

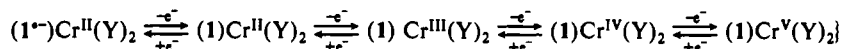
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Electrochemical Potentials and Associated pK_a Values for the Various Oxidation States of a Water-Soluble, Non μ -Oxo Dimer Forming Chromium Tetraphenylporphyrin in Aqueous Solution

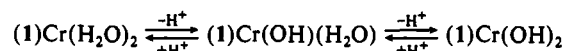
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Electrochemical studies of the water soluble, non μ -oxo dimer forming [5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)-porphinato]chromium(III) hydrate $\{(1)Cr^{III}(Y)_2, Y = H_2O \text{ or } HO^-\}$ have been carried out in aqueous solutions ($\mu = 0.2$ with $NaClO_4$). With an increase in pH, the proton dissociation of the ligated water molecules of $(1)Cr^{III}(H_2O)_2$ provides $(1)Cr^{III}(OH)(H_2O)$ and then $(1)Cr^{III}(OH)_2$. Nernst-Clark plots of the electrode potentials (E_m) vs pH for each of the stepwise $1e^-$ oxidations [i.e.,



provide the formal potentials (E°) for the interconversion of the various oxidation states of $(1)Cr(H_2O)_2$, $(1)Cr(OH)(H_2O)$, and $(1)Cr(OH)_2$. Also obtained from these Nernst-Clark plots are the pK_a values for the acid dissociations of



at each oxidation state. The best first and second pK_a values for the dissociation of protons from the ligated water molecules are as follows: $(1^{n-})Cr^{II}(H_2O)_2$ and $(1)Cr^{II}(H_2O)_2$, pK_{a1} 10.6; $(1)Cr^{III}(H_2O)_2$, pK_{a1} 9.4 and pK_{a2} 12.4; $(1)Cr^{IV}(H_2O)_2$, pK_{a1} 7.6 and pK_{a2} 10.2; and $(1)Cr^V(H_2O)_2$, pK_{a1} 7.1. The electrode potentials for the $1e^-$ reductions of the chromium(III) porphyrin π cation radical to chromium(III) porphyrin and $(1)Cr^{II}(Y)_2 \rightarrow (1^{n-})Cr^{II}(Y)_2$ are pH independent, due to the near equality of the pK_a values of water ligated to reduced and oxidized species. The near equality of the pK_a values of these two pairs results from the fact that the porphyrin ligand rather than the metal moiety is undergoing oxidation and reduction. Average values of E° for the interconversion of chromium(III) and chromium(IV) species are as follows: $e^- + (1)Cr^{IV}(H_2O)_2 \rightarrow (1)Cr^{III}(H_2O)_2$, 0.61 V; $e^- + (1)Cr^{IV}(H_2O)(HO) \rightarrow (1)Cr^{III}(H_2O)(HO)$, 0.50 V; $e^- + (1)Cr^{IV}(HO)_2 \rightarrow (1)Cr^{III}(HO)_2$, 0.39 V (SCE). Average values of E° for the interconversion of chromium(II) and chromium(III) species and chromium(III) and chromium(IV) and chromium(V) species could only be determined in the neutral and acidic pH range. The values of E° are as follows: $e^- + (1)Cr^{III}(H_2O)_2 \rightarrow (1)Cr^{II}(H_2O)_2$, -1.04 V; $e^- + (1)Cr^{III}(H_2O)(HO) \rightarrow (1)Cr^{II}(H_2O)(HO)$, -1.13 V; $e^- + (1)Cr^V(H_2O)_2 \rightarrow (1)Cr^{IV}(H_2O)_2$, 1.01 V; and $e^- + (1)Cr^V(H_2O)(HO) \rightarrow (1)Cr^{IV}(H_2O)(HO)$, 0.98 V.

Introduction

In a previous electrochemical investigation in aqueous solution between pH 2 and 12, we showed¹ that H_2O and HO^- serve as the axial ligands for iron(III) and iron(IV) tetraphenylporphyrins, iron(IV) tetraphenylporphyrin π -cation radical and manganese(III), manganese(IV) and manganese(V) tetraphenylporphyrins. The tetraphenylporphyrins employed were water soluble and did not form μ -oxo dimers. Further, we established that oxo ligation (i.e., $M=O$) can only occur in water at high pH.¹ The mechanisms of oxidation of chromium(III) porphyrins² and the use of Cr^V -ligated porphyrins in studies of the stoichiometric epoxidation of alkenes^{3,4} are of continuing interest. In order to understand these processes, a knowledge of the interconversion of the various oxidation states of chromium porphyrin is crucial. Most electrochemical studies on chromium porphyrins have been carried out in aprotic media.^{3d,5} There is little information on the

electrochemistry of water-soluble chromium porphyrins in aqueous solution. Electrode reactions that involve reactants or intermediates with ionizable protons and/or processes that involve proton transfer are best studied in aqueous solutions where pH and ionic strength are easily controlled. In aqueous media, and in the absence of strongly ligating external bases, the axial ligands are represented by either H_2O or HO^- , depending on the pH of the solution. From the pH dependence of the electrode potential (E_m) (i) acid dissociation constants of reactants and products may be determined, (ii) the direction and course of redox reactions may be predicted, (iii) the magnitude of the rate constants (k) for redox reactions occurring in different pH regions may be explained, and (iv) choices may be made between kinetically equivalent mechanisms. From $\log k$ vs pH profiles for the oxidation of metal(III) porphyrins with oxidants and a knowledge of the ionization constants of reactants, one can identify the reacting species at various acidities. We now report the results of an investigation of the pH dependence of the various redox potentials of chromium ligated by 5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin ($1H_2$) and the pK_a values for the dissociation of $(1)Cr^n(Y)_2$ ($n =$ oxidation state and $Y = H_2O$ or HO^-) in aqueous solutions.

