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Kinetics and Mechanism of the Reduction of Manganese Porphyrins: Reaction at the Periphery of the Porphyrin Ring

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The reduction of [tetrakis(*N*-methyl-4-pyridinium)porphinato]manganese(III) and [tetrakis(4-carboxyphenyl)-porphinato]manganese(III), Mn^{III}TMPyP and Mn^{III}TCPP, by cobalt(II) sepulchrate and sodium dithionite has been studied. The reduction of MnTMPyP by both reducing agents is strongly dependent on the ionic strength of the medium, and the reduction with Co(sep)$^{2+}$ is also catalyzed by chloride ion. The kinetic data are consistent with attack of reducing agent at the periphery of the porphyrin ring. For MnTCPP, the reduction by Co(sep)$^{2+}$ is biphasic, indicating two parallel reaction pathways—attack of Co(sep)$^{2+}$ at the periphery of the ring and at the axial waters. The data for the reaction of MnTCPP with dithionite are consistent with rate-determining formation of a radical anion followed by rapid intramolecular reduction of manganese(III) to manganese(II).

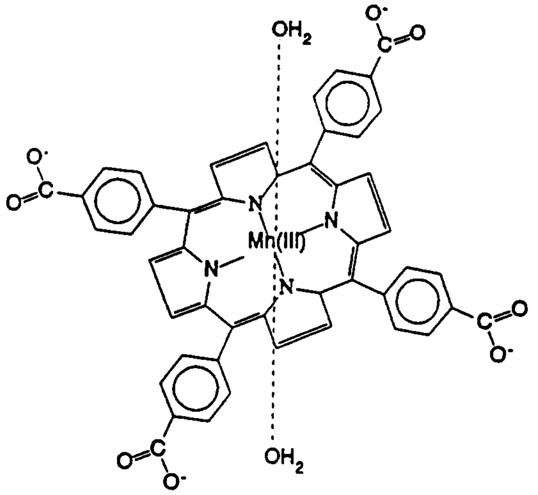
Introduction

Bimolecular electron-transfer reactions involving metalloporphyrins containing iron, cobalt, manganese, and other metals with both oxidizing and reducing agents have been well studied.[1-8] The redox agent can react with the metalloporphyrin in the vicinity of the axial water molecules or at the periphery of the porphyrin ring. The distinction between these two possible pathways is often difficult to determine especially for outer-sphere reactions. For the chromium(II) reduction of [tetrakis(*p*-sulfonatophenyl)-porphinato]cobalt(III) and [tetrakis(*N*-methyl-4-pyridiniumyl)-porphinato]cobalt(III), the kinetic data strongly imply reaction at the axial sites.[5,10] For the reduction of a series of manganese(III) porphyrins by dithionite, Duncan et al. favored a peripheral pathway.[7]

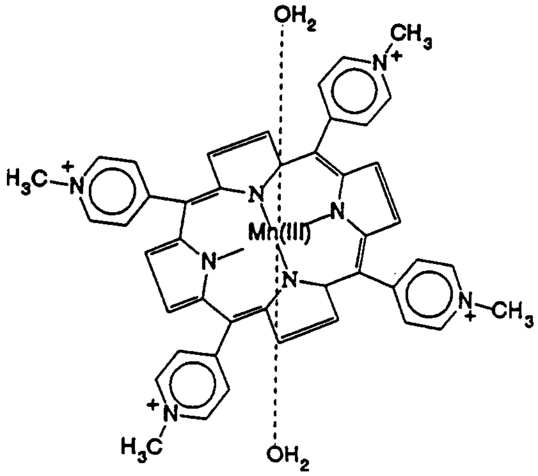
In an effort to provide evidence for electron transfer via the periphery of a porphyrin ring, we have studied the reduction of the manganese(III) porphyrins, MnTCPP and MnTMPyP, by dithionite and Co(sep)$^{2+}$. The manganese porphyrins are especially well suited for this investigation as they are water soluble over a wide pH range and remain monomeric at the concentrations used in this study. Also, it is well established that manganese porphyrins possess very weak axial bonds.[8,11,12]

Experimental Section

Materials. The complexes tetrasodium manganese(III) mesotetrakis-(4-(carboxylato)phenyl)porphinate acetate dihydrate (MnTCPP) and manganese(III) *meso*-tetrakis(*N*-methyl-4-pyridniumyl)porphinate pentaperchlorate dihydrate (MnTMPyP) were synthesized from *meso*-tetrakis(4-carboxyphenyl)porphine and *meso*-tetrakis(*N*-methyl-4-pyridiniumyl)porphine tetraiodide (Strem Chemicals) and manganese(II) acetate (Aldrich Chemical Co.) by published methods.[13] The complexes had satisfactory elemental analyses and UV–visible spectra.



MnTCPP



MnTMPyP

Manganese porphyrin solutions were stored in the dark and prepared by dilution from stock solution into buffer solutions.

