a of the coordinated imidazole (1.66) is considerably reduced from that of the free 4-nitroimidazole. A table of Mössbauer data in another recent publication[9] contains an entry for a complex formulated as a pentacyano(4-nitroimidazole)- rather than pentacyano(imidazolato)ferrate(II). The direct preparation of 4-nitroimidazole complexes is complicated in aqueous solution by pH considerations. 4-Nitroimidazole has a pK_a for the formation of the anion of 9.2.[10] At low pHs aqueous mixtures of 4-nitroimidazole and transition-metal salts show, by spectroscopic measurements, only very weak complex formation. At high pHs metal hydroxides are usually precipitated. Very marked color changes can be observed by dissolving KOH in dimethyl sulfoxide to which crown ether has been added and then adding transition-metal salts and 4-nitroimidazole. We attribute these color changes to the formation of 4-nitroimidazolato complexes and have isolated Cr(III) compounds. However, we have found that the most accessible 4-nitroimidazolate complex involves the pentacyanoferrate(II) moiety, and the present paper describes some chemistry of this compound.

Experimental Section

a. Synthesis of the Fe(II) Complex. The conventional method for the synthesis of pentacyanoferrate(II) complexes involves the preparation of the ammonia complex[11,12] followed by displacement of ammonia, initially by water and subsequently by the desired ligand.[13,14] The 4-nitroimidazolate complex can indeed be prepared by this method, but the purity and yield of the product are unsatisfactory. We have also prepared it by a one-step synthesis[15] in which aqueous nitroprusside is reacted with the 4-nitroimidazolate anion at high pH. However, our preferred method involves a procedure in which the intermediate pentacyanonitroferrate(II) is isolated from methanolic solution.

A 3-g sample of finely powdered sodium nitroprusside was added to 50 mL of methanol and the mixture stirred for 5 min to complete dissolution. A 4-g portion of potassium hydroxide was added with stirring. An exothermic reaction occurred, and the solution was heated and stirred for 10 min at 45 °C. A mustard yellow precipitate of the pentacyano nitro complex[16] formed rapidly, was cooled in ice for 60 min, and was filtered.

$$[Fe(CN)_5NO]^{2-} + 2OH^- = [Fe(CN)_5(NO_2)]^{4-} + H_2O$$

The precipitate was washed with 100 mL of methanol, dried at 60 °C for 2 h to remove methanol, and stored in a desiccator over calcium chloride. Anal. Calcd for $K_4[Fe(CN)_5(NO_2)]H_2O$: C, 14.78; N, 20.68; H, 0.50; Fe, 13.74; K, 38.49. Found: C, 14.78; N, 20.67; H, 0.53; Fe, 13.69; K, 38.75.

The electronic spectrum in alkaline solution showed a band at 396 nm in agreement with the literature report.[17] The infrared spectrum agreed with that reported by West,[16] with the exception of some additional bands and small shifts associated with the presence of the molecule of water of crystallization. To complete the preparation of the 4-nitroimidazole derivative, 3.5 g of 4-nitroimidazole and 3.5 g of potassium hydroxide were dissolved in 50 mL of methanol and the yellow nitro precipitates (not dried) from the previous reaction was added. These quantities represent approximately a 3-fold excess of the 4-nitroimidazole ligand. At this stage no reaction occurred. A 40–50-mL portion of water was slowly added, with continuous stirring at 45–50 °C until all the nitro compound just dissolved. A dark brown solution formed immediately. The solution was cooled to 10 °C in ice, 15 mL of cold methanol was added, and the resultant mixture was allowed to stand for 30 min to complete precipitation. After filtration the precipitate was washed with 100 mL of 4% methanolic KOH to remove excess 4-nitroimidazole and then with 100 mL of methanol to remove excess KOH. The complex was dried at 60 °C for 3 h to remove methanol and stored in a vacuum desiccator over calcium chloride. Anal. Calcd for $K_4[Fe(CN)_5(4\text{-}NIM)]\cdot 3H_2O$: C, 18.90; N, 22.04; H, 1.59; Fe, 10.98; K, 30.76. Found: C, 19.05; N, 22.05; H, 1.53; Fe, 11.04; K, 30.92. Yield: 81% based on starting nitroprusside.

The presence of three molecules of water of crystallization was confirmed by an NMR experiment. The complex was dissolved in D_2O, and the increase in the integrated area of the HDO peak, relative to that of "pure" D_2O, was compared with the integrated intensities of the 4-nitroimidazole protons. This method indicated three waters of crystallization. We note that 3 H_2O seems to be usual for the crystallization of pentacyanoferrate(II) complexes with heterocycle ligands.[14,18]

Several problems are commonly encountered in the synthesis of pentacyanoferrate(II) complexes from the ammonia complex. The aquo complex is thought to be an intermediate, and this complex is susceptible to a number of slow dimerization and oxidation reactions that lead to undesirable side products, giving poor yields and low purity. In the present synthesis the aquo compound is also a likely intermediate, since no reaction occurs until water is added to the methanolic reaction mixture. In this case though, only a limited amount of water is present and displacement by the incoming ligand occurs immediately, allowing no time for the formation of undesirable dimeric products. This procedure may prove useful in the synthesis of other pentacyanoferrate(II) derivatives.

b. Kinetic Measurements. (i) Formation of Pentacyano(4-nitroimidazolato)ferrate(II). The rates of formation of a large number of pentacyanoferrate(II) complexes have been measured and the problems involved in these measurements discussed.[13,19,20] Borghi et al.[21] have concluded that "by using the sulphito-complex as a starting reagent, pH's higher than 10 and concentrations up to 10^{-3} M can be reached without interference from dimerization and oxidation at least for half an hour after dissolution". We concur with this conclusion and have therefore used the sulfito complex to measure the rate of formation. Solutions of $Na_5[Fe(CN)_5(SO_3)]\cdot 2H_2O$ were freshly prepared in boiled, distilled water, deoxygenated with N_2. Initial measurements were made after 20 min, and syringes and flasks were covered with aluminum foil. Kinetic runs were carried out at pH 11.8 maintained with phosphate buffer. The high pH is necessary to ensure that all the 4-nitroimidazole is present in an anionic form. A temperature of 24 °C was maintained during the experiments. Following the recommendation of Borghi et al.[21] the total ionic strength was kept low (0.05 M with $NaClO_4$) to further inhibit the dimerization reaction. Sulfite solutions used at different aquation times ranging from 30 min to 2 h showed no significant differences in the pseudo-first-order rate constants obtained for a given concentration of 4-nitroimidazole. It is clear there is no significant distortion of the results due to dimerization or oxidation for aging periods up to 2.0 h. This result is in marked contrast to kinetic runs obtained on the ammonia complex. The concentration of $Na_5[Fe(CN)_5(SO_3)]$ was 5×10^{-4} M, and the 4-nitroimidazole concentrations varied from 5×10^{-3} to 5×10^{-2} M. At this concentration the published dissociation constant[22] for the sulfite complex[21] indicates 94% dissociation to the aquo compound. Aquation can be monitored by following the disappearance of the band at 360 nm and the appearance of a new band at 440 nm. The reaction was followed by monitoring the increase in absorption at 485 nm.

