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(15) While this work was in progress, another preparation of **4** was reported[5] but no melting point was given since the compound was isolated as a green oil which was not sublimed or purified by any other methods.

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Kinetics of the Reduction of Iron(III) Meso- and Deuteroporphyrin Esters by Chromium(II)

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Many kinetic studies have been done on the reduction to their divalent forms of cobalt(III), iron(III), and manganese(III) porphyrins by chromium(II),[1-4] vanadium(II),[1] europium(II),[1] dithionite,[5-7] hexaammineruthenium(II),[8] and tin(II).[9] The majority of this work has involved synthetic porphyrins of the *meso*-tetraphenyl type made water soluble by virtue of carboxylic acid, sulfonic acid, pyridinium, or *N*-methylpyridinium groups. In certain cases, this functionalization apparently provides pathways for electron transfer not available to natural porphyrins of the protoporphyrin type, and hence such synthetic adducts serve as poor models for heme-type proteins. Electron-transfer experiments on the reduction of iron(III) cytochrome *c*,[10-12] myoglobin,[13] and hemoglobin[13] have appeared. We report the kinetics of reduction of the iron(III) complexes of meso- and deuteroporphyrin IX dimethyl ester by chromium(II). These natural type porphyrins were solubilized and monomerized using the neutral detergent Triton X-100. Our results are compared with the kinetic behavior of related synthetic porphyrins.

Experimental Section

Meso- and deuteroporphyrin IX dimethyl ester (MPDME, DPDME) and their iron(III) dimer complexes were prepared by literature methods.[14] The iron porphyrins were dissolved in acetone and heated in a 2% Triton X-100 (spectroscopic grade, Research Products International Corp., Elk Grove, Ill.) solution until the acetone evaporated. The resulting solution was then filtered at room temperature through Metricel 0.45 μm filters and adjusted to the proper ionic strength.

Excellent isosbestic points were obtained in the Soret region from spectrophotometric acid–base titrations of the iron porphyrins in 2% Triton X-100, $\mu = 0.5$ ($NaClO_4/HClO_4$) at 25 °C. The pK_1 for the hydrolysis reactions

$$H_2O\text{-}Fe^{III}P \leftrightarrow HO\text{-}Fe^{III}P + H^+ \qquad K_1 \qquad (1)$$

were determined by standard means.[15] $pK_1 = 4.7$ for $Fe^{III}DPDME$ and 5.0 for $Fe^{III}MPDME$. "*n*", the number of protons dissociated, was 1.07 ± 0.07 for the iron meso complex and 0.99 ± 0.01 for the iron deutero ester.

The chromous solutions were prepared by zinc amalgam reductions of chromium(III) and analyzed spectrophotometrically by the permanganate method.[16] The kinetics were followed on a Durrum-Gibson stopped-flow apparatus using Hamilton gastight syringes to handle the air-sensitive, N_2 deaerated solutions. At pH 1, reoxidation by molecular oxygen of the chromium(II) reduced ferric porphyrins produced a mixture of the initial ferric porphyrin and the diprotonated porphyrin diacid, due to acid solvolysis of the iron(II) porphyrin form.

With the MPDME and DPDME iron(III) complexes, no evidence for ring reduction by Cr(II), as previously noted[6] in the Cr^{II}/M^{III}-tetrakis(4-*N*-methylpyridyl)porphyrin reactions, was found. In line
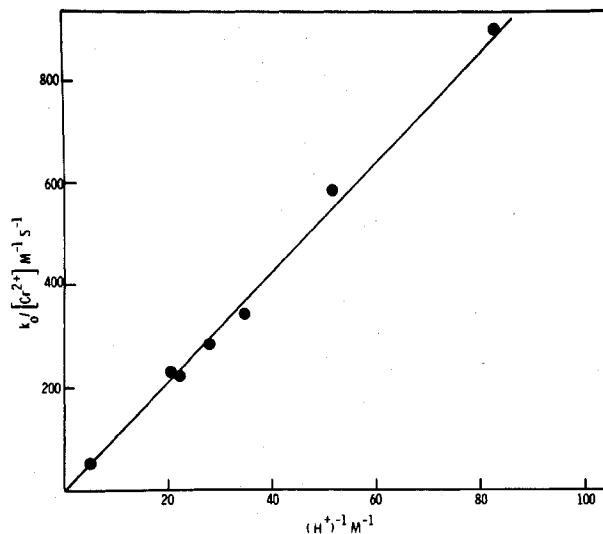

Figure 1. Plot of $k_{obsd}/(Cr^{2+})$ vs. $(H^+)^{-1}$ for the reaction of chromium(II) with iron(III) deuteroporphyrin dimethyl ester in 2% Triton X-100, 25 °C, $\mu = 0.5$ ($NaClO_4/HClO_4$).