Buffer solutions were prepared from 2-morpholinoethanesulfonic acid (MES) pK_a 6.1, 3-(tris(hydroxymethyl)methylamino)propanesulfonic acid (TAPS), pK_a 8.4, and 2-(cyclohexylamino)ethanesulfonic acid

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(CHES), pK_a 9.3 (Sigma Chemical Co.) and adjusted to the desired pH using sodium hydroxide and perchloric acid.

Solutions of cobalt(II) sepulchrate, Co(sep)$^{2+}$, were obtained by reduction of a stock solution of [Co(sep)](ClO$_4$)$_3$ over amalgamated zinc[14] in the appropriate buffer. The required amount of this solution was then transferred by syringe to a volumetric flask containing a solution of degassed buffer and LiClO$_4$.

Sodium dithionite was purchased from Fluka Chemie. The percent composition of $Na_2S_2O_4$ was determined spectrophotometrically by reduction of Fe(CN)$_6^{3-}$ (ϵ = 1026 M^{-1} cm^{-1} at 420 nm)[3] and found to be 80% pure. The concentrations of dithionite used in this work have been adjusted accordingly. Solutions were prepared by dissolving weighed quantities of $Na_2S_2O_4$ in degassed buffer/LiClO$_4$ solutions.

All solutions were made with distilled, deionized water obtained using a Millipore system. Solutions were deaerated using vanadium-scrubbed argon and kept free from oxygen using standard syringe techniques.

Physical Measurements. Electronic spectra were recorded with an HP8452A diode-array spectrophotometer.

Cyclic voltammetry measurements were carried out under an atmosphere of argon using a conventional three-electrode cell. The working electrode was highly oriented pyrolytic graphite (HOPG) having a circular area of 0.495 cm^2. Before each experiment, the HOPG electrode surface area was cleaned by removing several layers of the surface with a transparent adhesive tape. An SCE and a large platinum plate were used as reference and counter electrodes, respectively.

Stoichiometric Studies. The stoichiometries of the MnTCPP and MnTMPyP reactions with dithionite and Co(sep)$^{2+}$, respectively, were determined spectrophotometrically over the wavelength range 500–650 nm. Manganese porphyrin solutions (1.5 × 10^{-4} M) were titrated by adding known concentrations of reducing agent.

Kinetic Measurements. The reactions were followed at 25 °C using a Dionex stopped-flow spectrophotometer interfaced with an Olis kinetic data collection and fitting computer system. All reactions were carried out in buffered solutions maintained at a fixed ionic strength. The reactions were carried out under pseudo-first-order conditions, with at least 10-fold excess of reductant over manganese porphyrinate. The reductions of MnTCPP and MnTMPyP by Co(sep)$^{2+}$ were monitored at 390 and 378 nm, respectively. For the reduction of MnTCPP and MnTMPyP by dithionite, the wavelengths were 390 and 398 nm, respectively.

Results and Discussion

In aqueous solution the structures of the Mn(III) porphyrins are dependent on the pH. Harriman and Porter[13] have shown that there are two distinct pK_a's associated with deprotonation of the axial water molecules (ignoring the water solubilizing groups):

$$\mathrm{MnP(OH_2)_2^+} \rightleftharpoons \mathrm{MnP(OH_2)(OH)} + \mathrm{H^+} \quad \mathrm{p}K_{a1}$$

$$\mathrm{MnP(OH_2)(OH)} \rightleftharpoons \mathrm{MnP(OH)_2^-} + \mathrm{H^+} \quad \mathrm{p}K_{a2}$$

For Mn^{III}TMPyP and Mn^{III}TCPP spectrophotometric determination gave pK_{a1} and pK_{a2} as 8.0 and 10.6 and as 8.4 and 11.2, respectively. These authors also determined the overall charges on the complexes (including the water solubilizing group) by electrophoresis. These results indicated that at pH <7.5 two water molecules are coordinated to Mn(III). We also attempted to determine the pK_a's spectrophotometrically but were only able to observe spectral changes which corresponded to pK_{a2} above. For Mn^{III}TMPyP we determined a value of 10.3. Since the majority of our measurements were carried out at pH 6.1, the structure of the porphyrins in aqueous solution is Mn^{III}P(OH$_2$)$_2$ with two axially coordinated water molecules. It should also be noted that the half-wave potentials for Mn(III) porphyrins are independent of the pH in the range 5–11.[15] We also found that the reduction of Mn^{III}TMPyP and Mn^{III}TCPP by dithionite does not depend on the pH in the range 6–10. In the previous discussion we have assumed that the Mn porphyrins are monomeric in solution. Under the experimental conditions used, Beer's law plots were linear for manganese porphyrin concentrations from 1 μM to 1 × 10^{-4} M, indicating an absence of aggregation.[16] Also, it was recently shown by nuclear magnetic resonance dispersion that the porphyrins used in this study are not aggregated in aqueous solution.[17]