The sulfite complex used in this kinetic study was prepared according to the literature procedure.[23,30] Complete formation was demonstrated by the presence of the complexed sulfite band at 960 cm^{-1} in the infrared spectrum and the absence of the free sulfite band at 933 cm^{-1}.[23]

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Reaction rates were measured with the use of a Durrum Model D-110 stopped-flow spectrophotometer. The data were collected on a Nicolet-1170 signal averager. Hard copies of the decay curves were obtained from a Hewlett-Packard 7044A X-Y recorder. All experiments were run under pseudo-first-order conditions, and the resulting plots showed first-order behavior over 3–4 half-lives. Temperature was controlled by means of a thermostated water bath. The statistical errors in the rate constants are low, and the estimated errors of ±10% represent allowance for systematic errors.

(ii) Dissociation. Kinetic runs were carried out at pH 11.8 in phosphate buffer (μ = 0.05 M ($NaClO_4$)) in argon-degassed solutions at 25 °C. The concentration of $K_4[Fe(CN)_5$4-NIM] was 5×10^{-4} M, and a 50–200-fold excess of the incoming ligands imidazole, cyanide, or dimethyl sulfoxide was used.

(iii) Oxidation and Reduction. The kinetics of the oxidation of the Fe(II) complex by potassium peroxydisulfate were studied at pH 9.6 (μ = 0.025) in borax buffer at 25 °C. Both the decay of the 475-nm absorption and the growth of the bands at 425 and 525 nm were monitored. Reductions by dithionite were carried out in carefully degassed solutions using Tris buffer and were monitored at 475 nm.

c. Spectroscopic Measurements. Proton and carbon-13 NMR spectra were obtained on Bruker WM-250 and Varian EM-390 instruments. TSP ((trimethylsilyl)propionic acid) was used as an internal calibrant. A Bruker ER-100D spectrometer was used to obtain ESR spectra. UV/Visible spectra were measured on a Pye Unicam SP8-100 double-beam instrument or a Hewlett-Packard 8451A diode array spectrometer and infrared spectra on a Perkin-Elmer 283 spectrophotometer.

The preparation of the Fe(I) complex for ESR studies was carried out as follows. A 5.6-mL portion of dry acetonitrile was added to 0.5 g of $Na_2S_2O_4$ and 0.6 g of the 4-nitroimidazole complex, and 3.5 mL of deoxygenated water was injected below the acetonitrile. The yellow oil, which formed within 1 or 2 min, was removed with a syringe and a small quantity placed in a capillary tube for the ESR measurement. This operation was performed in an argon atmosphere.

Spectroscopic Properties of the Fe(II) Complex

a. NMR Spectra. The ^1H NMR spectrum of 4-nitroimidazole in D_2O at pH 12 shows two sharp lines at 7.34 and 7.93 ppm from Me_4Si. These resonances are assigned to protons at the 5- and 2-positions of the imidazole ring, respectively. In the complex at the same pH these lines move to 7.44 and 8.13 ppm. These downfield shifts on complexation are a little larger than those reported by Shepherd[24] for the analogous imidazole and methyl-substituted imidazole complexes. They are sufficiently large to provide an easy test for the presence of free ligand in impure samples of the complex. The observation of separate sharp resonances for free and complexed ligands demonstrates that exchange is slow on the NMR time scale.

The ^{13}C spectrum shows resonances at 178.8 and 176.1 ppm attributed to the cis and trans cyanides, repectively, and further lines at 151.0, 150.5, and 138.5 ppm assigned to the imidazole carbons. The line at 151.0 ppm is assigned to C4 since it lacks Overhauser enhancement, that at 150.5 ppm to C2, and that at 138.5 ppm to C5. The corresponding lines in the free ligand are found at 147.6, 147.3, and 133.0 ppm. The overlap between the C4 and C2 lines was avoided by running the proton-coupled spectrum. The observation of only one set of ^{13}C lines for the complexed imidazole indicates that a single isomer predominates. By analogy with the crystal structure of Storm et al.[8] for pentaammine(4-nitroimidazolato)cobalt(III) chloride and with the steric arguments presented by Shepherd[24] for methylimidazole complexes, coordination has probably occurred through the nitrogen not adjacent to the nitro substituent. Toma, Vanin, and Malin[25] have correlated the ^{13}C chemical shifts of the cyano groups of pentacyanoferrate(II) complexes with their Mössbauer and electronic spectra. These chemical shifts are therefore a measure of the ligand field strength of the 4-nitroimidazolato anion. On this basis it is a rather stronger field ligand than imidazole (cis shift 181.1 ppm, trans shift 179.1 ppm), about the same as pyridine (cis 179.5 ppm, trans 175.5 ppm) and pyrazole (cis 177.5 ppm, trans 173.5 ppm) and significantly weaker than the S-bonded dimethyl sulfoxide ligand (cis 170.0 ppm, trans 167.0 ppm). The observed ^{13}C shifts of 178.8 (cis) and 176.1 ppm (trans) suggest that the first ligand field transition should occur at about 26 300 cm^{-1} (380 nm) if the correlation of Toma et al. holds.