Experimental Section

Materials. 5,10,15,20-Tetrakis(2,6-dimethylphenyl)porphyrin was synthesized by the method of Lindsey et al.⁶ and converted to

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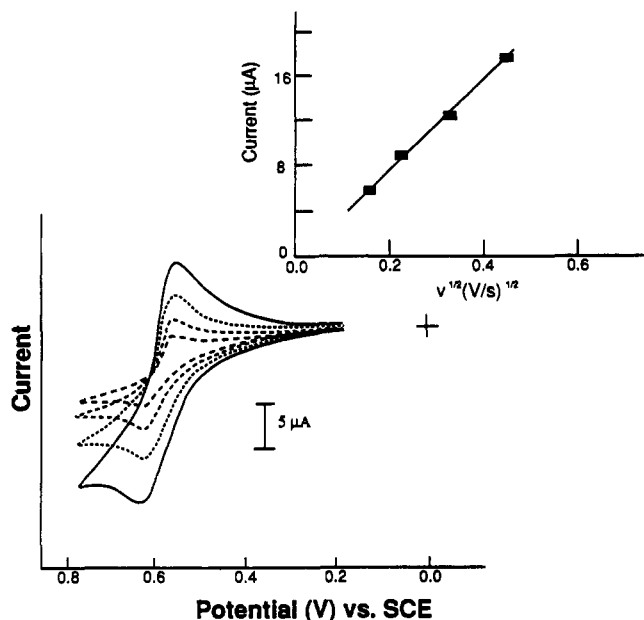


Figure 1. Cyclic voltammograms for the $1e^-$ oxidation of 4.12 mM (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ at scan rates of 0.025, 0.05, 0.1, and 0.2 V s^{-1} in a deaerated aqueous solution (pH 5, 0.2 N NaClO_4). The inset shows a plot of the anodic peak current as a function of the square root of the scan rate.

5,10,15,20-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrin ($1\text{H}_2\text{O}$) by the procedure of Zippies and Bruce.⁷ [5,10,15,20-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]chromium(III) hydrate ((1)- $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2$) was prepared by refluxing the free base with a 40-fold excess of chromium(II) chloride in DMF for 2 h.⁴ The water-soluble (1) $\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2$ was purified by ion-exchange chromatography, ultrafiltration, and size-exclusion chromatography.

Electrochemical Measurements. All aqueous solutions used for electrochemistry were prepared from distilled-deionized water which was boiled for at least $1/2$ h and stored under argon scrubbed free of O_2 , CO , and CO_2 . Preparations of all solutions were carried out under an argon atmosphere scrubbed free of O_2 , CO , and CO_2 . Metalloporphyrin concentrations ranged from 3.0 to 10.0 mM and contained 0.2 N NaClO_4 as electrolyte. Dilute solutions of carbonate-free HNO_3 and NaOH were used for the adjustment of pH. The pH values of solutions were measured before and after electrochemical experiments. The measured pH values were within ± 0.05 pH units. All reported potentials are with respect to saturated calomel electrode (SCE). All experiments were performed at room temperature.

The following buffers were employed in spectroelectrochemical experiments: (pH 3.1) $\text{ClCH}_2\text{COO}^-/\text{ClCH}_2\text{COOH}$, (pH 5.2) $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$, (pH 6.7) $\text{H}_2\text{PO}_3^-/\text{HPO}_3^{2-}$, (pH 9.3) $\text{HCO}_3^-/\text{CO}_3^{2-}$, (pH 10.6) $\text{HO}^-/\text{H}_2\text{O}$, (pH 11.5) $\text{HO}^-/\text{H}_2\text{O}$. Buffer concentrations were 0.1 M, and the ionic strength was maintained at 0.2 with NaClO_4 .

Instrumentation. The cyclic voltammetric measurements were accomplished with a three-electrode potentiostat (Bioanalytical Systems, Model CV-27) and a Houston Instruments Model 100 Omnigraphic recorder. A platinum-wire electrode separated from the analyte compartment by a medium-porosity glass fit was used as the auxiliary electrode. A Ag/AgCl electrode, filled with aqueous tetramethylammonium chloride solution and standardized to 0.00 V vs SCE,⁸ with a solution junction via a Pyrex-glass tube closed with a soft glass cracked bead contained in a Luggin capillary, was used as the reference electrode.