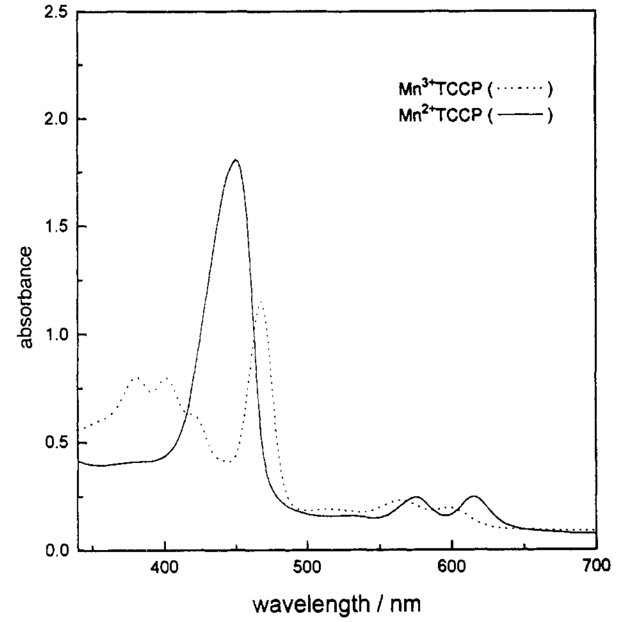

Figure 1. Spectral changes for the reduction of Mn^{III}TCCP with Co(sep)$^{2+}$. [Mn^{III}TCCP] = 1.5 × 10^{-5} M; [Co(sep)$^{2+}$] = 4.0 × 10^{-4} M.

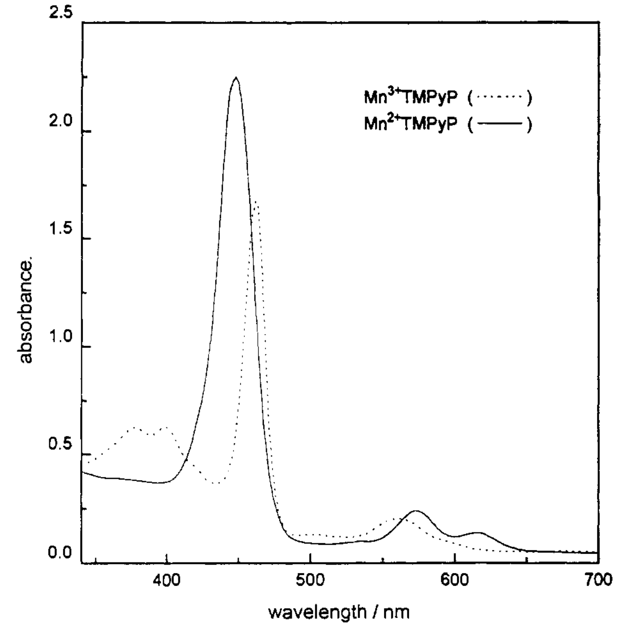

Figure 2. Spectral changes for the reduction of Mn^{III}TMPyP with Co(sep)$^{2+}$. [Mn^{III}TMPyP] = 1.0 × 10^{-5} M; [Co(sep)$^{2+}$] = 4.0 × 10^{-4} M.

The reductions of the manganese porphyrins by cobalt(II) sepulchrate and sodium dithionite were studied at pH ≥6 to avoid complications due to demetalation of the porphyrins which occurs in acidic media[18]. Furthermore, the dithionite ion is rapidly hydrolyzed in acid solution.[19] At pH 6.1 addition of excess reductant (Co(sep)$^{2+}$ or $S_2O_4^{2-}$) to a solution of manganese(III) porphyrin under anaerobic conditions results in rapid reduction of the complex with quantitative formation of the manganese(II) porphyrin. If the reduced solutions are allowed to stand under anaerobic conditions, the Soret band disappears irreversibly in

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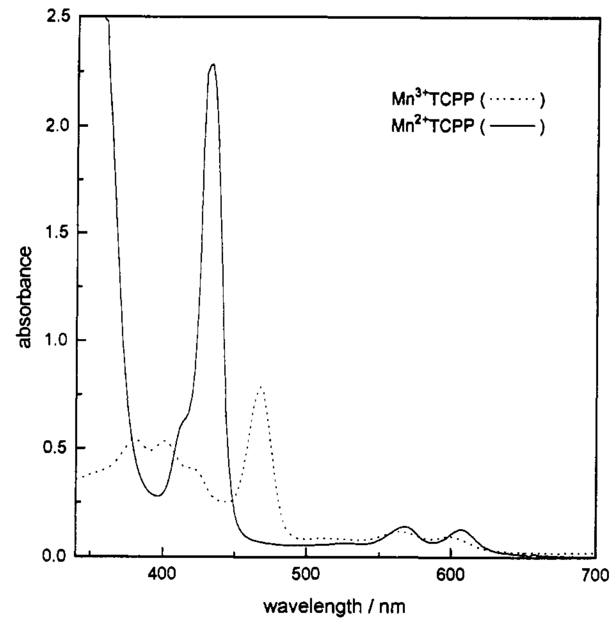

Figure 3. Spectral changes for the reduction of $Mn^{III}TCPP$ with $S_2O_4^{2-}$. $[Mn^{III}TCPP] = 1.0 \times 10^{-5}$ M; $[S_2O_4^{2-}] = 5.0 \times 10^{-4}$ M.