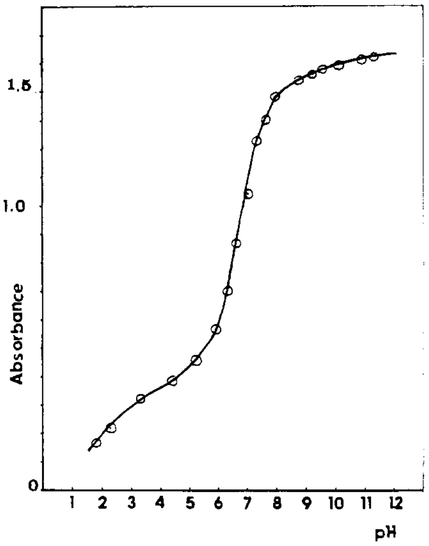

Figure 1. Absorbance vs. pH. Conditions: $[Fe(CN)_5(4\text{-NIM})]^{4-} = 1 \times 10^{-3}$ M; $\epsilon = 1520 \times 10^3$ M^{-1} cm^{-1} at pH 11.9; λ = 480 nm.

b. Electronic and Infrared Spectra. The complex shows two bands in the UV/visible spectrum, one at 480 nm (ϵ = 1520 M^{-1} cm^{-1}) and one at 350 nm (ϵ = 8320 M^{-1} cm^{-1}). The latter is almost certainly a π-to-π^* ligand transition since it has not shifted from the position in the free ligand. In light of the estimation of the first ligand field transition from the ^{13}C chemical shift, the band at 480 nm is probably a charge-transfer transition. The compilations of electronic spectra given by Toma et al.[26] and by Johnson and Shepherd[9] would indicate that a pentacyanoferrate(II) complex with a ligand field band at 480 nm would require a very weak-field sixth ligand. This is not in accord with the other chemical and physical properties of the compound under discussion. Toma and Malin[27] have assigned bands of pentacyanoferrate complexes of aromatic nitrogen heterocycles observed in the visible spectrum to metal-to-ligand electron-transfer transitions. They report extinction coefficients of 10^3–10^4 for these bands and have correlated the energies of the transitions with the oxidation potentials and ligand exchange rates of the complexes. They discuss their results in terms of dπ–pπ back-bonding to the aromatic ligand. In view of the similar extinction coefficient it seems very probable that the 480-nm band in the 4-nitroimidazolato complex is also a metal-to-ligand charge-transfer band. This assignment implies that this ligand is an effective π acceptor, comparable, for example, to 4-pyridylpyridinium, which bears a formal positive charge rather than a negative charge. The correlation between the electron-transfer band energy and the rate of ligand dissociation reported by Toma and Malin[27] leads to an estimate of 3.5×10^{-4} s^{-1} for the rate of ligand dissociation of the 4-nitroimidazole complex.

The infrared spectrum obtained of a KBr disk, shows a strong CN stretch at 2040 cm^{-1} with a weaker shoulder at 2080 cm^{-1}. In principle the CN stretching frequency should reflect the π-donor or -acceptor ability of the sixth ligand. A good donor should provide electrons for the π^* cyanide orbitals and lower the CN stretching frequency, and a good π acceptor should have the reverse effect. In practice, the stretching frequency seems to be quite insensitive to the nature of the sixth ligand. Thus, with the exception of the nitroprusside ion, all pentacyanoferrate(II) complexes show cyanide stretches in the 2030–2060-cm^{-1} region. The exact frequencies seem sensitive to the hydration of the complex. Thus, we observe that the aquated nitro complex prepared in the present work has a CN stretch at 2040 cm^{-1} compared

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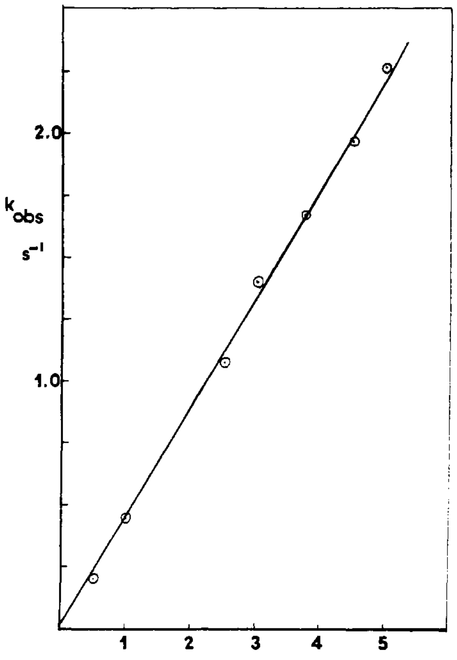

Figure 2. Plot of the observed rate constants vs. ligand concentration for the formation of $[Fe(CN)_5(4\text{-}NIM)]^{4-}$. Conditions: 24 °C; $\mu = 0.05$ M; pH 11.8; $\lambda = 485$ nm; $[Fe(CN)_5(4\text{-}NIM)]^{4-} = 5 \times 10^{-4}$ M.

to the value of 2060 cm^{-1} reported for the anhydrous compound.[16] Variations of 20 or 30 cm^{-1} in the CN stretches of Fe(II) cyanide complexes due to hydrogen-bonding effects have been reported previously.[28]

c. pK_a of Complexed 4-Nitroimidazole. Figure 1 shows a plot of absorbance at 480 nm vs. pH for pentacyano(4-nitroimidazole)ferrate(II). The changes of absorbance with pH are reversible, providing the solution is not allowed to stand for an extended period of time at low pH, when dissociation of the imidazole occurs, followed by slow irreversible dimerization and oxidation. Figure 1 indicates a pK_a for the 4-nitroimidazole complex of 6.8. This is less than the pK_a of the free ligand by 2.4 pK_a units,[10] consistent with the donation of negative charge from the ligand to the metal. Johnson et al.[29] have pointed out that the coordination of most transition-metal centers lowers the pK_a of imidazole by about 4 units and have fitted the data for a large number of such complexes to a formula involving the electronegativity and charge of the metal center. In the present case the observed lowering of 2.4 units is rather less than the usual decrease of 4 units or than that predicted by the formula for imidazole. This suggests that the donation of charge to the metal ion through the σ bond may be partly offset by π back-bonding in the case of the nitro ligand.

