Electrochemistry of Six-co-ordinate Cr^{III} Porphyrins

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Summary Electrochemical evidence is presented that two discrete paths of electron transfer are possible for reduction of TPPCrCl(L) where L is a substituted pyridine and TPP = tetraphenylporphryin, and that one of these involves the previously unobserved complex $[TPPCr(L)_2]^+$.

RECENTLY, Hoffman, Basolo, and co-workers[1,2] investigated the ligand binding behaviour of TPPCrCl (TPP = tetraphenylporphyrin) in a variety of solvents. Utilizing spectroscopic and conductometric techniques, they showed that TPPCrCl(S), where S is an oxygen donor solvent could be converted into TPPCrCl(L) upon complexation with a nitrogenous base, but would not form complexes of $[TPPCr(L)_2]^+$ in solution. In this communication we present the electron transfer mechanism for the reduction of TPPCrCl(L) in 1,2-dichloroethane and show conclusively that the electroreduction pathway may be made to go through the intermediate $[TPPCr(L)_2]^+$ whose reduction is thermodynamically favoured. The products of the electron transfer may be either the symmetrical bis-ligand adducts characterized by Reed and co-workers[3,4] or a novel mixed-halide-ligand complex of Cr^{II}, $[TPPCrCl(L)]^-$.

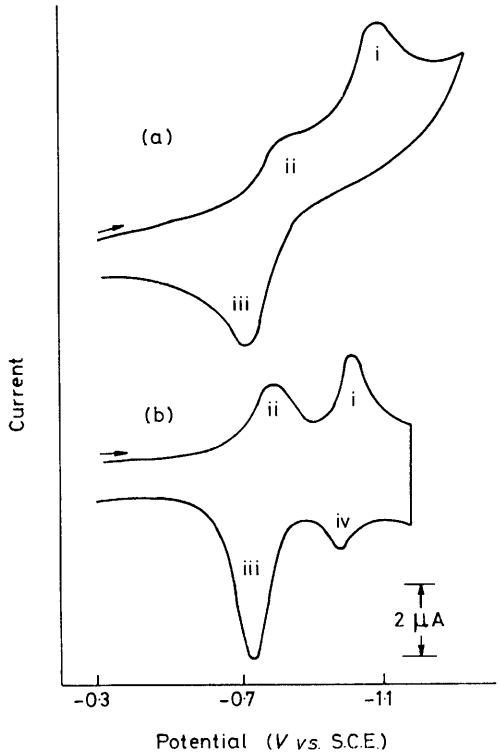
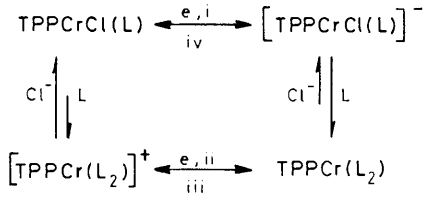


FIGURE 1. Current–voltage curves for the electro-reduction of TPPCrCl in $C_2H_4Cl_2$ which was 1·07 M in pyridine. Curve (a) depicts a cyclic voltammogram at a Pt button determined at a scan rate of 0·500 V/s. Curve (b) depicts a cyclic differential pulse voltammogram at a Pt button determined at a scan rate of 0·010 V/s, a modulation amplitude of 25 mV, and a pulse duration of 57 ms.

Figure 1(a) depicts a typical cyclic voltammogram of TPPCrCl obtained in $C_2H_4Cl_2$ which was 1·07 M in pyridine. On the first sweep from −0·3 to −1·3 V† one oxidation and two reductions were observed [peaks i—iii, Figure 1(a)]. On the second and all subsequent sweeps [not shown in Figure (1)] the current for reduction peak ii increased in proportion to a decrease in current measured for peak i. No significant changes were observed in the oxidation current for peak iii which was separated from peak ii by 60—80 nV. Based on earlier studies[4–6] of TPPCrCl and OEPCrOH (OEP = octaethylporphyrin) in dimethyl sulphoxide as well as TPPCrCl in CH_2Cl_2–pyridine mixtures[7] these processes may be assigned as the oxidation–reduction reaction $Cr^{III} + e \rightleftharpoons Cr^{II}$.

