Electron-transfer Kinetics and Mechanism of Di-imine Bond Formation in Tetracyano(ethylenediamine)ferrate(II)

Ana Maria da Costa Ferreira and Henrique E. Toma
Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brazil

The oxidative dehydrogenation of the ethylenediamine (en) ligand in the complex $[Fe(CN)_4(en)]^{2-}$ has been investigated by cyclic voltammetry, spectroelectrochemistry, and by stopped-flow kinetics with the $[Fe(CN)_6]^{3-}$ ion, at 25 °C, and $I = 0.100$ mol dm^{-3} (KCl). The first step in the oxidation process is assigned to a reversible electron-transfer reaction in the $[Fe(CN)_4(en)]^{2-}$ complex, with $E_{\frac{1}{2}} = 0.303$ V *versus* a normal hydrogen electrode. The oxidized ion undergoes successive electron transfer in the presence of OH^- ions (pH > 11), forming the red Fe^{II}–di-imine complex. The observed rate constant is given by $k_{obs.} = (1.9 \times 10^4)[Fe(CN)_6{}^{3-}][OH^-]$. The di-imine complex is further oxidized in the presence of $[Fe(CN)_6]^{3-}$ ions, with $k_{obs.} = (4.7 \times 10^3)[Fe(CN)_6{}^{3-}][OH^-]$. A mechanism is proposed involving Fe^{III} intermediate species which undergo induced electron transfer assisted by OH^- ions.

Transition metal ions can play a determining role in the reactivity of organic substrates.[1] Their influence is widespread, inhibiting or activating nucleophilic substitutions, promoting template synthesis, inducing ligand oxidations and introducing new patterns of reactivity in the substrates. A special case of ligand reactivity is exhibited by a number of Cu^{II}, Ni^{II}, Fe^{II}, and Ru^{II} amine complexes which undergo oxidation reactions yielding di-imine species.[2–5] The metal ion in this case seems to stabilize the normally reactive imine products; however, the mechanisms involved in the process remain little studied up to the present.

In this work we have investigated the oxidation of the complex tetracyano(ethylenediamine)ferrate(II). Earlier studies [6] have shown that under the action of oxidizing agents such as O_2, H_2O, Cl_2, OCl^-, $[Fe(CN)_6]^{3-}$ or quinone, tetracyano(ethylenediamine)ferrate(II) is converted to the deep red ethylenedi-imine derivative. To ascertain the route whereby the imine linkages are formed, we have carried out a detailed study on the kinetics, electrochemistry, and spectroelectrochemistry of the metal-assisted dehydrogenation of the coordinated ethylenediamine ligand.

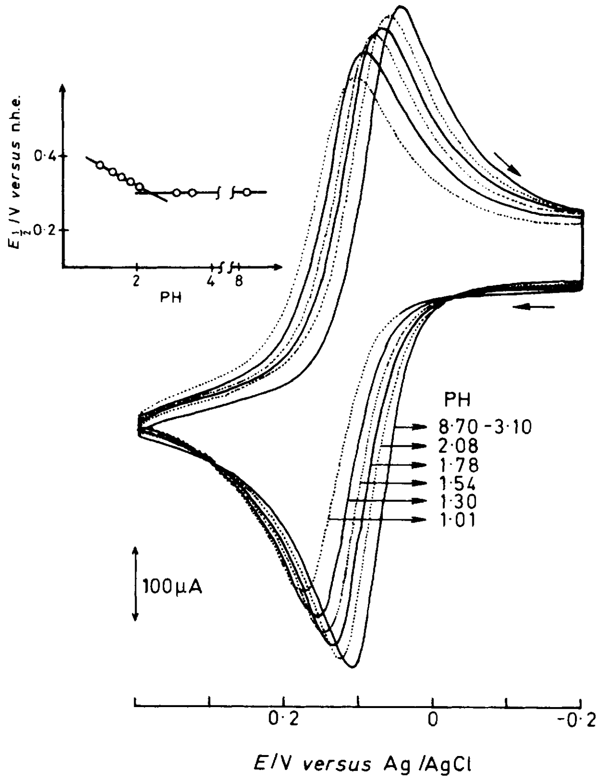


Figure 1. Cyclic voltammograms of $[Fe(CN)_4(en)]^{2-}$ (4.0×10^{-3} mol dm^{-3}) at 25.0 °C, at different pH. Inset: $E_{\frac{1}{2}}$ *versus* n.h.e. as a function of pH