Kinetics of Formation and Dissociation of the Fe(II) Complex

For the reasons set out in the Experimental Section the kinetics of the formation of the 4-nitroimidazole complex have been studied by reaction with the sulfito complex. Providing a period of about 30 min is allowed for aquation to occur, the actual reactant is the pentacyanoaquoferrate(II) ion and ligand displacement occurs at a rate that is first order in the incoming ligand. Figure 2 shows a plot of the pseudo-first-order rate constants vs. 4-nitroimidazole concentration. From the slope of this plot a value of 45.0 ± 3 $M^{-1}\ s^{-1}$ is obtained for the second-order rate constant. This value is comfortably within the range of 38–64 $M^{-1}\ s^{-1}$ reported by Bradic et al.[22] for the substitution of the pentacyanoaquoferrate(II) ion by singly negatively charged anions. The rate of substitution by uncharged ligands is considerably higher (200–300 $M^{-1}\ s^{-1}$) and that by doubly negatively charged anions substantially less (SO_3^{2-}, 3.3 $M^{-1}\ s^{-1}$). Bradic et al. argue that these differences are consistent with a dissociative exchange (D) mechanism if the dependence of the diffusion rate on the charge of the incoming ligand is taken into account. An interchange (I_d) mechanism is also compatible with the experimental data.

The rate of dissociation of the 4-nitroimidazolate was obtained from the rate of displacement by other ligands. With an excess of incoming ligand such reactions proceed at a rate that is independent of the concentration of the displacing ligand and is determined by the rate of dissociation of the leaving ligand.[19,31] The accepted mechanism is

$$Fe(CN)_5L^{3-} + H_2O \rightleftarrows Fe(CN)H_2O^{3-} + L$$

forward rate k_{-L}, backward rate k_L

$$Fe(CN)_5H_2O^{3-} + Y \rightleftarrows Fe(CN)_5Y^{3-} + H_2O$$

forward rate k_Y, backward rate k_{-H}

Under pseudo-first-order conditions this mechanism leads to an observed rate constant given by

$$k_{obsd} = \frac{k_{-L}k_Y[Y] + k_{-Y}k_L[L]}{k_Y[Y] + k_L[L]}$$

If $k_Y[Y] >> k_L[L]$, this expression reduces to $k_{obsd} = k_{-L}$. The displacement of 4-nitroimidazole by Me_2SO, imidazole, and CN^- ligands has been examined. Values of k_Y for the displacing ligands are known from the literature, and the concentrations of the reactants were chosen so that the condition necessary for $k_{obsd} = k_{-L}$ was easily satisfied. Displacement by Me_2SO, imidazole, or CN^- gives a value for k_{-L} of $(1.9 \pm 0.3) \times 10^{-4}\ s^{-1}$. This value is in reasonable agreement with the estimate of $3.5 \times 10^{-4}\ s^{-1}$ obtained above from the electronic spectrum and confirms the assignment of the band at 480 nm to a charge-transfer transition. We note that the dissociation rate is almost a factor of 10 less than that for the neutral imidazole ligand.[14] Combination of the association and dissociation rates gives an association constant of $2.1 \times 10^5\ M^{-1}$. Coincidentally, this is exactly the value quoted by Toma and Creutz[32] for neutral imidazole at low ionic strength. The differences in association rates and dissociation rates are compensatory.

Oxidation to the Iron(III) Complex

Pentacyanoferrate(II) complexes can be oxidized to the corresponding Fe(III) compounds. Toma and Creutz[32] have measured the oxidation/reduction potentials of a number of such complexes and have used this information to calculate the stability constants of the Fe(III) compounds. These authors point out that the range of stability constants for the Fe(III) complexes (6 orders of magnitude for the ligands considered) is much greater than that of the corresponding Fe(II) complexes (2 orders of magnitude). They found that for unsaturated nitrogen ligands there was a good correlation between the oxidation/reduction potentials and the first pK_a of the ligand. Taking the pK_a of the 4-nitroimidazolium ion to be −0.05,[33] this correlation predicts a value of around 0.6 V for the oxidation potential of the 4-nitroimidazole complex and a formation constant for the Fe(III) compound of around 100. These figures imply that the Fe(III) complex will be considerably less stable than the Fe(II) compound.

We find that the oxidation of the Fe(II) compound can be accomplished with potassium peroxydisulfate, potassium periodate, or hydrogen peroxide. There is evolution of oxygen during the last reaction, indicating that the reaction may be more complex than expected. Milder oxidizing agents such as bromine–water

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give some reaction but also appear to induce dimerization. The electronic spectrum of the product is independent of the oxidizing agent used, showing bands at 514, 412, and 335 nm. This spectrum is consistent with the spectroscopic data reported by Johnson et al.[29] and by Sheperd[24] for other pentacyanoferrate(III) imidazole and imidazolate complexes. The 335-nm band is clearly a ligand $\pi-\pi^*$ transition. The above authors assign the lowest energy band to ligand-to-metal charge transfer and the middle frequency to the ligand field transition. On this assignment the charge-transfer transition that occurs at 625 nm in the imidazolate complex has moved to 514 nm in the 4-nitroimidazolate complex. This is consistent with the expected reduced π-donor ability of the nitro derivative and complements the observation of a lower energy metal-to-ligand charge-transfer band in the corresponding Fe(II) complex. The ligand field band is observed at 412 nm in the nitro complex and 438 nm in the unsubstituted compound, indicating that 4-nitroimidazolate is a stronger field ligand than imidazolate.

As expected, the Fe(III) complex is paramagnetic and shows no ^{1}H NMR spectrum. The infrared spectrum shows a strong CN stretch at 2120 cm^{-1} and weaker bands at 2150 and 2200 cm^{-1}. The increase in stretching frequency on oxidation is similar to that observed for other pentacyanoferrate complexes. The exact frequency is not very sensitive to the nature of the sixth ligand. There is also a strong band at 1945 cm^{-1}. This band cannot be assigned to nitroprusside impurity since lower wavenumber bands expected for this compound are not observed. The frequency is very low for a CN stretch, and the intensity is high for a combination band. A magnetic moment of 1.4 μ_B was measured by the Gouy method. This value is rather lower than expected (1.7 μ_B) but confirms the spin-paired nature of the complex indicated by the electronic spectrum. The kinetics of the oxidation of the Fe(II) complex by peroxydisulfate have been qualitatively examined. Sulfab[34] has reported a kinetic study of the oxidation of pentacyano(sulfito)ferrate(II) by peroxydisulfate. This is a relatively slow reaction, and it is of interest to ask whether the rate will be similar for the nitroimidazolate derivative. Sulfab found the rate to be very sensitive to the ionic strength of the solution and attributed this to ion-pair formation. Under pseudo-first-order conditions we obtained a second-order rate constant of 0.7 ± 0.1 M^{-1} s^{-1}, which is quite similar to that obtained from the data of Sulfab under similar conditions. There is some evidence for a concurrent slower reaction as reported by Sulfab. The mechanism of these oxidation reactions is uncertain.