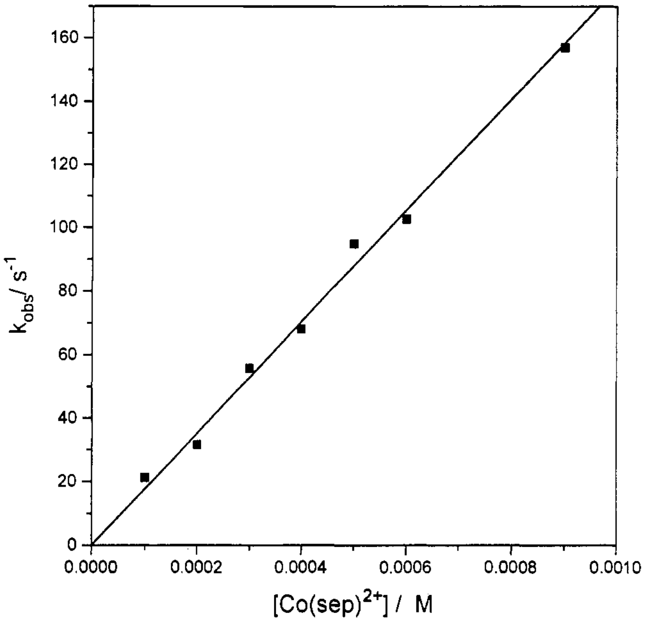

Figure 4. Variation of k_{obs} with $[Co(sep)^{2+}]$ for the reduction of $Mn^{III}TMPyP$ by $Co(sep)^{2+}$ in 0.05 M MES at pH = 6.14, T = 25 °C, and I = 0.1 M ($LiClO_4$).

approximately 1 h when 5.0×10^{-4} M $S_2O_4^{2-}$ is used and much more slowly for 5.0×10^{-4} M $Co(sep)^{2+}$. If oxygen is bubbled through the product solutions immediately after reduction, 100% regeneration of manganese(III) porphyrin is observed. In contrast, the Soret peak of the free porphyrins, TMPyP (420 nm) and TCPP (414 nm), is lost irreversibly in less than 2 min under the same conditions. Presumably, the loss of the Soret band is associated with reduction of the porphyrin ring in both cases. Typical spectral changes for these reactions are shown in Figures 1 and 2 for $Co(sep)^{2+}$ as reductant. A blue shift of the Soret band is observed upon reduction,[20] from 462 to 448 nm for MnTMPyP and from 468 to 448 nm for MnTCPP. With dithionite as reductant, the same behavior is observed with MnTMPyP. However, addition of dithionite to $Mn^{III}TCPP$ results in a larger blue shift of the Soret peak (from 468 to 432 nm) when compared to that observed for $Co(sep)^{2+}$ and an anomalous increase in the intensity of this band (See Figure 3). Pasternack and co-workers[3,10] have also observed an unusual blue shift for the reduction of $Co^{III}TMPyP$ by dithionite when compared to the reduction by chromium(II) and $Ru(NH_3)_6^{2+}$.

In the present study, addition of $Co(sep)^{2+}$ to a solution of $Mn^{II}TCPP$ produced with $S_2O_4^{2-}$ gave no change in the Soret band at 432 nm. However when $Mn^{III}TCPP$ was first reduced with $Co(sep)^{2+}$ (Soret band at 448 nm) and this solution then treated with dithionite, the Soret band shifted further to 432 nm. We have also found that addition of sodium sulfite or sodium sulfate to the $Co(sep)^{2+}$-reduced manganese porphyrin also causes the same shift (448 to 432 nm) and increase in intensity of the Soret band. Thus we attribute the "anomalous" shift in this study to coordination of SO_3^{2-} or SO_4^{2-} (from the dithionite solutions) to the manganese(II)porphyrin. A similar effect could also be responsible for the unusual shift reported for the dithionite reduction of $Co^{III}TMPyP$.[3,10] In nonaqueous media, the spectra of five-coordinate Mn(II) porphyrins show Soret band maxima at ~444 nm for anionic axial ligands and maxima at ~437 nm for neutral ligands.[21,22] In this study, the Soret maximum for $Mn^{II}TCPP$ at 448 nm results from axial coordination of water whereas the maximum at 432 nm is attributed to coordination of the dianionic ligands.

The stoichiometry of the reaction between $Co(sep)^{2+}$ and $Mn^{III}TCPP$ and $Mn^{III}TMPyP$ was determined to be 1 mol of reducing agent/mol of Mn(III) porphyrin. For dithionite the stoichiometry was 0.5 mol of dithionite/mol of porphyrin.