Experimental

The complex $Na_2[Fe(CN)_4(en)]\cdot 4H_2O$ was prepared under an argon atmosphere, according to methods previously described in the literature.[7] The solid was recrystallized from saturated aqueous solution, at 0 °C, in the presence of sodium iodide and ethanol. The observed composition and the electronic spectra were consistent with the literature data.[6] All other chemicals were reagent grade and used as supplied.

Cyclic voltammetry was performed with a Princeton Applied Research instrument consisting of a 173 potentiostat and a 175 universal programmer. A platinum working electrode was employed for the measurements with Ag/AgCl (1 mol dm^{-3} KCl) as the reference electrode, using the conventional Luggin capillary arrangement to minimize the ohmic drop. A platinum foil was used as the auxiliary electrode.

The electronic spectra were recorded on a Cary 14 spectrophotometer. For the spectroelectrochemical measurements the PAR 173 potentiostat was used in parallel with the Cary 14 spectrophotometer. A three-electrode system was designed for a rectangular quartz cell of 0.06 mm internal optical pathlength. A platinum net, or a gold minigrid, was used as transparent working electrode, in the presence of a small Ag/AgCl reference electrode and of a platinum auxiliary electrode. The experiments were carried out at 25 °C under semi-infinite diffusion conditions, as described Kuwana and Winograd.[8]

The stopped-flow kinetics were carried out with a Durrum D-150 instrument, equipped with a Kel-F flow system. Most of the data were obtained under pseudo-first-order conditions, at 25 °C, $I = 0.100$ mol dm^{-3} (KCl), in the presence of a high excess of the reactants over the $[Fe(CN)_4(en)]^{2-}$ complex. The reactions were monitored at the absorption band of the di-imine product at 520 nm ($\varepsilon = 3.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The rates of the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_4(en)]^{2-}$ electron-transfer reaction were close to the limit of the stopped-flow technique.

The rate constants were obtained under second-order conditions, following the decay of the $[Fe(CN)_6]^{3-}$ ion at 420 nm.

Results and Discussion

Tetracyano(ethylenediamine)ferrate(II) is stable in neutral or slightly acidic solutions. The cyclic voltammograms of this complex show a single anodic peak, with the corresponding cathodic peak separated by 60 mV (Figure 1). The peak currents ratio was typically 1.00 ± 0.02. A linear dependence was observed for a plot of peak currents *versus* the square root of the potential sweep rate, or the concentration of the complex. The data can be fitted in the Randles–Sevcik equation for a one-electron reversible process,[9] with a diffusion coefficient of $(5.1 \pm 0.2) \times 10^{-6}$ cm² s⁻¹ at 25 °C, $I = 0.100$ mol dm⁻³ KCl. The half-wave potential of the $[Fe^{III}(CN)_4(en)]^-/[Fe^{II}(CN)_4(en)]^{2-}$ couple was +0.303 ± 0.005 V, *versus* a normal hydrogen electrode (n.h.e.).

In acidic solutions, systematic variations in the peak potentials and diffusion coefficients were noted as a function of pH (Figure 1). The plot of $E_{\frac{1}{2}}$ *versus* pH shown in the inset of Figure 1 indicates that only one proton is involved in the equilibrium, with a pK_a of 2.3. This value is typical of protonation of a cyanide ligand, as in $[Fe^{II}(CN)_5L]^{n-}$ complexes, where L = H_2O (pK_a 2.75),[10] pyridine (2.10),[11] 4-methylpyridine (2.20),[11] or dithio-oxamide (2.13).[12] At pH < 1, bluish species similar to colloidal Prussian blues are formed in solution.