Reduction of the Iron(II) Complex

A number of papers have discussed the radicals formed by the reduction of 4-nitroimidazole derivatives that are radiosensitizers.[2,3] Whillans et al.[4] have examined the ESR spectra of radicals formed by radiolytic reduction of the parent compound. They found different spectra in the pH regions 1–3, 6–10, and 13–14 and assigned them to neutral radicals, monoanions, and dianions formed by successive deprotonation steps as the pH is increased. All of these radicals showed a characteristic large hyperfine coupling constant (14.4–16.68 G) for the nitrogen of the nitro group and *g* values typical of organic free radicals (2.004 41–2.004 68). A recent paper by Ozawa and Kwan[35] has demonstrated that aromatic nitro compounds can be reduced by dithionite. 4-Nitroimidazole can also be reduced in this manner. Figure 3b shows the spectrum obtained at high pH. It agrees well with that obtained by Whillans et al. by radiolysis.

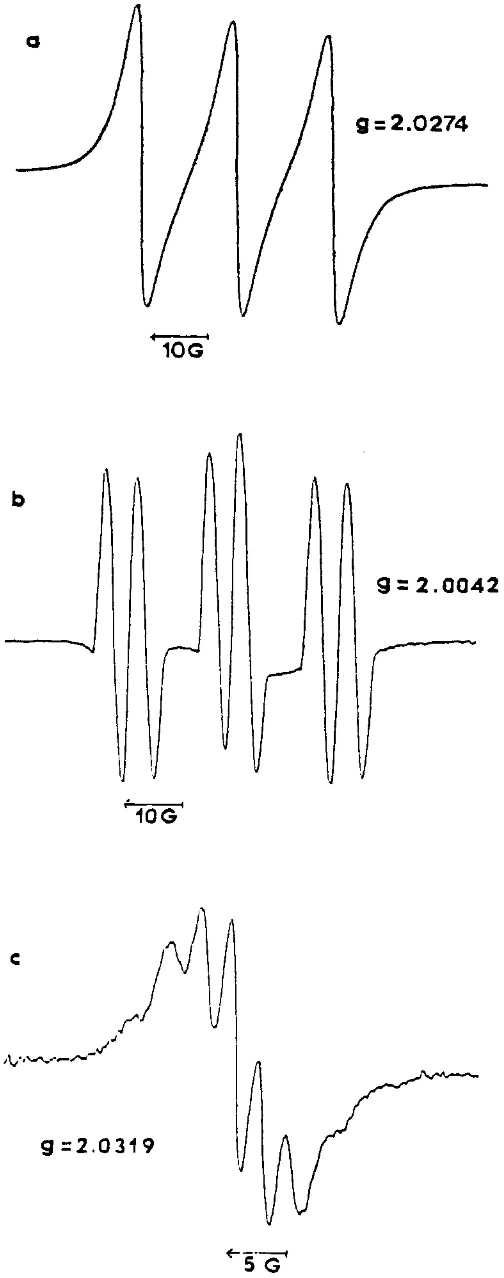

Figure 3. ESR spectra: (a) of the nitroprusside radical formed in an 80% DMF solution with SO_2^-; (b) of the 4-nitroimidazole radical formed in aqueous solution with SO_2^- (pH 13); (c) of the Fe(I) radical formed by reduction of $[Fe(CN)_5(4\text{-}NIM)]^{4-}$ with SO_2^- in aqueous solution at pH 6.6.

The reduction of the nitroprusside ion to give radical species has been accomplished by electrolytic,[36,37] photolytic,[38] and chemical[39] means. The chemistry of these reactions has been extensively investigated. There are two principal types of radical products. One is blue, has a *g* value of 2.027, and has been shown by X-ray crystallography[40] to be the five-coordinated complex $Fe(CN)_4NO^{2-}$ with a square-pyramidal geometry. The second type of radical is six-coordinated $Fe(CN)_5NO^{3-}$ and gives a brown solution and a *g* value of 1.979. The electronic structures of these compounds, particularly the question as to whether they are best described as Fe(I) compounds with NO$^+$ ligands or Fe(II) compounds with neutral NO ligands, have been discussed by several authors.[41,42] The possible existence of d^7 Fe(I) compounds was suggested some years ago on the basis of experiments on the electrolysis of the ferrocyanide ion.[43] Such compounds have also

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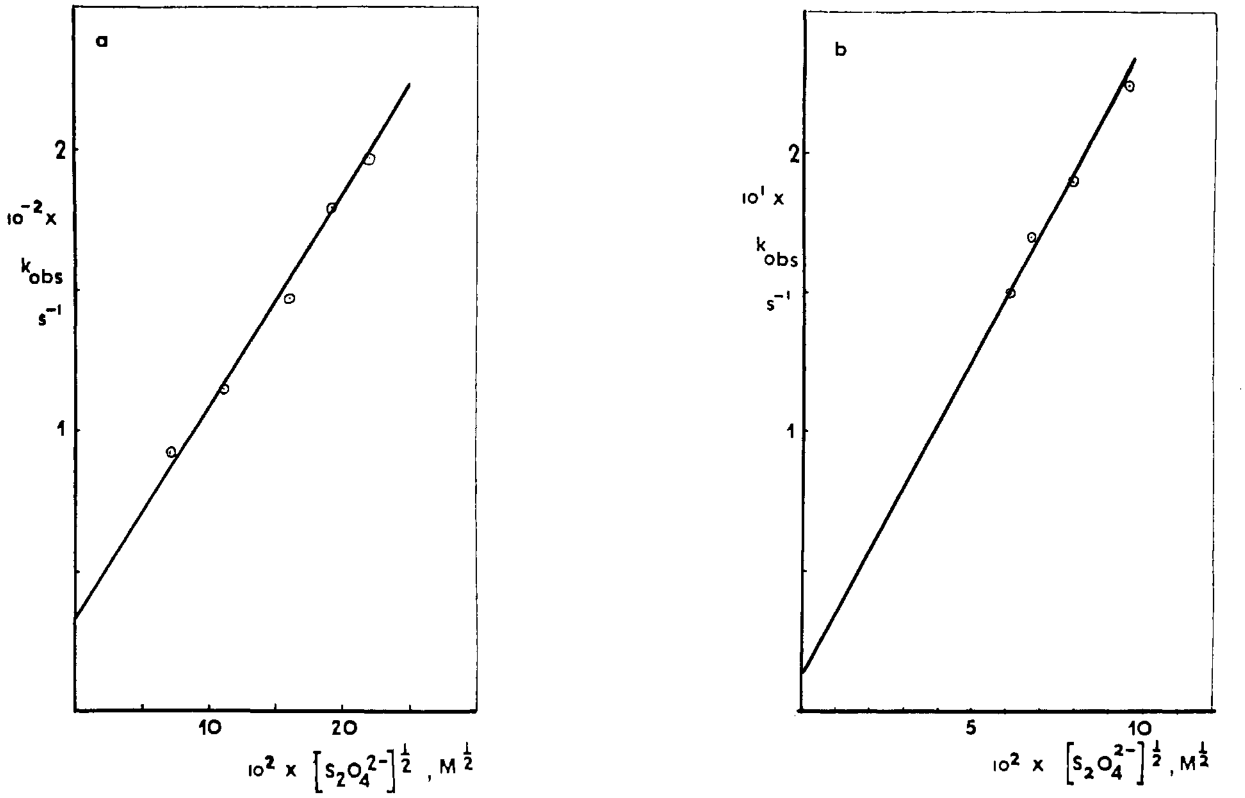