A 2.8-mm-diameter glassy-carbon or a 1.0-mm-diameter Pt disk electrode was employed as the working electrode for the determination of the pH dependence of potentials in aqueous solution. All working electrode surfaces were highly polished with Al_2O_3 paste prior to each experiment. The reproducibility of individual potential values was ± 5 mV. A Pt-mesh working electrode was used in spectroelectrochemical experiments. The design of the spectroelectrochemical cells employed has been described.⁹ Absorption spectra were recorded on a Cary 14

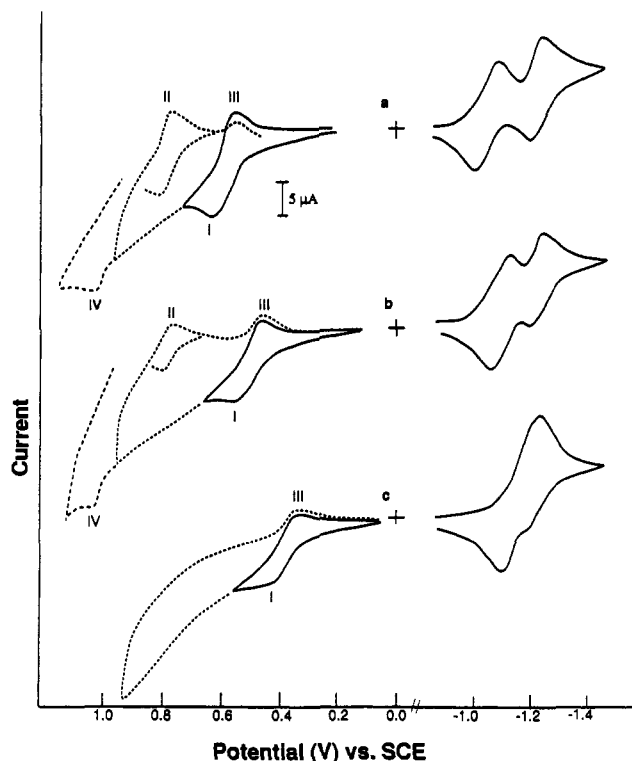


Figure 2. Cyclic voltammograms of 4.12 mM (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ in water (0.2 N NaClO_4) at various pH values at a scan rate 0.1 V s^{-1} : (a) pH 5.0; (b) pH 9.5; (c) pH 11.5. At pH 5, wave I is oxidation of (1) $\text{Cr}^{\text{III}}(\text{Y})_2$, wave II is reduction of the chromium(III) porphyrin π -cation-radical species, wave III is reduction of (1) $\text{Cr}^{\text{IV}}(\text{Y})_2$, and wave IV is oxidation of (1) $\text{Cr}^{\text{IV}}(\text{Y})_2$.

spectrophotometer interfaced to a Zenith computer equipped with OLIS (On-Line Instrument System Inc.) data acquisition and processing software.

Results and Discussion

The oxidation and reduction of (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ in aqueous solutions ($\mu = 0.2$ with NaClO_4) were studied between pH 2 and 12 under an argon atmosphere. Typical cyclic voltammograms for the first oxidation of (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ at pH 5.0 at various scan rates are shown in Figure 1. The well-defined waves represent a quasi-reversible oxidation as shown from the peak separation (ΔE_p) between the anodic and cathodic potentials ($E_{p,a}$ and $E_{p,c}$ respectively). The dependence of the anodic peak current ($i_{p,a}$) as a function of the square root of the scan rate (v) is linear as expected from a diffusion-controlled process (Figure 1, inset). This peak current at a constant scan rate is linearly proportional to the concentration of chromium(III) porphyrin. The diffusion coefficient (D) for the $1e^-$ oxidation (vide infra) of (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ at pH 5.0 can be calculated¹³ as $(3.1 \pm 0.3) \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

Figure 2 illustrates cyclic voltammograms (+1.2 to -1.5 V vs SCE) for (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ at different pH values. Examination of Figure 2 shows that the first oxidation peak current (i_p) is pH dependent. The maximum i_p is at pH < 7 and is associated with a well-defined redox couple. With an increase in pH, i_p decreases. It has previously been reported¹⁰ that i_p increases with pH above pH 8.5 with [meso-tetrakis(*N*-methyl-4-pyridiniumyl)porphinato]manganese(III). The electrochemistry of (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ and [meso-tetrakis(*N*-methyl-4-pyridiniumyl)porphinato]manganese(III) can not be compared, at alkaline pH, because the latter exists as a μ -oxo dimer between pH 8.5 and 11.5 while (1) $\text{Cr}^{\text{III}}(\text{Y})_2$ remains monomeric.