The kinetic studies were carried out under pseudo-first-order conditions with the reductant in at least a 10-fold excess. The observed rates were independent of the wavelengths selected to monitor the reactions. All reactions gave excellent single-exponential traces except for the reaction of $Mn^{III}TCPP$ with $Co(sep)^{2+}$ which was biphasic. The kinetic data for the $Co(sep)^{2+}$ reduction of $Mn^{III}TMPyP$ at pH 6.14 are given in Figure 4. The data conform to the simple rate law

$$k_{obs} = k_2[Co(sep)^{2+}]$$

where k_2 is equal to the slope of the line in Figure 4. At 25 °C and I = 0.1 M ($LiClO_4$), $k_2 = (1.8 \pm 0.1) \times 10^5$ M^{-1} s^{-1}. The effect of ionic strength on this reaction was also investigated, and the data are given in Table 1. The very strong increase in observed rate with an increase in ionic strength is indicative of a reaction between two positively charged reactants. The reaction was also found to be catalyzed by chloride ion (Figure 5) with the observed rate changing by more than a factor of 10 by the addition of 0.06 M LiCl.

The reduction of $Mn^{III}TCPP$ by $Co(sep)^{2+}$ at pH 6.14 was biphasic, but both reactions apparently conform to the simple rate law above (see Figure 6). The reactions were difficult to separate, and the data are not as precise as for the other reactions. At 25 °C and I = 0.1 M ($LiClO_4$), the k_2 values were $(3.6 \pm 0.3) \times 10^4$ and $(2.5 \pm 0.3) \times 10^4$ M^{-1} s^{-1}, respectively. For this reaction, a change in ionic strength or addition of chloride ion did not affect the observed rate constant.

The kinetic data for the reduction of $Mn^{III}TCPP$ and $Mn^{III}TMPyP$ by dithionite are consistent with eqs 1–3, in which parallel

$$S_2O_4^{2-} \rightleftharpoons 2SO_2^- \qquad K_1 = k_1/k_{-1}, \text{ rapid} \tag{1}$$

$$SO_2^- + Mn^{III}P + H_2O \rightarrow Mn^{II}P + HSO_3^- + H^+ \quad k_2 \tag{2}$$

$$S_2O_4^{2-} + Mn^{III}P \rightarrow Mn^{II}P + S_2O_4^- \quad k_3 \tag{3}$$

reactions with SO_2^- and $S_2O_4^{2-}$ are rate-determining. The reactions are first order in $Mn^{III}P$ and half order and first order in $[S_2O_4^{2-}]$ for (2) and (3). The reactions gave reasonable pseudo-

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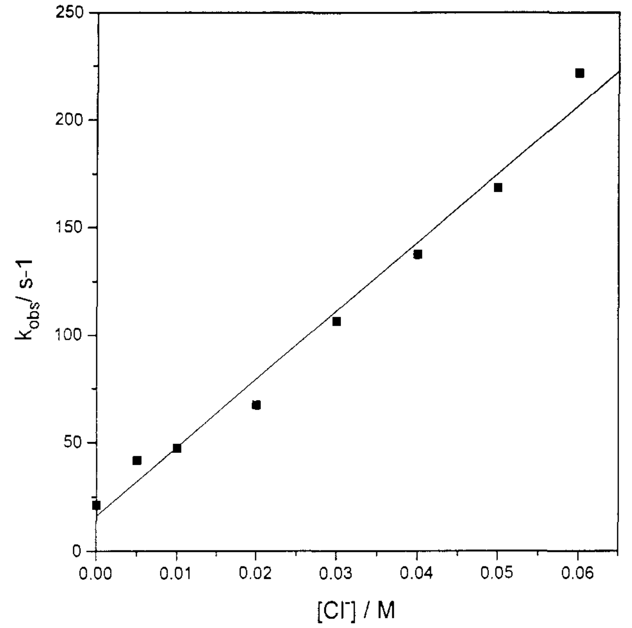

Figure 5. Variation of k_{obs} with added lithium chloride for the reduction of Mn^{III}TMPyP by Co(sep)$^{2+}$ in 0.05 M MES at pH = 6.14, T = 25 °C, [Co(sep)$^{2+}$] = 0.0004 M, and I = 0.1 M (LiClO$_4$).