In basic solutions, the $[Fe(CN)_4(en)]^{2-}$ complex becomes susceptible to autoxidation, and reacts even with mild oxidizing agents, such as $[Fe(CN)_6]^{3-}$. The starting yellow solutions turn gradually red, as a function of the pH and the concentration of the oxidizing agent. The product has been isolated as a solid of composition [6] $Na_2[Fe(CN)_4(C_2H_4N_2)]\cdot 4H_2O$, exhibiting a red colour characteristic of the iron(II) di-imines.[13] The electronic spectrum of the product shows an absorption band at 520 nm (ε = 3 600 dm³ mol⁻¹ cm⁻¹) which arises from a d_π–p_π charge-transfer transition, involving the highest occupied d_π orbitals of Fe^{II} and the lowest unoccupied π orbital of the di-imine ligand.

Formation of the ethylenedi-imine (diim) ligand requires four electron equivalents and a pH above 11. The stoicheiometry of the oxidation reaction with the $[Fe(CN)_6]^{3-}$ ion was confirmed spectrophotometrically by the molar ratio method as shown in equation (1). However, when the oxidizing agent

$$[Fe(CN)_4(en)]^{2-} + 4[Fe(CN)_6]^{3-} + 4OH^- \longrightarrow [Fe(CN)_4(diim)]^{2-} + 4[Fe(CN)_6]^{4-} + 4H_2O \quad (1)$$

is present in high excess, the $[Fe(CN)_4(diim)]^{2-}$ complex is further oxidized with a gradual decay of the typical red colour.

The cyclic voltammograms of the complex in alkaline solution indicate three successive steps of oxidation, involving a complex compromise between the potential scan rates and the pH. These steps are referred as A, B, and C in Figure 2. At pH 11.6 it is possible to show that the anodic peak A, at 0.35 V *versus* n.h.e., is associated with a reverse cathodic peak. Based on the similarity with the cyclic voltammograms obtained at pH 7, we have assigned this peak to the one-electron oxidation of the $[Fe^{II}(CN)_4(en)]^{2-}$ complex, equation (2).

$$[Fe^{II}(CN)_4(en)]^{2-} \longrightarrow [Fe^{III}(CN)_4(en)]^- + e \quad (2)$$

The reversible wave A becomes less pronounced as the potential scan rates decrease. In contrast, the successive irreversible waves B and C are intensified. At pH 12.7 and above, no evidence of peak A has been observed, even at scan rates as rapid as 200 mV s⁻¹. The relative intensity of peak C diminishes as the scan rate is decreased, in contrast with the results obtained at pH 11.6.

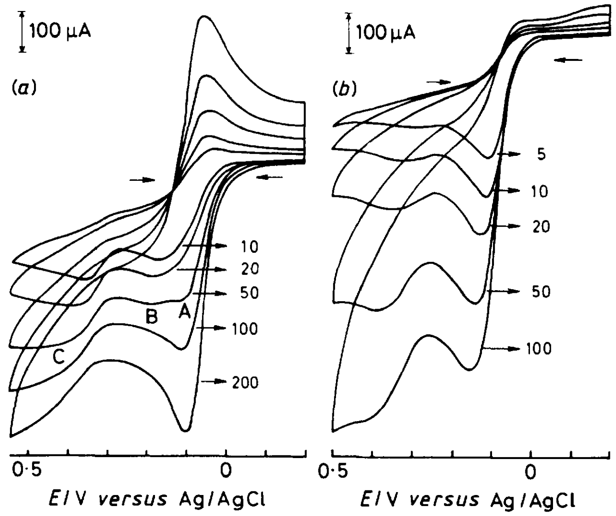


Figure 2. Cyclic voltammograms of $[Fe(CN)_4(en)]^{2-}$ (4.2×10^{-3} mol dm⁻³) at 25.0 °C at different scan rates (mV s⁻¹): (*a*) $I = 0.50$ mol dm⁻³ (KCl), pH 11.6; (*b*) $I = 1$ mol dm⁻³ (KCl), pH 12.7

It seems logical that the second wave, B, should be associated with an OH^- dependent oxidation of $[Fe^{III}(CN)_4(en)]^-$, produced in step A. At pH 11.6, the rates of the electrochemical process are controlled by a chemical mechanism involving OH^- ions; however, at low scan rates or above pH 12.7, the chemical process becomes fast enough to yield a single wave, corresponding to the sum of steps A and B.