with this observation, polarographic studies[9] in DMF/0.1 M *n*-Pr$_4$NClO$_4$ indicate that the free base form of tetrakis(4-*N*-methylpyridyl)porphyrin is reduced more easily ($E_{1/2} = -1.02$ V vs. Ag|Ag$^+$ (0.1 M)) than either the corresponding H_2MPDME (-1.82 V) or H_2DPDME (-1.76 V).
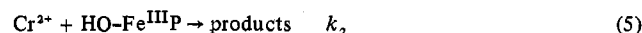
Results

The kinetics of the reduction of the iron(III) porphyrins by chromium(II)

$$Fe^{III}P + Cr^{2+} \rightarrow Fe^{II}P + Cr^{3+} \qquad (2)$$

were studied at 25 °C, $\mu = 0.5$ ($NaClO_4/HClO_4$) in 2% Triton X-100 between pH 0.2 and 2. Under pseudo-first-order conditions with at least 100-fold excess of Cr^{2+} to porphyrin, the reactions were first order in porphyrin over at least 2.5 half-lives. The reactions at constant pH were first order in chromium(II). The specific rate constant ($k_{obsd}/(Cr(II))$) increased with an increase in pH. Figure 1 shows a linear plot of the specific rate constant vs. $(H^+)^{-1}$ for $Fe^{III}DPDME$. The observed rate law is of the form $k_{obsd} = k(Cr(II))(H^+)^{-1}$. For $Fe^{III}DPDME$, $k = 11.0 \pm 0.3$ s^{-1}, and for $Fe^{III}MPDME$, $k = 1.6 \pm 0.2$ s^{-1}.

One overall mechanism for this reaction might be

$$H_2O\text{-}Fe^{III}P = HO\text{-}Fe^{III}P + H^+ \qquad K_1 \qquad (3)$$

$$Cr^{2+} + H_2O\text{-}Fe^{III}P \rightarrow products \qquad k_1 \qquad (4)$$

$$Cr^{2+} + HO\text{-}Fe^{III}P \rightarrow products \qquad k_2 \qquad (5)$$

The derived rate law would be

$$[k_{obsd}/(Cr(II))][1 + K_1/(H^+)] = k_1 + k_2K_1(H^+)^{-1} \qquad (6)$$

If $k_1 = 0$ and, under our conditions, $[1 + K_1/(H^+)] = 1$, then our calculated rate constant, k, would equal k_2K_1. For $Fe^{III}DPDME$, $k_2 = 5.5 \times 10^5$ M^{-1} s^{-1} and for $Fe^{III}MPDME$, $k_2 = 1.7 \times 10^5$ M^{-1} s^{-1}.

Discussion

In terms of proton affinity (pK_3 for the monocation/free base equilibria), H_2MPDME ($pK_3 = 5.9$) is more basic[17] than H_2DPDME (5.5). It is thus not unexpected that H_2O-$Fe^{III}MPDME$ ($pK_1 = 5$) is a weaker acid (more iron(II) porphyrin character) than the corresponding iron deuteroporphyrin (4.7). The more basic $Fe^{III}MPDME$ is reduced the slowest by chromium(II), and similar results have been found for the dithionite[5] and tin(II)[9] reductions of manganese(III) and cobalt(III) porphyrins.

Table I. Iron(III) and Cobalt(III) Porphyrin Reduction
Rates by Chromium(II)

Porphyrin[a,b]	k_1, $M^{-1} s^{-1}$	k_2, $M^{-1} s^{-1}$	k, s^{-1}	pK_1
Fe^{III}DPDME	0	5.5×10^5	11.0	4.7
Fe^{III}MPDME	0	1.7×10^5	1.6	5.0
Fe^{III}TPyP[c]	270	4×10^5	8.0	4.7[e]
Co^{III}TPyP[d]	49	3.2×10^5	0.4	5.9[f]
Co^{III}TMPyP[c]	16	13×10^5	1.6	5.9[f]
Co^{III}TPPS$_4$[d]	0	24×10^5	4.9	5.7[g]
Co^{III}TPPC$_4$[d]	0	753×10^5	3.0	7.4[h]

[a] Rate = $[k_1(M^{III}P) + k_2(HO-M^{III}P)](Cr(II))$, $k = k_2K_1$. [b] Key: DPDME and MPDME, deutero- and mesoporphyrin IX dimethyl esters; TPyP, tetrakis(4-pyridyl)porphine; TMPyP, tetrakis(4-*N*-methylpyridyl)porphine; TPPS$_4$, tetrakis(4-sulfonatophenyl)porphine; TPPC$_4$, tetrakis(4-carboxyphenyl)porphine. [c] Reference 6. [d] Reference 3. [e] While this pK_1 is for Fe^{III}TMPyP, it is assumed to be similar to that of Fe^{III}TPyP, which is insoluble above pH 4. [f] Reference 22. [g] Reference 18. [h] Reference 19.