Figure 4. Plots of the observed rate constants vs. the square root of dithionite concentration for the reduction of $[Fe(CN)_5(4\text{-NIM})]^{4-}$ (conditions: 25 °C, $\mu = 0.5$ M (K_2SO_4); Tris buffer; measured at 475 nm): (a) first fast reduction, pH 8.7; (b) second slow reduction, pH 7.1.

been suggested as intermediates in pulse-radiolysis experiments.[44] More recently, organometallic "sandwich" compounds containing benzene and cyclopentadienyl rings associated with an Fe(I) ion have been described.[45]

The chemistry quoted above suggests that pentacyanoferrate(II) complexes with good π-accepting sixth ligands may be reduced by a moderately powerful reducing agent such as dithionite. Figure 3c shows an ESR spectrum obtained by the dithionite reduction of the pentacyano(4-nitroimidazolato)ferrate(II) ion. This spectrum is clearly incompletely resolved but shows at least seven lines, with a splitting of 2.4 G corresponding to three ^{14}N splittings. The relative intensities are not inconsistent with a nine-line pattern arising from splitting by four cyano nitrogens. The g value is 2.0319. The spectrum does not show the large N-hyperfine splitting found for the free 4-nitroimidazole radical and has a g value similar to that of the five-coordinated reduced nitroprusside complex rather than to that of an organic free radical or the six-coordinated complex. Figure 3a shows the ESR spectrum obtained by the dithionite reduction of sodium nitroprusside for comparison. This spectrum was obtained in dimethylformamide to which a minimum amount of water was added to increase the solubility of the reactants. It has a g value of 2.0274 and a nitrogen hyperfine coupling constant of 14.8 G, both of which agree with the parameters reported for the five-coordinated radical obtained by photolytic or electrolytic reduction. This radical is very stable with no noticeable decrease in ESR intensity over a period of several days.

On the basis of the high g vlaue we assign the ESR spectrum obtained by the reduction of the 4-nitroimidazole complex to a five-coordinated Fe(I) compound.[40] The failure to observe the 4-nitroimidazole radical spectrum of Figure 3b suggests that free 4-nitroimidazole is not present. We are able to obtain the ESR spectrum only at pHs around 6.5–7.5. This suggests that protonation of the 4-nitroimidazole ligand occurs concurrently with reduction. Assignment to the ion $Fe(CN)_4(4\text{-NIMH})^{3-}$ is therefore preferred, but $Fe(CN)_5^{4-}$ is also possible. The failure of $Fe(CN)_6^{4-}$ to react with dithionite suggests the latter is less likely. The nitroprusside radical has a square-pyramidal structure,[40] but a very recent paper[49] describes Fe(I) carbonyl complexes with trigonal-bipyramidal geometry. The seven-line pattern of Figure 3c is more consistent with the latter alternative. A more detailed discussion of the interpretation of the ESR spectra of this and related complexes will be presented in a subsequent paper.

The above ESR results demonstrate the formation of an Fe(I) complex by dithionite reduction. The addition of the dithionite is accompanied by a change in color from brown to bright yellow, and a new band appears at 368 nm. The kinetics of this reaction have been examined by stopped-flow spectrophotometry. As is usual with dithionite reactions it is necessary to carefully deoxygnate all solutions to obtain consistent and reproducible results. The reaction was examined in the pH range 6.5–9 in Tris buffer, at temperature 25 °C, and at ionic strength 0.4–0.5 M. Pseudo-first-order conditions were used with the dithionite in excess. The reaction proved to be biphasic, but the difference in rates of the two reactions is sufficiently large to allow easy separation of the two processes. The initial fast reaction gives an increase in absorption at 475 nm. The subsequent slower reaction was followed by the decrease in absorption at 475 nm. Observed pseudo-first-order rate constants for both reactions are given in Table I.

Kinetics of Dithionite Reductions. The kinetics of dithionite reductions have been considered by Lambeth and Palmer.[46] They showed that the effective reducing agent could be either $S_2O_4^{2-}$ or SO_2^-. The latter results from the equilibrium

$$S_2O_4^{2-} \rightleftarrows 2SO_2^- \quad K$$

Lambeth and Palmer measured both the equilibrium constant and the forward and reverse rates for this reaction. In certain circumstances the formation of SO_2^- ions can be the rate-determining

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Table I. Pseudo-First-Order Rate Constants of the Reduction of $[Fe(CN)_5(4\text{-NIM})]^{4-}$ with Dithionite[a]

fast reaction		slow reaction	
$10^2[S_2O_4^{2-}]$, M	k_{obsd}, s^{-1}	$10^2[S_2O_4^{2-}]$, M	k_{obsd}, s^{-1}
0.50	84.3	0.37	0.150
1.25	116	0.45	0.170
2.50	148	0.62	0.190
3.75	181	0.91	0.224
5.00	197		

[a] Conditions: $\mu = 0.50$ M (K_2SO_4); $T = 25$ °C; $\lambda = 475$ nm; [Fe] = 5×10^{-4} M; Tris buffer. [b] pH 8.7. [c] pH 7.1.