Analogously, the third wave C should be assigned to an OH^- dependent oxidation of the species generated in B. At pH 11.6 the rates of the electrochemical process are controlled by a slow chemical reaction, responsible for the poorly defined shape of the wave observed at high potential scan rates. Around pH 12.7, other parallel reactions appear to contribute to the decay of peak C at low scan rates.

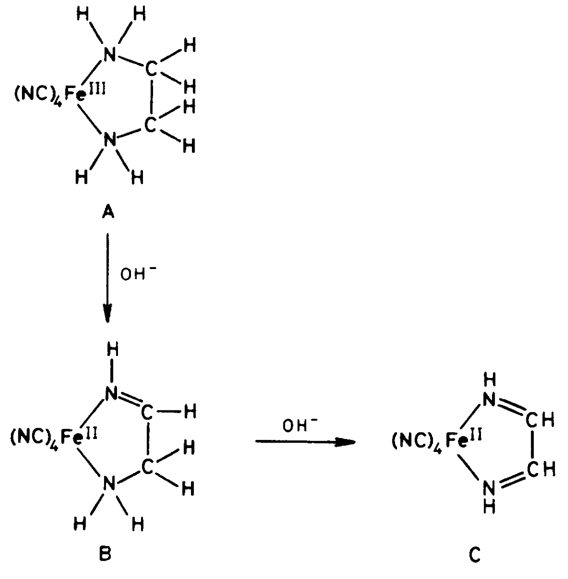
The electrochemical behaviour can be summarized by the sequence of reactions (3). Species A corresponds to the

$$[Fe^{II}(CN)_4(en)]^{2-} \xrightarrow[0.35\text{ V}]{} A \xrightarrow[0.41\text{ V}]{OH^-} B \xrightarrow[0.57\text{ V}]{OH^-}$$
$$C \xrightarrow{OH^-} \text{Decomposition products} \quad (3)$$

$[Fe^{III}(CN)_4(en)]^-$ complex; the assignment of the species B and C to the monoimine and di-imine products would seem reasonable on a qualitative basis, Scheme 1.

In order to substantiate the analysis of the cyclic voltammograms, we have made a careful spectroelectrochemical study on the complex $[Fe(CN)_4(en)]^-$. The electronic spectra recorded under controlled potentials are shown in Figure 3. The red di-imine complex generated electrochemically can be readily detected in the electronic spectra. Formation of the di-imine complex reaches a maximum at 0.37 V, close to the peak potential of species B in the cyclic voltammograms at low scan rates. As the potential increases up to 0.57 V, there is a gradual decay of the di-imine complex, with an isosbestic point at 458 nm.

The spectroelectrochemical measurements rule out definitely the tentative assignment of the cyclic voltammograms shown in Scheme 1. Therefore, in alkaline solution, peaks B and C should be assigned to formation and oxidation of the di-imine complex, respectively



Scheme 1.

