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Electron-Transfer Kinetics of Chlorotetrakis(p-chlorophenyl)porphinatomanganese(III) in Dimethyl Sulfoxide–Imidazole Mixtures

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The electron-transfer reactivity of chlorotetrakis(p-chlorophenyl)porphinatomanganese(III) was investigated by the technique of cyclic voltammetry at a platinum electrode. Less than a 50-mV shift was observed in half-wave potentials for the Mn(III) ⇄ Mn(II) and Mn(II) ⇄ anion radical reactions upon imidazole complexation indicating a relative stability between Mn(III), and Mn(II), and the anion radical which was virtually identical in dimethyl sulfoxide–imidazole solvents. In a dimethyl sulfoxide–imidazole mixed-solvent system the rate constant for electroreduction of Mn(III) at the standard potential was dependent on the imidazole concentration and varied between 1×10^{-3} cm/s in the absence of imidazole and 4×10^{-6} cm/s at 1.0 M ligand concentration. This latter value is the slowest rate constant ever measured for a metalloporphyrin electron transfer.

Introduction

In the last 5 years a number of papers have been published which report electron-transfer rate constants for the oxidation–reduction of metalloporphyrins in terms of their physical and chemical properties.[2-8] The majority of these investigations have focused on characterizing the electron-transfer kinetics of either cobalt or iron complexes. This was done with an aim toward obtaining model systems which exhibit extremely rapid rates similar to those found in the oxidation–reduction of cytochrome *c* or extremely sluggish rates similar to those observed for oxidation of myoglobin or hemoglobin. For the iron and cobalt complexes it has been shown that electron-transfer rate constants are a function of the metal spin state,[2,3] type and degree of axial complexation,[4-6] basicity of the porphyrin ring,[7] and solvent system.[2,3,8] However, despite these extensive investigations of model cytochrome *c* and hemoglobin systems, very little is known regarding the specific factors which influence and control electron-transfer kinetics of other transition-metal porphyrins. For example, at this time, only one paper has been published which reports the heterogenous rate constant for conversion of a manganese(III) to a manganese(II) porphyrin.[2]

Thus, in order to complement the existing thermodynamic data[9,10] on manganese porphyrin redox reactions and to obtain kinetic information for comparison with iron and cobalt systems, we have undertaken a comprehensive study of the oxidation–reduction kinetics of several manganese(III) and manganese(II) complexes in nonaqueous media. Our aim was to obtain and characterize extremely rapid or extremely sluggish electron-transfer processes as a function of both axial ligand complexation and porphyrin ring basicity.

Previous to this study, all rate constants for metalloporphyrin redox reactions, with a single possible exception,[6] have been measured in the range of 1.0×10^{1}–8×10^{-4} cm/s. In the course of our investigations we were able to obtain electron-transfer rate constants for several porphyrin complexes which were slower than 8×10^{-4} cm/s by up to 2 orders of magnitude.

We present in this paper electrochemical results on the reduction of chlorotetrakis(p-chlorophenyl)porphinatomanganese(III), (p-Cl)TPPMnCl, in dimethyl sulfoxide and dimethyl sulfoxide–imidazole mixtures. This mixed-solvent system is unique in that the rate constant significantly decreases with increase of imidazole concentration (presumably due to axial complexation) and in the presence of 1 M imidazole is almost 3 orders of magnitude slower than the corresponding standard rate constant in neat Me_2SO. The rate constant obtained is, in fact, the slowest rate constant yet measured for a metalloporphyrin electron transfer.

Experimental Section

Chlorotetrakis(p-chlorophenyl)porphinatomanganese(III) was synthesized by the method of Adler et al.[11] Dimethyl sulfoxide, Me_2SO ("Spectroquality", MCB), tetrabutylammonium perchlorate, TBAP (Eastman Kodak Co.), and imidazole, Im (MCB) were used without further purification.

Cyclic voltammetric measurements were obtained with a three-electrode system utilizing a PAR Model 174 polarographic analyzer and a Houston Instruments Model 2000 X-Y recorder. The working electrode and counterelectrode were constructed from platinum. A commercial calomel electrode (SCE) was used as the reference electrode and was separated from the bulk of the solution by a fritted glass disk.

Deaeration was accomplished by passing high-purity nitrogen or argon through the solution for 10 min, and a stream of gas was passed above the solution during analysis. All potentials are reported vs. the standard calomel electrode.