Thin-layer coulometric experiments were performed to verify the number of electrons involved in the first oxidation of (1)-

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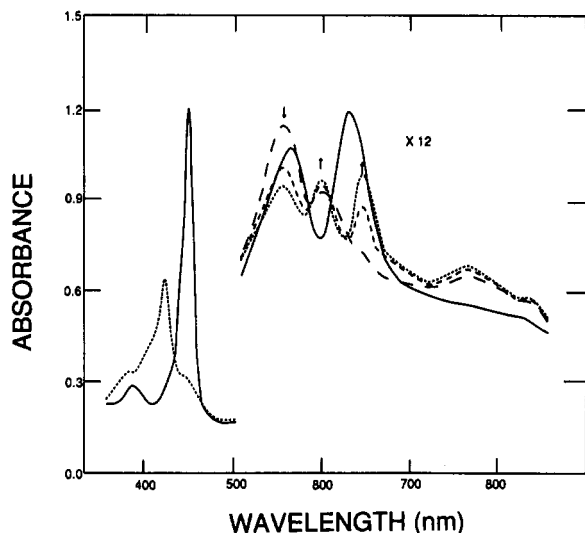
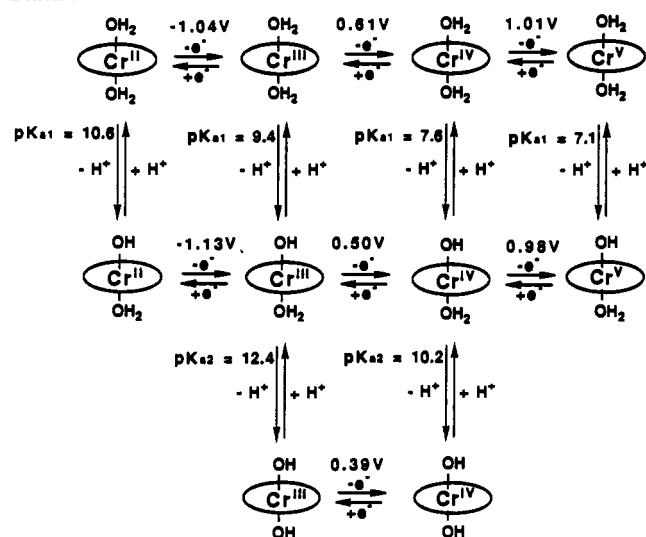


Figure 3. Comparison of the electronic absorption spectra of (1)Cr^{III}(Y)₂ at pH 5.2 (—) to the spectra of its 1e⁻ oxidation product at pH 5.2 (···), 9.3 (---), and 11.5 (-·-). All spectroelectrochemical controlled-potential oxidations were carried out in water with 0.2 N NaClO₄ as supporting electrolyte using an initial concentration [(1)Cr^{III}(Y)₂]⁰ = 0.5 mM. The applied potential remained some 250 mV more positive than the oxidation potential for (1)Cr^{III}(Y)₂ at any given pH.

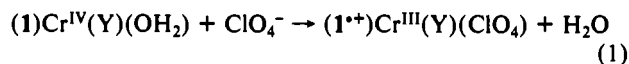
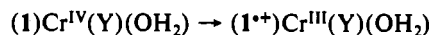
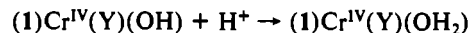
Cr^{III}(Y)₂. Integrated currents were recorded for the first oxidation of (1)Cr^{III}(Y)₂, and the oxidations were considered to be complete when the current flow was about that for a blank solution of electrolyte. These experiments established the transfer of one electron between pH 2 and 12. A single wave accompanies the 1e⁻ oxidation of (1)Cr^{III}(Y)₂ → (1)Cr^{IV}(Y)₂ on scanning from 0.0 to +0.9 V (pH 5, wave I in Figure 2a). However, two reduction processes (waves II and III in Figure 2a) are observed on the reverse scan at lower pH's (Figure 2a,b). On the time scale of the experiment, the 1e⁻ oxidation (wave I in Figure 2a) at E_{p,a} = +0.64 V is coupled to wave III (Figure 2a). The value of i_{pc}/i_{pa} is dependent on the potential at which the reverse scan is initiated. This result implies that the direct product ((1)Cr^{IV}(Y)₂) of the initial oxidation undergoes a chemical transformation during the scanning time. It is proposed that this transformation is initiated by an axial ligand exchange of (1)Cr^{IV}(Y)₂ (vide infra), which leads to an intracomplex electron transfer and the formation of a chromium(III) porphyrin π-cation-radical species ((1^{•+})Cr^{III}). Only one redox couple is observed on scanning from 0.0 to +0.9 V at higher pH (Figure 2c at pH 11.5). Thus, the rate of conversion of (1)Cr^{IV}(Y)₂ to a (1^{•+})Cr^{III} species increases as the pH is decreased from 12.0 to 2.0.