Our postulated mechanism assumes that these $Cr^{2+}/Fe^{III}P$ reactions take place through the hydrolyzed $HO-Fe^{III}P$ form. Studies on the Cr^{2+} reductions of the synthetic water soluble tetrakis(4-carboxyphenyl)porphine- and tetrakis(4-sulfonatophenyl)porphinecobalt(III) complexes are also found to proceed exclusively by the inverse (H^+) pathway.[3] Although the species $HO-Co^{III}P$ was present,[18,19] the inverse hydrogen ion pathway was ascribed[3] to deprotonation of sulfonic acid and carboxylic acid functional groups present in the para positions of these metalloporphyrins. Reduction of the cobalt(III) center was assumed to proceed via an inner-sphere mechanism with a demonstrated incorporation of chromium(III) at the remote functional groups and electron transfer through the porphyrin ring.[3,4] The iron porphyrin esters that we have studied are without peripheral substituents capable of ionization, and since $CrOH^+$ is not generally invoked as a reactant, $HO-Fe^{III}P$ is our suggested oxidant.

In the $Cr^{2+}/[(NH_3)_5CoOH_2]^{3+}$ system, it has been demonstrated[20] that $[(NH_3)_5CoOH]^{2+}$ is the sole reactant. One explanation was that $-OH$ was a better bridging group with Cr^{2+} than $-OH_2$ and that an inner-sphere pathway was involved. A similar mechanism could be followed in the present case, with a $Cr(OH)FeP$ bridged intermediate. If this hydroxy-bridged species is the activated complex in our reaction, and since $H_2O-Fe^{III}P$ is unreactive, the implication is that electron transfer with these natural porphyrin derivatives does not occur via a remote attack at the porphyrin edge with Cr^{2+}, as has been suggested[11] for certain pathways with oxidized cytochrome *c*.

Preliminary results[23] indicate that the rate law for SCN^- addition to the water-soluble cobalt(III) complexes of TPPS$_4$ and TMPyP is the same in the presence and absence of the neutral detergent Triton X-100 (2% solution). In addition, the anation rate constants and equilibrium constants increased by only a factor of 2 when going from water to the neutral detergent media. Thus, the indication is that this detergent does not strongly alter porphyrin reactivity parameters.

Table I shows results for several $Cr^{2+}/iron(III)$ or -cobalt(III) porphyrin reductions. The rates are factored such that the inverse hydrogen ion dependence is ascribed to $HO-M^{III}P$ as the reactant. With the exception of the cobalt(III) tetrakis(4-carboxyphenyl)porphyrin, the rates by the assumed k_2 pathway are surprisingly similar to one another, irrespective of the porphyrin type or the coordinated metal ion. Since the reported pK_1 values show some apparent inconsistencies, similar conclusions are reached by consideration of k ($=k_2K_1$).

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Strength of Metal–Metal Interactions in Some Substituted Dimetal Carbonyls

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The strengths of metal–metal bonds in dinuclear metal carbonyls can be defined and inferred in a number of ways. The length of the Mn–Mn bond in $Mn_2(CO)_{10}$ was originally thought to imply that the bond was weak[1a] and the lengths of metal–metal bonds have recently been used to provide estimates of metal–metal bond orders and strengths.[1b] Force constants for metal–metal stretching vibrations have also been used to provide qualitative estimates of relative bond strengths.[2] Thermochemical[3] and mass spectrometric[4] measurements can, in principle, provide numerical estimates of metal–metal bond strengths. Not many values have been obtained in these ways and those that have suffer, in practice, from imprecision,[3] dependence on arbitrary assumptions,[4] or ambiguities of definition.[4,5] A substantial number of values of activation enthalpies, ΔH_{hf}^*, have recently been assigned to homolytic fission of metal–metal bonds in the complexes $M_2(CO)_{10-n}L_n$ (M_2 = Mn_2, MnRe, Tc_2, Re_2; n = 1 or 2; L = P- or As-donor ligand).[6] These are the energies needed to stretch the bonds to the breaking point and they provide a very useful quantitative measure of the metal–metal bond strengths and of the dependence of the strengths on the nature of M and L. Thus, for example, a pronounced steric effect is observed in substituted dimanganese complexes.[6]

A very readily made measurement that is related quantitatively to the strength of these metal–metal bonds has been demonstrated by Gray et al.[7] The band at 343 nm in the electronic spectrum of $Mn_2(CO)_{10}$ was assigned to the $\sigma \rightarrow \sigma^*$ transition involving orbitals along the metal–metal bond axis. Corresponding bands were assigned by analogy to the same transitions in several closely related complexes. The

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