Results and Discussion

A cyclic voltammogram of (p-Cl)TPPMnCl in Me_2SO is shown in Figure 1A. Both reduction and reverse oxidation peaks are well defined and can be assigned to the diffusion-controlled one-electron transfers yielding initially Mn(II) and then the anion radical.[10] Absence of chemical reactions coupled to the electron transfer was verified by the invariance of peak potential with sweep rate, as well as the dependence on the square root of scan rate for both the anodic and the cathodic peak currents. In addition, the ratio of anodic and cathodic peak currents, i_{pa}/i_{pc}, was equal to unity as predicted for a diffusion-controlled reaction.[12]

Imidazole was then added to the solution, and the cyclic voltammograms were taken at various concentrations of the complexing ligand. From 10^{-3} to 10^{-2} M imidazole no change was observed in the current–voltage curve. However, when the concentration of imidazole became greater than 10^{-2} M, the first reduction peak began to shift cathodically while the reverse oxidation peak shifted anodically from $E_{1/2} = -0.23$ V in Me_2SO. Concomitantly, the reduction peak geometry broadened from a quasi-reversible electron-transfer shape of $|E_p - E_{p/2}| = 70$ mV to an irreversible $|E_p - E_{p/2}| = 100$ mV. These changes in geometry and position are shown in Figures 1 and 2. Figure 1B shows the cyclic voltammogram in Me_2SO containing 1.0×10^{-1} M imidazole. At this imidazole concentration, the Mn(III) reduction has become less reversible than in neat Me_2SO, while in Me_2SO containing 1.0 M imidazole (Figure 1C) the reduction is totally irreversible. Although the range of the solvent system has decreased with imidazole addition, no change in reversibility or peak position was observed for the anion radical reaction up until the overlap of the peak by the solvent reduction. Futher evidence for changeover of the initial reduction from a quasi-reversible to

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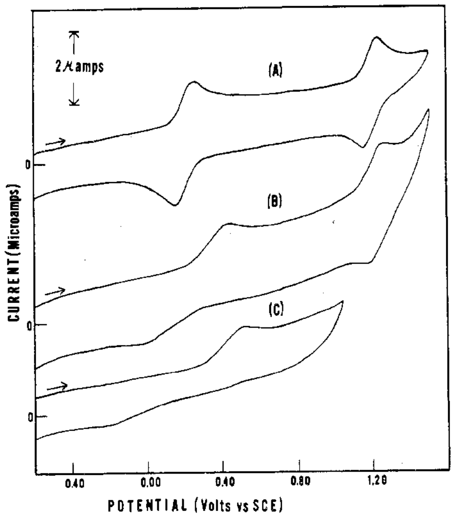

Figure 1. Cyclic voltammograms of 1.0×10^{-3} M (p-Cl)TPPMnCl in Me_2SO (0.1 M TBAP) containing varying imidazole concentrations: (A) 0.00 M imidazole, (B) 1.0×10^{-1} M imidazole, (C) 1.0 M imidazole. The scan rate was 0.10 V/s.

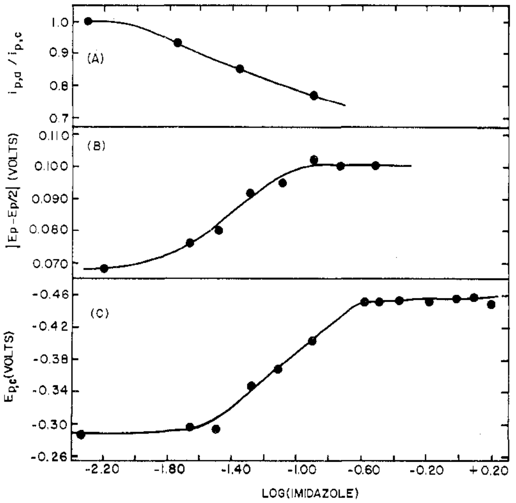

Figure 2. Plot showing (A) ratio of anodic and cathodic peak currents, (B) cathodic peak geometry, and (C) cathodic peak potential as a function of imidazole concentration. The scan rate was 0.05 V/s.

an irreversible electron transfer is found in Figure 2 which gives diagnostic plots of $i_{p,a}/i_{p,c}$, $|E_p - E_{p/2}|$, and the cathodic peak potential, $E_{p,c}$, as a function of imidazole concentration. As seen from this figure (and Figure 1) the electron-transfer kinetics became progressively more sluggish above 10^{-2} M Im. No further shifts in potential or peak broadening were observed above 0.25 M imidazole indicating a similar rate of electron transfer from 0.25 M to the upper concentration investigated, which was 2.0 M Im.