Characterization of (1)Cr^{IV}(Y)₂ as the 1e⁻ oxidation product of (1)Cr^{III}(Y)₂ was carried out by rapid thin-layer spectroelectrochemical controlled-potential one-electron oxidation using a platinum mesh electrode. These spectroelectrochemical one-electron oxidations were carried out at pH 3.1, 5.2, 6.7, 9.3, 10.6, 11.5, and 12.5. Figure 3 illustrates typical absorption spectra of (1)Cr^{III}(Y)₂ (392 nm, 450 (Soret), 566, 637, 826) and the one-electron oxidation product at pH's 5.2, 9.3, and 11.5. The Soret peak (424 nm) of the product is independent of pH. However, with a decrease in pH, the peaks at 595 and 647 nm increase while the peak at 554 nm decreases. It is known that the peaks at 424 nm and about 595 and 650 nm characterize the chromium(III) porphyrin π cation radical.¹¹ The rate of formation of this species increases with decrease in pH. These results support the conclusion drawn from the cyclic voltammetry experiments, that the rate of intracomplex electron transfer from porphyrin ring orbitals to chromium d orbitals in (1)Cr^{IV}(Y)₂ to yield the chromium(III) porphyrin π cation radical increases as the pH decreases. Transition-metal oxidation states of IV are stabilized by -OH and =O ligation. It is not surprising to find, therefore, that the

Scheme I



exchange of one or more -OH axial ligands for HOH and/or ClO₄⁻ is accompanied by oxidation of the porphyrin ligand by the Cr(IV) moiety (eq 1). Equation 1 correctly predicts that chromium(III) porphyrin π-cation-radical formation becomes more favorable as the pH is decreased.



The second 1e⁻ oxidation of (1)Cr^{III}(Y)₂ at pH 5.0 (wave IV in Figure 2a) is irreversible and characterized by decreased current, compared with that of the first oxidation. It is not surprising to find that the current of wave IV (Figure 2a) is dependant on the scan rate, knowing that the first oxidation product ((1)Cr^{IV}(Y)₂) is converted to the chromium(III) porphyrin π cation radical during the scanning time. Also, the second oxidation product ((1)Cr^V(Y)₂) was found to be unstable in aqueous solution. We were able to show, by rapid thin-layer spectroelectrochemical controlled-potential oxidation of (1)Cr^{III}(Y)₂ at +1.1 V and pH 5.2, that 2e⁻ oxidation of (1)Cr^{III}(Y)₂ provides the UV/vis spectra characteristic of (1)Cr^V(Y)₂ (λ_{max} = 410 nm).⁴ The (1)Cr^V(Y)₂ product generated in this fashion decomposes very rapidly in aqueous solution.

The reduction of the chromium(III) porphyrin π cation radical to chromium(III) porphyrin at pH 5.0 is associated with wave II (Figure 2a) at E_{pc} = +0.81 V. This reduction process is coupled to an oxidation process (E_{pa} = +0.87 V) on the reverse scan at +0.65 V. The first reduction wave of (1)Cr^{III}(Y)₂, corresponding to the formation of (1)Cr^{II}(Y)₂, is quasi-reversible and separable from the reversible second reduction at lower pH (Figure 2a). On the basis that the peak currents for the first and second reductions are the same as the first oxidation peak current of (1)Cr^{III}(Y)₂, it can be concluded that they involve one-electron transfer. At a higher pH of 11.5 (Figure 2c), the first and second reduction waves merge to a single wave with 2e⁻ peak current, but the oxidation waves of reduced species are slightly separable.

pH Dependence of the Electrode Potentials for Oxidation and Reduction of (1)Cr^{III}(Y)₂ in Aqueous Solutions. Cyclic voltammetry was used to measure the electrode potentials as a function of pH (glassy carbon electrode at 0.1 V/s) and the results are shown in Figure 4 as Nernst-Clark plots. The points of Figure 4 are experimental, and the lines generated to fit the experimental points were obtained by computer fitting of the Nernst-Clark¹²

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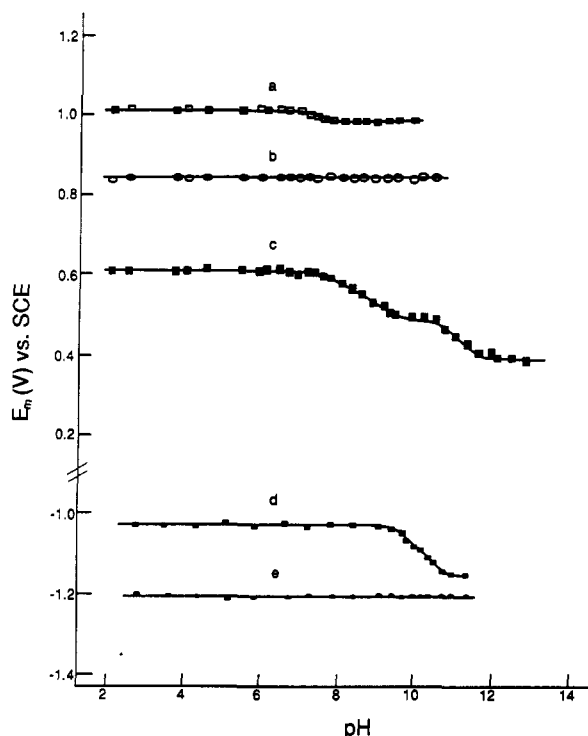


Figure 4. Nernst-Clark plots of potential (E_m) vs pH, where solid lines represent theoretical fits to the experimental points: (a) $1e^-$ oxidation of $(1)Cr^{IV}(Y)_2$; (b) $1e^-$ reduction of the chromium(III) porphyrin π -cation-radical derivative to the chromium(III) porphyrin derivative; (c) $1e^-$ oxidation of $(1)Cr^{III}(Y)_2$ to $(1)Cr^{IV}(Y)_2$; (d) $1e^-$ reduction of $(1)Cr^{III}(Y)_2$; (e) $1e^-$ reduction of $(1)Cr^{II}(Y)_2$.

equations (eqs 2–4) derived by use of the equilibria in Scheme I (where the ellipses represent the porphyrin ligand).