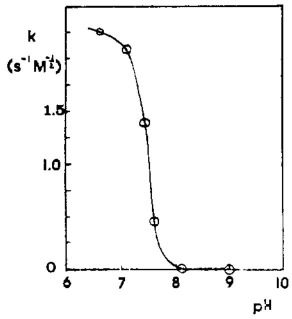

Figure 5. Plot of second-order rate constants vs. pH for the second, slow reduction of $[Fe(CN)_5(4\text{-NIM})]^{4-}$ with dithionite. Conditions: Tris buffer and K_2SO_4; $T = 25$ °C; $\lambda = 475$ nm.

step in dithionite reductions. If this is the case, the reaction becomes zero order in the substrate. The present reactions show good first-order dependence on Fe complex concentration. If SO_2^- is the reducing agent, the observed pseudo-first-order rate constants should increase with the square root of the dithionite concentration.

The rates of both reactions increase with the square root of dithionite concentration, as is shown by the plots of Figure 4, and are also pH dependent. The form of the pH dependence of the second reaction is shown in Figure 5. No reaction occurs above pH 8. The pH behavior of the rapid reaction is similar, but the quality of the data at low pH makes quantitative study of the pH dependence more difficult. Consistent with the failure to observe an ESR spectrum at high pH, no rapid reaction can be detected above pH 9. In the case of the initial reaction the plot does not go through the origin (Figure 4). From the pH dependence we deduce that SO_2^- reduces the 4-nitroimidazole complex not the 4-nitroimidazolato complex

$$Fe(CN)_5(4\text{-NIMH})^{4-} + SO_2^- \rightleftarrows Fe(CN)_4(4\text{-NIMH})^{4-} + CN^-$$

but the reaction does not go to completion. The slope represents the rate of the forward reaction and the intercept that of the backward reaction. The implications is that the reduction potentials of the SO_2^- ion and the Fe(I) complex are similar. The data of Figure 4 give a forward rate of 750 ± 50 $M^{-1/2}$ s^{-1} and a reverse rate of 30 ± 3 s^{-1}. Using the value of Lambeth and Palmer[46] for K, we obtain a value of 2.0×10^7 M^{-1} s^{-1} for the forward rate and 6.4×10^5 for the equilibrium constant of the above reaction.

Since the rate of reduction is clearly very rapid compared to the rate of ligand dissociation, electron transfer occurs by an outer-sphere mechanism. The absolute rate observed is quite similar to that previously reported[1] for the 4-nitroimidazole derivative of metmyoglobin (8.0×10^6) and to those reported[46] for lumiflavin-3-acetate (2.6×10^7), horse heart ferricytochrome (3.9×10^7), and spinach plastocyanin (2.9×10^7). It seems likely that as suggested for the metmyoglobin complex the SO_2^- radical attacks the nitro group and the electron is subsequently transferred through the π system to the Fe atom. The loss of the sixth cyanide ligand seems to be concurrent with the electron transfer, as in the case for the nitroprusside radical.

Since the second reaction also shows a dependence on the square root of the dithionite concentration, it therefore represents a further reduction by SO_2^- radicals. The data of Figure 5 indicate that reduction only occurs below pH 8. These results imply that only the protonated species is further reduced, allowing the nonprotonated species to be observed by ESR in predominantly nonaqueous solution. The second reduction is much slower than the first reaction ($k = 3.7 \times 10^4$ M^{-1} s^{-1}) and does not appear to go to completion. The five-coordinated Fe(I) complex is isoelectronic with the well-known complex $Co(CN)_5^{3-}$. This suggests that the further reduction product may be the hydride $HFe(CN)_4(4\text{-NIMH})^{3-}$ isoelectronic with the known hydride $HCo(CN)_5^{3-}$. The ^1H NMR spectrum of the reduced product was therefore examined in the region to high field of Me_4Si. A single line was observed at δ −20.5. This line moves to even higher fields (δ −23.2 and −25.0) with increasing acidity. These chemical shifts are in excellent agreement with the range reported (δ −20 to −25) for organometallic iron hydrides.[47] The pH dependence could indicate an equilibrium between the hydride and its conjugate anion. The infrared spectrum has also been examined for an Fe–H stretching vibration. Additional bands are observed at 2350 and 2370 cm^{-1}. Although rather high, assignment of these bands to hydride stretches is possible. Experiments in D_2O to confirm the assignment were inconclusive because of overlap with the intense OD stretch.

Conclusions

The above results have demonstrated the existence of iron complexes with cyano and 4-nitroimidazole ligands involving four discrete oxidation levels connected by one-electron redox reactions. The complexes are assigned as pentacyano(4-nitroimidazolato)ferrate(III), pentacyano(4-nitroimidazolato)ferrate(II), tetracyano(4-nitroimidazole)ferrate(I), and hydridotetracyano(4-nitroimidazole)ferrate(II) ions.

The (4-nitroimidazolato)ferrate(II) complex is a stable compound, with spectroscopic properties and ligand exchange characteristics corresponding to those expected for a pentacyano complex with an additional strong-field ligand. The Fe(III) complex is less stable. The two reactions observed in the dithionite reduction are represented by

$$Fe(CN)_5(4\text{-NIM})^{4-} + SO_2^- + H^+ \rightleftarrows Fe(CN)_4(4\text{-NIMH})^{3-} + CN^- + SO_2$$

$$Fe(CN)_4(4\text{-NIMH})^{3-} + SO_2^- + H^+ \rightleftarrows HFe(CN)_4(4\text{-NIMH})3^- + SO_2$$

Rates have been determined for both these reactions, and the equilibrium constant has been measured for the first reaction. Most ligands give stable iron complexes in only the +3 and +2 oxidation states. The existence of multiple oxidation states in a single-ligand system is unusual. It must be ascribed to the combination of the good σ-donor properties and moderate π-acceptor properties of the 4-nitroimidazolate anion. The complexes of other ligands with similar electronic properties will probably show analogous reactions. It is clear that the +2 oxidation state is the most stable, but the σ-donor ability is sufficient to give some stability to the +3 state and the π-acceptor properties suffice to allow the formation of an unstable +1 compound. The properties of the latter complex are of particular interest. It is a d^7 compound, isoelectronic with pentacyanocobaltate(II) and with the Fe(I) complex formed from nitroprusside. The ESR spectrum suggests that it also resembles these compounds in being five-coordinate. The hydride formed by further reduction is isoelectronic with $HCo(CN)_5^{3-}$. The catalytic properties of pentacyanocobaltate(II) and its associated hydride are well documented,[48] and it is therefore of interest to ask whether the present Fe(I) compound will show similar, or possibly more pronounced, catalytic activity. Preliminary experiments have given positive results.