In order to further confirm the electrochemical irreversibility of the (p-Cl)TPPMnCl reduction, the cyclic voltammograms were also recorded as a function of scan rate. As the scan was increased, both the cathodic and the anodic peak shifted in opposite directions yielding a larger $|E_{p,a} - E_{p,c}|$ with higher scan rates, v (Figure 3). At the same time plots of $i_p/v^{1/2}$ remained constant indicating a straightforward oxidation–reduction in which the kinetics are controlled by the rate of charge transfer.[12]

Rates of heterogeneous electron transfer for the Mn(III) ⇄ Mn(II) reaction in neat Me_2SO were measured by the cyclic voltammetric technique of Nicholson.[13] When the anodic and cathodic peak potentials are larger than the reversible value of 59 mV, the rate of electron transfer can be calculated by measuring the peak separations as a function of potential sweep rate. Use of this method gave an experimental electron-transfer rate constant $k^0 = 1 \times 10^{-3}$ cm/s for the reduction of (p-Cl)TPPMnCl in Me_2SO. While slower than OEPMnOH (6×10^{-3} cm/s) or TPPFeCl (2×10^{-2} cm/s) in Me_2SO,[2] these are still sufficiently fast to yield an anodic and cathodic peak separated by less than 150 mV on the cyclic voltammogram. In contrast, however, rate constants for reduction of (p-Cl)TPPMnCl in solutions containing imidazole are slower by up to several orders of magnitude. In these cases the electron-transfer rate constant may be determined in terms of the cathodic peak potential, E_p, using eq 1[12] where E^0 is the standard potential, D the diffusion coefficient in cm^2/s, v the sweep rate in V/s, k^0 the electron transfer rate constant, and α the transfer coefficient, which will usually vary from 0.3 to 0.8. As seen from the above equation, there is a $30/\alpha n$ mV cathodic shift in peak potential at 25 °C for every 10-fold increase in scan rate v. From the experimental cathodic slope of 52 mV/log v, Figure 3, an αn = 0.58 was determined. This value of αn was then inserted into eq 1 and electron-transfer rate constants of 4.0×10^{-5} cm/s at 0.10 M Im and of 4.0×10^{-6} cm/s at 1.0 M Im were calculated. These values are listed in Table I and are based on a measured diffusion coefficient of 1×10^{-6} cm^2/s and an $E^0 = -0.20$ V (which was obtained by extrapolation of the anodic and cathodic peak shifts to a theoretical 60-mV separation at low scan rates).

$$E_p = E^0 - \frac{RT}{\alpha nF}\left[0.780 + \ln\left(\frac{D\alpha nFv}{RT}\right)^{1/2} - \ln k^0\right] \qquad (1)$$

It is interesting to note that complexation of (p-Cl)TPPMnCl by imidazole produces less than a 50-mV shift in the Mn(III) ⇄ Mn(II) half-wave potentials indicating an almost equal stabilization of Mn(II) and Mn(III). This agrees with results obtained for TPPFeCl complexation with imidazole[14] (less than a 90-mV shift is observed in DMF) but differs significantly from TPPCo where, upon nitrogeneous base complexation, an anodic shift of over 1.0 V may be noted.[4a]

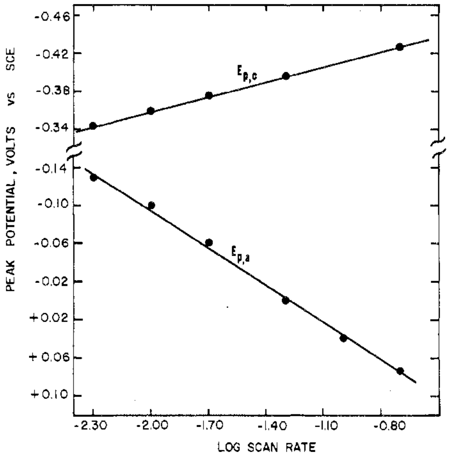

Figure 3. Plot of cathodic, $E_{p,c}$, and anodic, $E_{p,a}$, peak potentials as a function of scan rate; (Im) = 0.125 M.