Equation 2 applies to the couple $(1)Cr^{III}(Y)_2/(1)Cr^{IV}(Y)_2$. The terms K_{a1}^{III} , K_{a2}^{III} , K_{a1}^{IV} , and K_{a2}^{IV} are the first and second acid dissociation constants of $(1)Cr^{III}(Y)_2$ and $(1)Cr^{IV}(Y)_2$, respectively.

$$E_m = E^{o'} + \frac{RT}{F} \ln \left[\frac{a_{H^+}^2 + K_{a1}^{III}a_{H^+} + K_{a1}^{III}K_{a2}^{III}}{a_{H^+}^2 + K_{a1}^{IV}a_{H^+} + K_{a1}^{IV}K_{a2}^{IV}} \right] \quad (2)$$

Equation 3 applies to the couple $(1)Cr^{IV}(Y)_2/(1)Cr^V(Y)_2$.

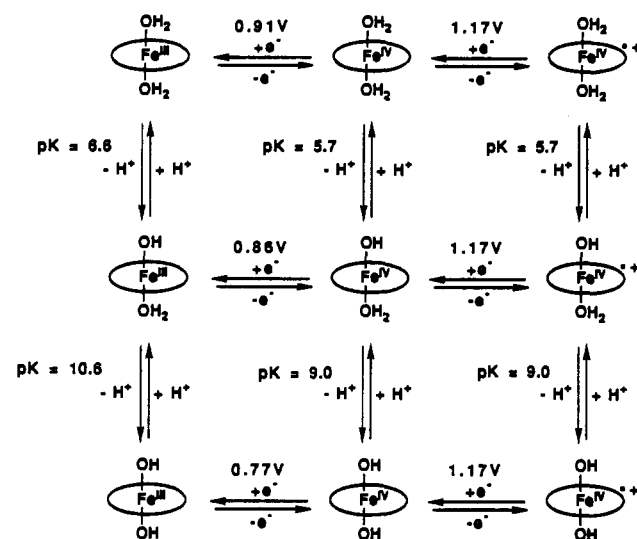
$$E_m = E^{o'} + \frac{RT}{F} \ln \left[\frac{a_{H^+}^2 + K_{a1}^{IV}a_{H^+} + K_{a1}^{IV}K_{a2}^{IV}}{a_{H^+}^2 + K_{a1}^V a_{H^+} + K_{a1}^V K_{a2}^V} \right] \quad (3)$$

Equation 4 applies to the couple $(1)Cr^{III}(Y)_2/(1)Cr^{II}(Y)_2$.

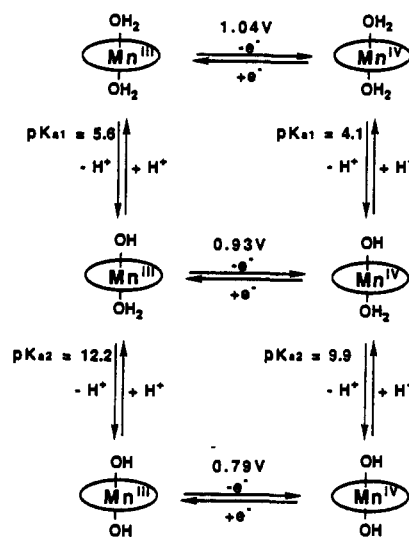
$$E_m = E^{o'} + \frac{RT}{F} \ln \left[\frac{a_{H^+} + K_{a1}^{III}}{a_{H^+}^2 + K_{a1}^{III}a_{H^+} + K_{a1}^{III}K_{a2}^{III}} \right] \quad (4)$$

The pH dependence of the first and second $1e^-$ oxidations of $(1)Cr^{III}(Y)_2$ are similar to the pH dependence observed for the metal-centered oxidation of $(1)Fe^{III}(Y)_2$ and $(1)Mn^{III}(Y)_2$ (Schemes II and III¹). The electrode potential (Figure 4c) of the first oxidation of $(1)Cr^{III}(Y)_2$ shifts from +0.61 V below pH 7 to +0.39 V above pH 12. The pH dependence of E_m relates to the ionization of ligated H_2O and suggests metal-centered oxidation of $(1)Cr^{III}(Y)_2$ to $(1)Cr^{IV}(Y)_2$. Three pH-independent regions are observed, one [$E_{1/2} = +0.61$ V, $E_{1/2} = (E_{pc} + E_{pa})/2$] below pH 7, a smaller second plateau ($E_{1/2} = +0.50$ V) around pH 10, and a plateau ($E_{1/2} = +0.39$ V) above pH 12. These three pH-independent regions can be thought of as apparent formal potentials ($E^{o'}$) for $(1)Cr^{IV}(H_2O)_2 + e^- \rightarrow (1)Cr^{III}(H_2O)_2$, for $(1)Cr^{IV}(H_2O)(HO^-) + e^- \rightarrow (1)Cr^{III}(H_2O)(HO^-)$, and for $(1)Cr^{IV}(HO^-)_2 + e^- \rightarrow (1)Cr^{III}(HO^-)_2$, respectively. The electrode potential ($E_m = E_{1/2}$) decreases with a slope of about 55 mV/pH between pH 7.6 and 9.6 and between pH 10.2 and 12.4. Thus,