The second point of interest is the linkage between the oxidation/reduction reactions and the acid/base equilibria. Wang[7] has pointed out the potential importance of such linkage to biologically important processes such as oxidative phosphorylation. In the present case, in both of the dithionite reduction steps, the addition of the electron is accompanied by protonation to keep the overall charge on the complex constant. In the first reduction step the protonation occurs on the ligand, and in the second step it takes place on the metal.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for financial support of this research and to K. Moffat and V. Stratton for performing some of the initial experiments in this area.

Registry No. $K_4[Fe(CN)_5(NO_2)]$, 14709-58-1; $K_4[Fe(CN)_5(4\text{-}NIM)]$, 95531-72-9; $Na_5[Fe(CN)_5(SO_3)]$, 12169-60-7; $[Fe(CN)_5(4\text{-}NIM)]^{4-}$, 95531-73-0; $[Fe(CN)_4(4\text{-}NIMH)]^{3-}$, 95531-74-1; $[Fe(CN)_5NO]^{2-}$, 15078-28-1; imidazole, 288-32-4; cyanide, 57-12-5; dimethyl sulfoxide, 67-68-5.

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Oxidative Electrochemistry of Iron–Selenocarbonyl Porphyrins

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The oxidation of selenocarbonyl(5,10,15,20-tetraphenylporphinato)iron(II), (TPP)FeCSe, was studied in 1,2-dichloroethane solution at a Pt-button electrode. Results from detailed voltammetric and spectroelectrochemical experiments (both electronic and infrared) indicated that (TPP)FeCSe can be oxidized in two chemically reversible, one-electron transfers. This is comparable to thiocarbonyl iron porphyrin but is in marked contrast with the analogous carbonyl iron(II) porphyrin derivative. The latter complex loses CO concomitantly with the removal of the first electron. The product of the first oxidation of (TPP)FeCSe is a selenocarbonyl iron(III) porphyrin whereas the second oxidation step occurs at the periphery of the porphyrin ring, producing the selenocarbonyl iron(III) porphyrin cation radical. Addition of nitrogenous bases to solution generated the monoadduct, (TPP)FeCSe[nitrogenous base]. This adduct was also oxidized in two discrete, one-electron transfers. The product of the first oxidation, $\{(TPP)Fe^{III}CSe[\text{nitrogenous base}]\}^+$, was stable for hours. The product of the second oxidation, however, readily underwent nucleophilic attack by uncomplexed nitrogenous base present in solution. The electronic effects generated by the ligand trans to the selenocarbonyl moiety are discussed in the context of their influence on the spectral, electrochemical, and thermodynamic properties of the selenocarbonyliron porphyrin.

Introduction

The interaction of neutral diatomic molecules (O_2, CO, NO, CS, CSe) with synthetic iron porphyrins is being intensively investigated.[1,2] Until recently little attention has been directed toward the electrooxidation of porphyrin Fe^{II} diatomic molecule complexes. This was due, in part, to the observation of only ferrous porphyrin complexes in vivo and, in part, to unsuccessful attempts to chemically generate oxidized forms of these complexes in the laboratory. Brown et al.,[3] Gurira and Jordan,[4] and Buchler et al.[5] have attempted to electrochemically generate $[(Por)FeCO]^+$ (Por = porphyrin) complexes. In each case, oxidation of CO-bound iron(II) porphyrins proceeded with loss of CO. Similarly, oxidation of $(Por)Fe^{II}O_2$ complexes initiates a chemical reaction pathway that eventually leads to formation of either the μ-oxo dimer or the ferric monomer, depending upon conditions.[6]

Recently, both Buchler[7] and Kadish[8] have independently observed the reversible electrooxidation of $(Por)Fe^{II}NO$ complexes. The formal valence of Fe in the oxidized nitrosyl species has yet to be determined.[8b] Electrooxidation of six-coordinate $(Por)Fe^{II}NO[L]$ (L = nitrogenous base) complexes occurs irreversibly, producing the $[(Por)Fe^{II}[L]_2]^+$ species.

The reversible electrooxidations of $(Por)Fe^{II}CS$ complexes have been well documented.[5,9,10] Bottomley and co-workers[10] have demonstrated that both $(TPP)Fe^{II}CS$ and $(TPP)Fe^{II}CS[L]$ undergo two chemically reversible one-electron-transfer reactions. The electrode product resulting from the first oxidation step was found to be an extremely stable cationic ferric porphyrin. The product of the second oxidation was an Fe^{III} radical cation, whose lifetime in solution decreased in the presence of nitrogenous bases. Both electron-transfer reactions proceeded with full retention of the diatomic ligand. Gorce[11] has reported voltammetric results that indicated that the electrooxidation of $(TPP)Fe^{II}CSe$ probably proceeds by a pathway similar to that of $(TPP)Fe^{II}CS$. The uniqueness of the $Fe^{II}CSe$ moiety and the possibility of observing an $Fe^{III}CSe$ species prompted this study.

Experimental Section

Caution! The chemicals used were or were presumed to be highly toxic. Selenium-containing compounds gave off an extremely obnoxious odor. All reactions were carried out in a well-ventilated hood. Selenium-containing waste products were disposed of after treatment with sodium hypochlorite solution.

Materials. Benzylselenocyanate ($C_6H_5CH_2SeCN$) was obtained via modification of the procedure put forth by Jackson.[12] A melting point of 72–73 °C was obtained (lit.[12] mp 71.5 °C). This product was obtained in a 74% yield based on potassium selenocyanate. ^1H NMR in $CDCl_3$ referenced to $(CH_3)_4Si$ (ppm): 7.40 (s, 5 H), 4.33 (s, 2 H).

Benzyl trichloromethyl selenoether, ($C_6H_5CH_2SeCCl_3$) was obtained by following the general procedure presented by Makosza and Fedorynski[13] for their synthesis of the analogous sulfur compound. ^1H NMR

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