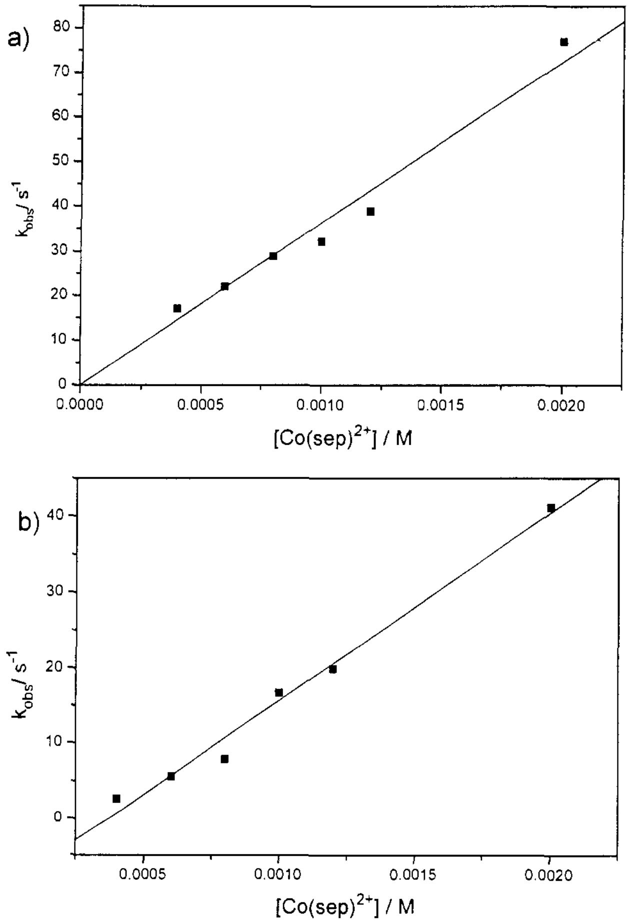

Figure 6. Variation of k_{obs} with [Co(sep)$^{2+}$] for the reduction of Mn^{III}-TCPP for (a) faster reaction and (b) slower reaction at 25 °C in 0.05 M MES at pH = 6.14 and I = 0.1 M (LiClO$_4$).

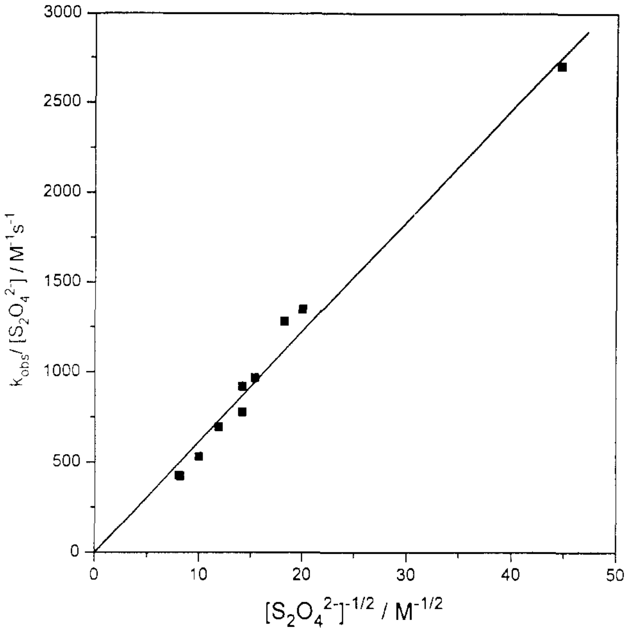

Figure 7. Plot of k_{obs}/[$S_2O_4^{2-}$] vs [$S_2O_4^{2-}$]$^{-1/2}$ for the reduction of Mn^{III}-TCPP by dithionite at 25 °C in 0.05 M MES at pH = 6.14, I = 0.1 M (LiClO$_4$), and [Mn^{III}TCPP] = 1 × 10^{-5} M.

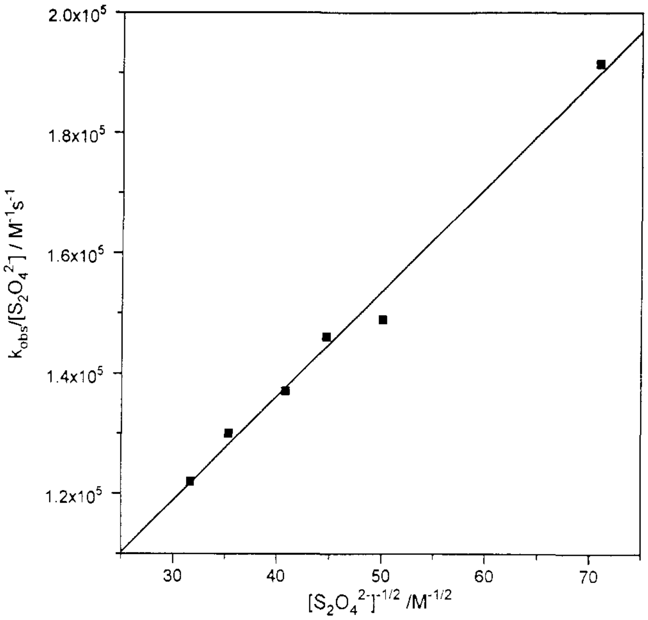

Figure 8. Plot of k_{obs}/[$S_2O_4^{2-}$] vs [$S_2O_4^{2-}$]$^{-1/2}$ for the reduction of Mn^{III}-TMPyP by dithionite at 25 °C in 0.05 M MES at pH = 6.14, I = 0.1 M (LiClO$_4$), and [Mn^{III}TMPyP] = 1 × 10^{-5} M.

first-order kinetic traces and the rate law can be expressed as (4).