Scheme II



Scheme III



in these two pH ranges the oxidation of $(1)Cr^{III}(Y)_2$ involves dissociation of one proton per one electron transferred. This pH dependence of E_m establishes the correctness of the structures $(1)Cr^{III}(H_2O)_2$, $(1)Cr^{III}(H_2O)(HO^-)$, and $(1)Cr^{III}(HO^-)_2$ and the pH dependence of their formation (Scheme I). The deprotonation of $(1)Cr^{III}(H_2O)(HO^-)$ most likely provides $(1)Cr^{III}(HO^-)_2$, rather than $(1)Cr^{III}(H_2O)(O)$, because the pK_a of ligated (H_2O) is a much smaller number than is the pK_a of ligated (OH) in 55 M H_2O solvent.

The electrode potential for one-electron reduction of chromium(III) porphyrin π -cation-radical species (produced by ligand exchange of $(1)Cr^{IV}(Y)_2$, loc. cit.) is almost constant (+0.84 V) between pH 2 and 12 (Figure 4b). This is to be expected since the pK_a values for proton dissociation of ligated H_2O in $(1)^{+}Cr^{III}(H_2O)_2$ and $(1)Cr^{III}(H_2O)_2$ are anticipated to be virtually the same.

The means to approximate $E_{1/2}$ from E_{pa} of an irreversible process is provided by Bard and Faulkner.¹³ With the appropriate equations, the $E_{1/2}$ for the first oxidation of $(1)Cr^{IV}(Y)_2$ was calculated and found to decrease slightly from 1.01 to 0.98 V between pH 7.2 and 7.6 with a slope of about 60 mV/pH. Potentials can only be determined below pH 10 due to the intervention of the HO^- envelope at higher pH values. The finding that one-electron transfer is associated with a proton transfer near the pK_a of ligated H_2O indicates that $(1)Cr^{IV}(Y)_2$ undergoes

(13) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; Wiley: New York, 1980; Chapter 6.

Table I. Acid Dissociation Constants, Calculated from the Nernst-Clark Plots of Figure 4, for Water Molecules Ligated to the Various Oxidation States of the Chromium 5,10,15,20-Tetrakis-(2,6-dimethyl-3-sulfonatophenyl)porphyrin Species

species	pK_{a1}	pK_{a2}
(1 ⁻)Cr ^{II} (H ₂ O) ₂	10.6 ± 0.3 ^{a,f}	NO ^b
(1)Cr ^{III} (H ₂ O) ₂	10.6 ± 0.3 ^c	NO ^b
(1)Cr ^{III} (H ₂ O) ₂	9.1 ± 0.3 ^c	NO ^b
	9.6 ± 0.3 ^d	12.4 ± 0.3 ^d
(1 ⁺)Cr ^{III} (H ₂ O) ₂	9.6 ± 0.3 ^{a,d}	12.4 ± 0.3 ^{a,d}
(1)Cr ^{IV} (H ₂ O) ₂	7.6 ± 0.2 ^d	10.2 ± 0.3 ^d
	7.5 ± 0.2 ^e	NO ^b
(1)Cr ^V (H ₂ O) ₂	7.1 ± 0.2 ^e	NO ^b

^a Acid dissociation constants of the π cation radical and the π anion radical are identical with those of same oxidation states of chromium porphyrins. ^b NO means not observed. ^c Determined from the one-electron reduction of (1)Cr^{III}(Y)₂. ^d Determined from the one-electron oxidation of (1)Cr^{III}(Y)₂. ^e Determined from the one-electron oxidation of (1)Cr^{IV}(Y)₂. ^f Determined from the one-electron reduction of (1)Cr^{II}(Y)₂.

metal-centered oxidation to (1)Cr^V(Y)₂. That 1e⁻ oxidation of (1)Cr^{IV}(Y)₂ provides (1)Cr^V(Y)₂ is, therefore, supported by both the pH dependence of E_m and the observation of the spectrum of (1)Cr^V(Y)₂ product under the conditions of rapid thin-layer spectroelectrochemical controlled potential oxidation (loc. cit.).

The electrode potential of the first reduction of (1)Cr^{III}(Y)₂ shifts from -1.04 V below pH 9 to -1.13 V above pH 10 (Figure 4d). The electrode potential decreases with a slope of about 60 mV/pH between pH 9 and 12. The pH dependence of E_m establishes the reduction as metal-centered to provide (1)Cr^{II}(Y)₂. The reversible second reduction of (1)Cr^{III}(Y)₂ is pH independent with $E_{1/2}$ at -1.21 V (Figure 4e). This pH independence of E_m shows that the second 1e⁻ reduction may be assigned to the reduction of the porphyrin ring ((1)Cr^{II}(Y)₂ + 1e⁻ → (1⁻)Cr^{II}(Y)₂).