Conventional analysis[8] of the peak shape and the dependence of peak current and peak potential on scan rate for processes i and ii in Figure 1(a) indicate the presence of chemical reactions coupled to reversible electron transfers. Process i has been analysed as a reversible electron transfer which is followed by a reversible chemical reaction (EC mechanism). Process ii has also been analysed as a reversible electron transfer which in this case is preceded by a reversible chemical reaction (CE mechanism). Based on these results the electron transfer mechanism shown in the Scheme is proposed where the Roman numbers correspond to the peaks in Figure 1.



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In theory,[8] slow scan rates should enable isolation of the reversible reactions i and iv. For the systems investigated, however, this was not possible and no reverse peak iv was obtained by cyclic voltammetry in the range of scans between 0·020 and 100 V/s.

The reversibility of the electron transfer processes i and iv and the presence of four distinct Cr species at the electrode surface could be confirmed, however, by results of cyclic differential pulse voltammetry (CDPV) shown in Figure 1(b). Scanning through the same potential region as in the cyclic voltammogram [Figure 1(a)] two reduction peaks (i and ii)

† All potentials in this report are referenced to the saturated calomel electrode.

and two oxidation peaks (iii and iv) are observed with CDPV. On the cyclic voltammetric time scale, process iv is not observed, indicating that the symmetrically substituted Cr^{II} species is thermodynamically favoured over the asymmetrically substituted species $[TPPCrCl(L)]^-$. However, at slow scan rates, a measurable amount of $[TPPCrCl(L)]^-$ is oxidized (peak iv). This species is not present in the bulk of the solution but is produced by the slow reassociation of Cl^- before electron transfer. The driving force behind this reassociation is the relative ease with which $[TPPCrCl(L)]^-$ can be oxidized with respect to $TPPCr(L)_2$, that is, the 300 mV difference in oxidation potentials between the two complexes. In the same manner, $[TPPCr(L)_2]^+$ is not present initially in the bulk of solution but is formed at the electrode surface by dissociation of TPPCrCl(L) prior to electron transfer. Without the application of a potential this species would not be observed.

Standard thin-layer spectroelectrochemical techniques[9] were employed in an attempt to characterize the reactants and products of each process. At an applied potential of 0·00 V, the spectrum observed corresponded to TPPCr(Cl)(L).[1,2] After complete reduction at potentials more negative than −1·3 V, the spectrum was comparable to that reported for $TPPCr(L)_2$.[3,4] An identical spectrum was obtained for a new solution reduced at −0·95 V, thus confirming the equilibrium between the reactants in peak ii and those in peak i. The spectrum taken after complete reoxidation of $TPPCr(L)_2$ at −0·40 V initially indicated a mixture of several species but decayed over the course of several minutes to the spectrum of the starting material, TPPCr(Cl)(L).

Finally, to rule out the possibility that peaks ii and iii might involve competitive equilibria between the counterions Cl^- and ClO_4^- (as available from the supporting electrolyte), a TPPCrCl solution containing 1·07 M pyridine in $C_2H_4Cl_2$ with a 50-fold excess of Cl^- was prepared and tested. The current–voltage relationship obtained on this solution was identical to that obtained in the absence of added Cl^-.

Similar oxidation–reduction mechanisms were obtained for twelve variously-substituted pyridines and the only difference observed was a cathodic shifting of all potentials as the pK_a of the complexed axial ligand increased.‡ Plots of $E_{1/2}$ *vs.* pK_a of the axially complexed ligand have been shown to be linear for reduction of $[TPPFe(L)_2]^+$, $TPPFe(L)_2$, $[TPPMn(L)]^+$, and TPPMn(L) where L is a substituted pyridine.[10,11] Similar linear plots are depicted in Figure 2 for reduction of TPPCrCl(L) and $[TP[Cr(L)_2]^+$ to yield $[TPPCrCl(L)]^-$ and $TPPCr(L)_2$, respectively.