$$k_{obs} = k_2K_1^{1/2}[S_2O_4^{2-}]^{1/2} + k_3[S_2O_4^{2-}] \qquad (4)$$

Equation 4 can be rearranged to give (5). Thus a plot of k_{obs}/[$S_2O_4^{2-}$] vs [$S_2O_4^{2-}$]$^{-1/2}$ should be linear with slope equal to $k_2K^{1/2}$ and intercept k_3. The plots are shown in Figures 7 and 8. Values

$$k_{obs}/[S_2O_4^{2-}] = k_2K_1^{1/2}[S_2O_4^{2-}]^{-1/2} + k_3 \qquad (5)$$

of k_2 were calculated using K_1 = 1.4 × 10^{-9} M[23] and are (4.6 ± 0.3) × 10^7 M^{-1} s^{-1} for MnTMPyP and (1.6 ± 0.1) × 10^6 M^{-1} s^{-1} for MnTCPP. For the latter reaction the intercept was zero within experimental error, and as expected, the simpler plot of k_{obs} versus [$S_2O_4^{2-}$]$^{1/2}$ was also linear. The value of k_3 for MnTMPyP was (6.7 ± 0.4) × 10^4 M^{-1} s^{-1}. Our values of k_2 are in good agreement with those obtained by Duncan et al.[7] (2.3 × 10^7 M^{-1} s^{-1} for MnTMPyP and 4.0 × 10^6 M^{-1} s^{-1} for MnTCCP) although these authors apparently did not observe a k_3 term for MnTMPyP. The reactions were also investigated as a function of ionic strength, and the data are given in Table 2. For Mn^{III}-TMPyP, the strong inverse dependence of k_{obs} on ionic strength indicates a reaction between a positively charged and a negatively charged reactant. For Mn^{III}TCPP, k_{obs} increases slightly for an

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Table 1. Effect of Ionic Strength on the Reduction of Mn^{III}TMPyP by Co(sep)$^{2+}$ [a,b]

I/M[c]	k_{obs}/s^{-1}	I/M[c]	k_{obs}/s^{-1}
0.10	41 ± 3	0.40	163 ± 3
0.20	83 ± 3	0.50	199 ± 5
0.30	126 + 3		

[a] pH = 6.14, [MnP] = 1.0 × 10^{-5} M, [Co(sep)$^{2+}$] = 2.2 × 10^{-4} M, T = 25 °C. [b] A plot of log k_{obs} vs $I^{1/2}$ is linear with a slope of +1.1. [c] LiClO$_4$

Table 2. Effect of Ionic Strength on the Reduction of Mn^{III}TMPyP and Mn^{III}TCPP by Dithionite[a]

Mn^{III}TMPyP[b]		Mn^{III}TCPP[c]	
I/M[d]	k_{obs}/s^{-1}	I/M[d]	k_{obsd}/s^{-1}
0.10	430 ± 11	0.10	3.9 ± 0.1
0.20	291 ± 5	0.20	4.4 ± 0.1
0.50	154 ± 3	0.40	4.9 ± 0.1
0.80	104 ± 3	0.60	5.2 ± 0.1
1.00	73 ± 3		

[a] pH = 6.14, [MnP] = 1.0 × 10^{-5} M, T = 25 °C. [b] [S$_2$O$_4^{2-}$] = 5.0 × 10^{-4} M. A plot of log k_{obs} vs $I^{1/2}$ is linear with a slope of −1.1. [c] [S$_2$O$_4^{2-}$] = 5.0 × 10^{-3} M. A plot of log k_{obs} vs $I^{1/2}$ is linear with a slope of +0.3. [d] LiClO$_4$.

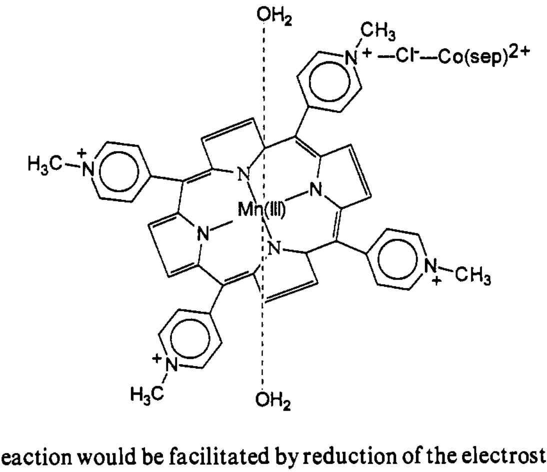
Table 3. Second-Order Rate Constants (M^{-1} s^{-1}) for the Reduction of Manganese Porphyrins by Co(sep)$^{2+}$, SO$_2^-$, and S$_2$O$_4^{2-}$ at 25 °C, pH = 6.14, 0.05 M MES, and I = 0.1 M (LiClO$_4$)

	Co(sep)$^{2+}$	SO$_2^-$	S$_2$O$_4^{2-}$
MnTMPyP	1.8 × 10^5	4.6 × 10^7 [a]	6.7 × 10^4
MnTCPP	3.6 × 10^4 2.5 × 10^4	1.6 × 10^6	

[a] Reactions carried out at I = 1.0 M (LiClO$_4$).