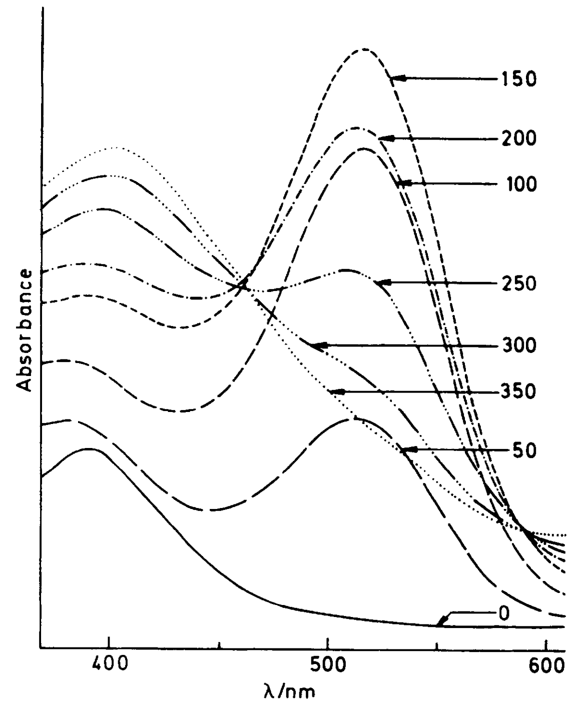


Figure 3. Spectroelectrochemical measurements, at different controlled potentials (mV) *versus* Ag/AgCl, I = 1 mol dm^{-3} (KCl), of $[Fe(CN)_4(en)]^{2-}$ at pH = 12.7, and 25.0 °C ($\lambda_{max.}$ = 520 nm)

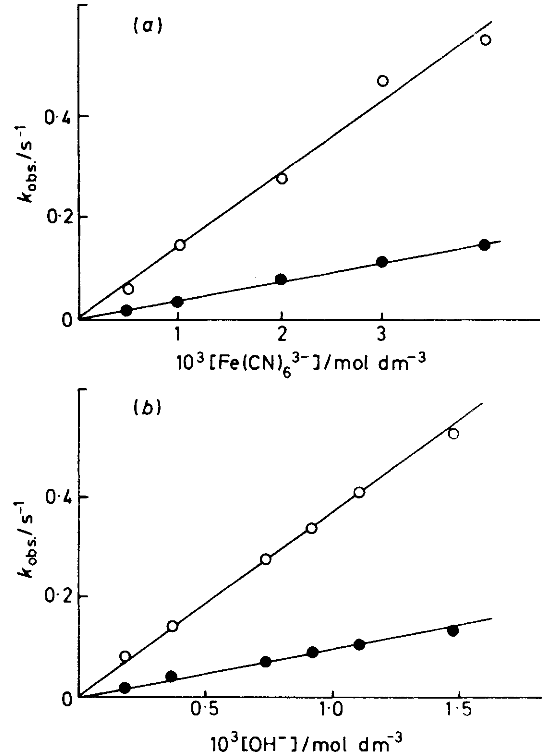


Figure 4. Dependence of $k_{obs.}$ of the oxidation of $[Fe(CN)_4(en)]^{2-}$ (3.02×10^{-5} mol dm^{-3}) at 25.0 °C and 0.100 mol dm^{-3} (KCl), on the concentration of (*a*) $[Fe(CN)_6]^{3-}$, $[OH^-] = 7.41 \times 10^{-4}$ mol dm^{-3}; (*b*) OH$^-$, $[Fe(CN)_6{}^{3-}] = 2.00 \times 10^{-3}$ mol dm^{-3}: (○) k_2 (formation of the di-imine complex), (●) k_3 (oxidation of the di-imine complex)

At this point we know that the monoimine complex cannot be detected as a stable intermediate in the oxidation reaction of the $[Fe(CN)_4(en)]^{2-}$ complex; however, little can be said about the mechanisms involved in the process. To evaluate this point we have studied the stopped-flow kinetics of the homogeneous electron-transfer reaction (1).