As seen in Figure 2, reversible half wave potentials are more negative by 15 mV per pK_a unit for reduction of the former complex and by 39 mV per pK_a unit for reduction of the latter complex. Thus, reduction of the symmetrically substituted Cr^{III} complex is $2\frac{1}{2}$ times more sensitive to σ effects than the asymmetric mono-pyridine Cr^{III} complex. In the latter case, both the electrode reactant and product have Cl^- as an invariant sixth ligand. The negative slope of both plots (Figure 2) suggests that the higher oxidation state shows a greater sensitivity to the σ donor ability of the ligand than that of the lower oxidation state.

The $2\frac{1}{2}$-fold decrease in sensitivity to the ligand pK_a on going from symmetrically to unsymmetrically substituted Cr^{III} complexes may indirectly reflect the dominating influence of the counterion (as has been shown for the reaction of Fe^{III} porphyrins)[12] or may reflect the destabilizing effect of a monovalent anion co-ordinated to the Cr^{II} species (as has been shown for the reactions of Mn^{II} porphyrins).[13] Alternatively, the increase in ligand sensitivity for the symmetrically substituted complexes may suggest a substantial *trans*-stabilization by the formation of six-co-ordinate, ion-paired Cr^{III} species. At present, with electrochemical evidence, we are unable to determine the predominant factors involved.

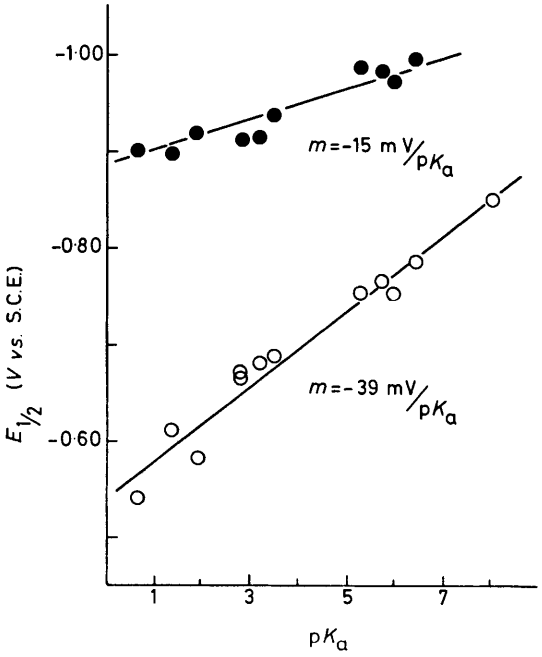

FIGURE 2. Plot of potential dependences on ligand pK_a for the electron transfer reactions of $[TPPCr(L_2)]^+$ (lower trace) and of TPPCrCl(L) (upper trace) at a ligand concentration of 1·00 ± 0·07 M in the substituted pyridines listed in footnote ‡.

Preliminary results of further work indicate that two discrete electron transfer pathways may also exist for complexes of TPPCrX(S) where S is a solvent molecule and X an halide. In many cases it appears that the actual species in solution is not that which is thermodynamically favoured in the electroreduction, and that a dissociation or re-association of the halide must occur before ready electron transfer is achieved. This dual mechanism of electro-oxidation–reduction is of interest not only in terms of Cr^{III} porphyrins but also in terms of understanding the factors which determine electron transfer pathways during the electroreduction of synthetic Fe^{III} and Mn^{III} porphyrins, where the product has been shown to be axially complexed by a halide molecule.[12,13] Finally, thermodynamic know-

‡ pK_a Values (from K. Schoefield, 'Hetero-Aromatic Nitrogen Compounds,' Plenum Press, New York, N.Y., 1967) for substituted pyridines employed as axial adducts of TPPCrCl and TPPCr: pyridine, pK_a, 3,5-Cl_2 0·67, 3-CN 1·40, 4-CN 1·86, 3-Cl 2·81, 3-Br 2·84, 3-MeCO 3·18, 4-MeCO 3·51, pyridine 5·23, 3-Me 5·79, 4-Me 5·98, 3,4-lutidine 6·46, and 4-NMe_2 9·71.

ledge of the halide dissociation/association kinetics should allow 'tuning' of a given pathway by shifting of solution equilibria or by modification of the time required for the electro-reduction.

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