Table I. Electron-Transfer Rate Constants for the Oxidation-Reduction of (p-Cl)TPPMnCl in Dimethyl Sulfoxide-Imidazole Mixtures

concn of Im, M	$E_{1/2}$, V vs. SCE	$E_{p,a} - E_{p,c}$, [a] V	k^0, cm/s
0.00	−0.23	0.141	1.0×10^{-3}
0.10	−0.20	0.470	4.0×10^{-5}
1.0	−0.20	0.690	4.0×10^{-6}

[a] Scan rate = 0.200 V/s.

It is not clear at this time which step in the electron-transfer process is rate controlling. Both d^4 Mn(III) and d^5 Mn(II) are high-spin complexes[15] and thus no change in spin state would be observed. It is possible that the slow electron transfer rate is due to a rate-determining ligand exchange associated with electron transfer. However, no definite information has been obtained on the exact coordination number of the manganese(II) or manganese(III) complexes. Attempts by La Mar and Walker[16] to determine the nature of the pyridine or *N*-methylimidazole complex with TPPMnCl using NMR or optical spectroscopy proved inconclusive, and the absence of isosbestic points indicated the presence of several species in solution. Similarly, quantitative information could not be obtained for either Mn(III) or Mn(II) by electrochemical methodologies as in previous studies[17] due to the irreversibility of the electron transfer and the fact that, in both the presence and absence of imidazole, an almost identical half-wave potential is obtained.

The structure of TPPMn(1-MeIm) has been obtained by X-ray analysis.[18] The manganese(II) is displaced 0.56 Å from the mean porphyrin plane. In aqueous solution, bis ligand complexes of Mn(II) porphyrins have been suggested[9] but these have not been observed in nonaqueous media or in the crystalline state,[19] where no concrete evidence exists for other than five-coordinate complexes with high-spin manganese(II).

X-ray data have also been obtained for several five- and six-coordinate complexes of manganese(III). In the absence of strongly coordinating ligands TPPMnCl is five-coordinate with the manganese removed from the mean porphyrin plane by about 0.27 Å.[19] On complexation with pyridine, a six-coordinate complex results where the manganese(III) ion is now displaced only 0.145 Å out of the mean porphyrin plane.[20] Generally six-coordinate complexes of high-spin Mn(III) are obtained in which the manganese(III)–porphyrin plane distance is significantly reduced with respect to that for high-spin Mn(II).[19]

We know from the spectroscopic results of Boucher[9b] and have also confirmed electrochemically[21] that in Me_2SO a solvent molecule replaces the axially bound halide (in this case chloride) to yield the six-coordinate complex (*p*-Cl)TPPMn$(Me_2SO)_2^+$. Presumably the complex in 1.0 M imidazole would also be six-coordinate (either (*p*-Cl)TPPMn$(Me_2SO)(Im)^+$ or (*p*-Cl)TPPMn$(Im)_2^+$[22] and would have a shortened manganese–porphyrin plane distance compared to the five-coordinate Mn(II) complex. Thus the addition of an electron to Mn(III) would involve both the removal of an axial ligand (either Me_2SO or imidazole) and a movement of the Mn atom by up to 0.4 Å upon reduction from Mn(III) to Mn(II). This large out-of-plane movement and displacement of an axial ligand does not occur during reduction of the low-spin imidazole complexes of TPPFeCl or $TPPCo^+$ where both the oxidized and reduced forms of the complex contain the metal atom in the plane of the porphyrin ring. Likewise, a significantly smaller change in porphyrin–manganese plane distance probably occurs for the reduction of (*p*-Cl)TPPMnCl in the nonbonding solvent CH_2Cl_2. (Crystallographic measurements of TPPMnCl and its reduced product show Mn(III) to be 0.27 Å out of plane[19] and Mn(II) to be 0.18 Å out of plane.[24]) In this case electron transfer is relatively rapid ($k^0 = 3 \times 10^{-3}$ cm/s).

Electron-transfer studies with other manganese porphyrin complexes are now in progress to determine if the decrease in rate is a general phenomona or is specific to the imidazole complexes of (*p*-X)TPPMnCl.

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