Analogously to the electrochemical process, three steps can be detected in the kinetics of oxidation of the $[Fe(CN)_4(en)]^{2-}$ complex by the $[Fe(CN)_6]^{3-}$ ion. The first reaction corresponds to the rapid outer-sphere electron transfer between the reactants, as shown in equation (4). The second

$$[Fe(CN)_4(en)]^{2-} + [Fe(CN)_6]^{3-} \longrightarrow [Fe(CN)_4(en)]^- + [Fe(CN)_6]^{4-} \quad (4)$$

reaction (5) leads to the red di-imine product. The third

$$[Fe(CN)_4(en)]^- + 3[Fe(CN)_6]^{3-} + 4OH^- \longrightarrow [Fe(CN)_4(diim)]^{2-} + 3[Fe(CN)_6]^{4-} + 2H_2O \quad (5)$$

reaction (6) is associated with the decomposition of the di-imine complex induced by OH$^-$ ions, in the presence of the $[Fe(CN)_6]^{3-}$ oxidizing agent.

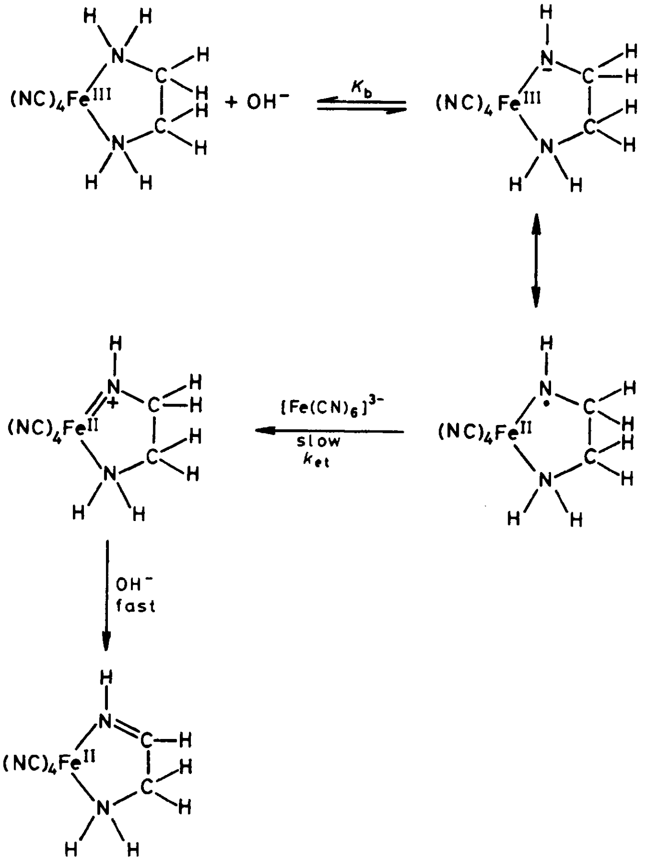
$$[Fe(CN)_4(diim)]^{2-} + [Fe(CN)_6]^{3-} + OH^- \longrightarrow \text{Oxidation products} \quad (6)$$

The outer-sphere electron transfer (4) was investigated at pH 7, to minimize the interference of reaction (5). The second-order rate constant obtained for this process was $(9 \pm 1) \times 10^6$ dm^3 mol^{-1} s^{-1}.

Formation of the di-imine complex [reaction (5)] was followed at 520 nm. First-order kinetics were observed for at least two half-lives. The dependence of $k_{obs.}$ on the concentration of the $[Fe(CN)_6]^{3-}$ and OH$^-$ ions, illustrated in Figure 4(*a*), leads to consistent results, expressed by the rate law (7) where $k_2 = (1.9 \pm 0.1) \times 10^4$ dm^6 mol^{-2} s^{-1}.

$$\frac{d[Fe(CN)_4(diim)^{2-}]}{dt} = k_2[Fe(CN)_6{}^{3-}][Fe(CN)_4(en)^-][OH^-] \quad (7)$$

The participation of the OH^- in the mechanism can be represented as shown in Scheme 2.



Scheme 2.

By acting as a Lewis acid, the metal ion should enhance the acidity of the co-ordinated NH_2 group, as observed in the case of ruthenium(III) and platinum(IV) amines. For instance, the pK_a decreases from 34, in free NH_3, to 12.4 in the $[Ru(NH_3)_6]^{3+}$ complex.[14] Therefore, since $k_2 = k_{et} . K_b$, from the maximum value allowed for $k_{et} = 10^9$ dm^3 mol^{-1} s^{-1}, the limiting value of p$K_a < 19$ can be estimated for the $[Fe^{III}(CN)_4(en)]^-$ complex.