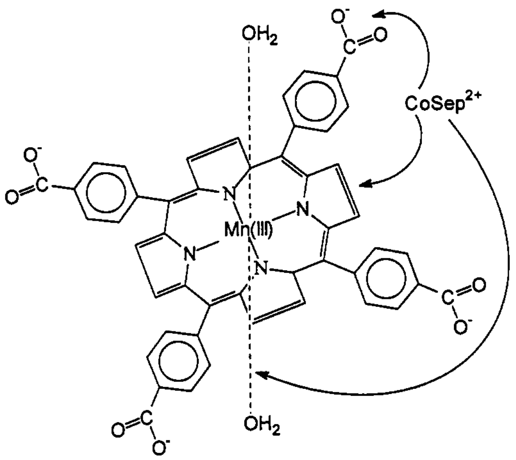
increase in ionic strength, implying reaction between two negatively charged species. This small dependence on ionic strength implies that the negative charge is delocalized in the porphyrin ring system if in fact the reductant reacts at the periphery of the ring as argued later. Both of these reactions showed no dependence on added chloride and were also independent of pH in the range pH 6–10. The rate constants for the reactions studied are collected in Table 3.

On the basis of the known properties of Co(sep)$^{2+}$ as a reductant, the reactions of Co(sep)$^{2+}$ with both Mn^{III}TMPyP and Mn^{III}TCPP are assumed to be outer-sphere. For Mn^{III}TMPyP the slope of a plot of log k_{obs} vs $I^{1/2}$ is +1.1, indicating that Co(sep)$^{2+}$ attacks the oxidant at the periphery of the porphyrin ring in the vicinity of the positive charge on the methylpyridine substituent. Further evidence for this pathway comes from the chloride ion-catalyzed reaction. It is well-known that Mn(III) porphyrins show little tendency to complex with added inorganic anions.[8,11,12] In this case no changes in the spectrum of the Mn(III) porphyrins were observed for addition of large excesses (0.01–0.50 M) of LiCl. However, the reduction of Mn^{III}TMPyP by Co(sep)$^{2+}$ is catalyzed by addition of 0.010–0.060 M LiCl. This strongly suggests reaction at the periphery of the porphyrin ring near the methylpyridine substituent via an ion pair involving Mn^{III}TMPyP, Cl$^-$, and Co(sep)$^{2+}$:



The reaction would be facilitated by reduction of the electrostatic repulsion between the porphyrin and Co(sep)$^{2+}$.

In an attempt to clarify the position of the ion pair and provide further evidence for the reaction pathway shown above, we investigated the reduction of Mn^{III}TCPP (negatively-charged substituents on the periphery of the porphyrin ring) by Co(sep)$^{2+}$. The biphasic behavior observed for this reaction suggests two parallel reaction pathways, one at the periphery of the porphyrin ring and the other in the vicinity of the axial water molecules:



In this reaction there is no discernible change in either of the observed rate constants with a change in ionic strength or with added LiCl. If one of the reactions involves peripheral attack, the lack of specific charge interactions as observed for Mn^{III}TMPyP implies that the negative charge is delocalized over the porphyrin ring. The results also indicate that for Mn^{III}TMPyP the positive charges on the substituents are localized.

These reactions were also probed using the negatively-charged reductant sodium dithionite. For both MnTMPyP and MnTCPP the active form of the reducing agent is the SO$_2^-$ radical. Since it is unlikely that SO$_2^-$ bonds directly to Mn(III) and since we have no evidence for adduct formation between SO$_2^-$ and a pyrrole ring, it is assumed that the reduction reaction is outer-sphere. For the reduction of Mn^{III}TMPyP the large negative salt effect implies that SO$_2^-$ attacks near the localized positive charge on the substituents. The slope of a plot of log k_{obs} vs $I^{1/2}$ gives the charge product of the "reactants" as −1.1. In this case no effect was observed due to added chloride as expected. For Mn^{III}TCPP there was a small positive salt effect (charge product +0.3), indicating negatively charged reactants. This supports the assertion above that the negative charge is delocalized in the porphyrin ring system. Duncan et al.[7] arrived at a similar conclusion by comparing relative rates for manganese porphyrins with different charged substituents. Thus our kinetic data are consistent with peripheral attack in these systems where formation of the Mn(III) porphyrin radical anion is rate-determining. The radical then rapidly reduces Mn(III) to Mn(II). Duncan, Harriman, and Porter[7] have also proposed a detailed mechanism for the reduction of water-soluble Mn(III) porphyrins by dithionite involving the initial production of a Mn(III) porphyrin π-radical anion which then undergoes electron redistribution to form the Mn(II) porphyrin. Since no intermediate absorption spectrum was observed, the electron rearrangement was assumed to be fast and the rate-determining step production of the radical anion.

In summary, this study has provided evidence for reaction via the periphery of the porphyrin ring in the outer-sphere reduction of Mn(III) porphyrins by Co(sep)$^{2+}$ and dithionite.