The acid dissociation constants for (1⁻)Cr^{II}(Y)₂, (1)Cr^{II}(Y)₂, (1)Cr^{III}(Y)₂, (1)Cr^{IV}(Y)₂, (1⁺)Cr^{III}(Y)₂, and (1)Cr^V(Y)₂, which are determined from the fit of the Nernst-Clark plots to the experimental data for the reductions and oxidations of (1)Cr^{III}(Y)₂, are provided in Table I.

Of considerable importance is the understanding that H₂O and HO⁻ are the axial ligands of the chromium porphyrin derivative of various oxidation states in aqueous solutions. The electrochemically measured pK_{a1}^{III} (9.4) and pK_{a2}^{III} (12.4) values for acid dissociation of (1)Cr^{III}(H₂O)₂ compare favorably to values determined by spectrophotometric titration (9.0 and 12.6) at an ionic strength of 0.2 M (NaClO₄).⁴ The decrease of pK_{a1} with an increase in the oxidation state of chromium is reasonable and has precedence¹ in studies with (1)Fe^{III}(Y)₂. The pH independence of the electrode potentials in the reductions of chromium(III) porphyrin π cation radical → chromium(III) porphyrin derivative and (1)Cr^{II}(Y)₂ → (1⁻)Cr^{II}(Y)₂ is explained on the basis that the electron added to or removed from the porphyrin ring in the course of these reactions is delocalized over the porphyrin 24-atom framework such that the electron density of the Cr^{III} and Cr^{II} water ligation centers are not much altered. Therefore, the pK_a values of the chromium(III) porphyrin π cation radical and (1⁻)Cr^{II}(Y)₂ are almost the same as those of the chromium(III) porphyrin derivative and (1)Cr^{II}(Y)₂, respectively.

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Registry No. (1)Cr^{II}(H₂O)₂, 136536-89-5; (1)Cr^{II}(H₂O)(HO⁻), 136536-90-8; (1)Cr^{II}(HO⁻)₂, 136536-91-9; (1⁻)Cr^{II}(H₂O)₂, 136536-92-0; (1⁻)Cr^{II}(H₂O)(HO⁻), 136536-93-1; (1⁻)Cr^{II}(HO⁻)₂, 136536-94-2; (1)Cr^{III}(H₂O)₂, 136536-95-3; (1)Cr^{III}(H₂O)(HO⁻), 136536-96-4; (1)Cr^{III}(HO⁻)₂, 136536-97-5; (1)Cr^{IV}(H₂O)₂, 136536-98-6; (1)Cr^{IV}(H₂O)(HO⁻), 136536-99-7; (1)Cr^{IV}(HO⁻)₂, 136537-00-3; (1)Cr^V(H₂O)₂, 136537-01-4; (1)Cr^V(H₂O)(HO⁻), 136545-26-1; (1)Cr^V(HO⁻)₂, 136537-02-5; Pt, 7440-06-4; carbon, 7440-44-0.

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Iron(III) Porphyrins Substituted with Highly Electron-Withdrawing CF₃ Groups: Electronic Absorption, MCD, and EPR Spectral Study

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Electronic absorption, MCD, and EPR spectra of iron(III) complexes of etioporphyrin I and electron-deficient porphyrins with one, two, or four CF₃ groups at pyrrole β -positions of the porphyrin have been measured. The overall equilibrium constants of the reaction of the iron(III) porphyrin chloride with imidazole and 1-methylimidazole were evaluated from the electronic spectral changes on addition of the bases. The equilibrium constants for imidazole have a slight tendency to decrease with the number of CF₃ group, and those for 1-methylimidazole have a marked such tendency. The effects of highly electron-withdrawing substituents at the porphyrin periphery were revealed more obviously in the MCD spectra of the (porphyrinato)iron(III) chloride than in the electronic spectra. MCD spectral results indicated that the Soret region is sensitive to minor changes in the redox potential of the porphyrin. In the EPR spectra of both low-spin complexes with imidazole and 1-methylimidazole, the g anisotropy was apparently lowered and the tetragonality μ/λ was increased with an increase in the number of CF₃ groups. The rhombicity R/μ for CF₃-substituted porphyrin complexes was larger than that for the unsubstituted analogues. These EPR spectral results were discussed in relation to the electron-withdrawing ability of peripheral substituents.

Introduction

The introduction of highly electron-withdrawing groups at the periphery of a porphyrin can affect the redox property of the porphyrin ligand and its respective metalloporphyrins and its affinity for metal ions or axial ligands.²⁻⁵

Electron-deficient porphyrins with chemically inert CF₃ groups at pyrrole β -positions have been shown to have a considerably reduced affinity for metal ions, arising from significant reduction in the electron density on pyrrole nitrogens.⁶⁻⁸ Paramagnetic ¹⁹F

NMR spectra of iron(III) porphyrins substituted with CF₃ groups and reconstituted metmyoglobin have been measured and the ¹⁹F

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