The mechanism of electron transfer may involve a case of induced electron transfer, analogous to those previously reported by Taube.[15] In these reactions, the co-operative action of an internal and of an external one-electron oxidizing agent produces a two-electron oxidation of a co-ordinated ligand. It is important to note that the induced electron-transfer process should be favoured in a complex such as $[Fe^{III}(CN)_4(en)]^-$, since one of the canonical structures already has a radical character.

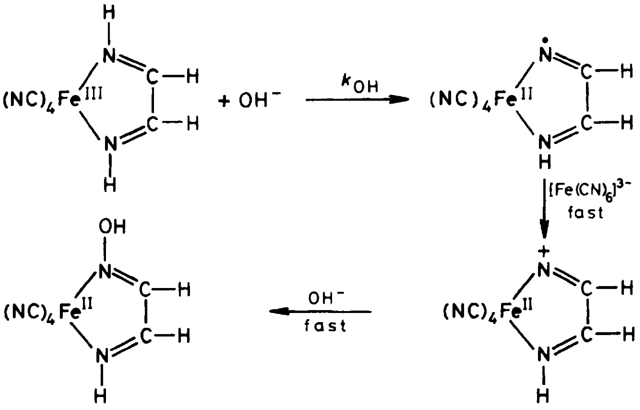
After the rate-determining step, the electron-deficient product can transfer a proton to the solvent or OH^- ions, forming a monoimine intermediate. The sequence of electron transfer and deprotonation reactions takes place once more, to produce the di-imine complex. These reactions, however, should be accelerated by the greater driving force introduced by the special stability of the iron(II)–di-imine bond. In this way they do not contribute to the observed rate law.

The di-imine complex is further oxidized by the $[Fe(CN)_6]^{3-}$ ion, in the presence of OH^-, according to first-order kinetics. The dependence of $k_{obs.}$ on the concentration of the $[Fe(CN)_6]^{3-}$ and OH^- ions (Figure 4) supports the rate law (8) where $k_3 = (4.7 \pm 0.1) \times 10^3$ dm^6 mol^{-2} s^{-1}.

$$\frac{-d[Fe(CN)_4(diim)^{2-}]}{dt} = k_3[Fe(CN)_4(diim)^{2-}][Fe(CN)_6{}^{3-}][OH^-] \quad (8)$$

The oxidation of the di-imine complex by the $[Fe(CN)_6]^{3-}$ ion [equation (9)] has an unfavourable equilibrium constant (4.0×10^{-4}), estimated from the redox potentials of the reactants {E^0 for $[Fe(CN)_4(diim)]^{2-/-} = 0.63$ V, at pH 7}. It is possible that the hydroxide ion helps to drive the reaction to completion, as shown in Scheme 3. By removing a proton from the oxidized di-imine complex, a highly reactive intermediate is generated which can undergo further electron-transfer reactions with the excess $[Fe(CN)_6]^{3-}$ complex. According to this mechanism, $k_3 = k_{OH} \cdot K/[Fe(CN)_6{}^{4-}]$; therefore $k_{OH} = 1.4 \times 10^3$ dm^3 mol^{-1} s^{-1}.

$$[Fe(CN)_6]^{3-} + [Fe(CN)_4(diim)]^{2-} \overset{K}{\rightleftharpoons} [Fe(CN)_6]^{4-} + [Fe(CN)_4(diim)]^- \quad (9)$$



Scheme 3.

A typical reaction expected for the deprotonated di-imines is the induced electron transfer leading to oxime, or hydroxylated products,[16,17] as in Scheme 3. This kind of reaction is quite possible in the present case; however, it cannot be detected kinetically as it does not contribute to the observed rate law. Further work is in progress to elucidate the terminal steps of the oxidation mechanism.

Acknowledgements

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