constants from these potentiometric data.

In most cases the values of the oxygenation constants calculated by varying the value of K_{A_2} were determined to precisions within the limits of experimental error, so that the introduction of a second adustable parameter, K_{A_1}, cannot be justified. The small average deviations observed in most systems is taken as strong evidence that the first amide dissociation can be neglected without introducing any appreciable error. However, in the glycylglycine and glycyltyrosine systems, where amide dissociation does not occur until higher pH values are attained, the larger average deviations may be due to incomplete deprotonation of the first amide group.

Morris and Martin[21] have recently described a cobalt(II) promoted amide dissociation in dipeptides involving a spin-state equilibrium between high- and low-spin complexes, both of which have both amides deprotonated. They cite as primary evidence of the change to a low-spin complex a color change from pink to blue around pH 11.5 for cobalt glycylglycine solutions containing a 20-fold excess of ligand. However, our own efforts to reproduce these data result in precipitation of cobalt(II) hydroxide around pH 10.5, as indicated in Figure 2. Upon going to a 40-fold excess of glycylglycine, which prevents any precipitation of cobalt, no blue color was observed even at pH 11.5. Although the absence of a visible blue color could be the result of using more dilute solution, the fact that a 20:1 excess is not sufficient to prevent precipitation above pH 10.5 casts serious doubt upon any spectral data obtained at these conditions. For this reason we have omitted any spin-state equilibria from consideration in our calculations.

References and Notes

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Mechanisms of Reduction of Cobaltic Porphyrins with Various Reducing Agents

Everly B. Fleischer* and Stephen K. Cheung

Contribution from the Department of Chemistry, University of California, Irvine, California 92717.

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Abstract: In this paper, tetra(*p*-sulfonatophenyl)porphinatocobalt(III), tetra(*p*-carboxyphenyl)porphinatocobalt(III), and tetra(4-pyridyl)porphinatocobalt(III) were reduced with hexaaquochromium(II), hexaaquovanadium(II), and hexaammineruthenium(II). The reduction kinetics were studied with stopped-flow techniques. The rate law is: rate = k[reductant][cobaltic porphine] = $\{k_1' + (k_1^*/[H^+]) + k_2[Cl^-] + k_2'[SCN^-]\}$ [reductant][$Co^{III}P$]. For the vanadium(II) reductions, the term k_1' was of the order of 1350 $M^{-1}\,s^{-1}$ for all three of the cobaltic porphines and the mechanism was proposed to be an outer-sphere pathway. For the chromium(II) reduction of Co^{III}-TPPS, $k_1' = 0.0$, $k_1^* = 4.9\ s^{-1}$, and $k_2 = 2.9 \times 10^4\ M^{-2}\,s^{-1}$ and $k_2' = 1.1 \times 10^6\ M^{-2}\,s^{-1}$. For the chromium(II) reduction of Co^{III}-TCPP, $k_1^* = 3\ M^{-1}\,s^{-1}$, $k_2 = 4.4 \times 10^4\ M^{-2}\,s^{-1}$, and $k_2' = 1.3 \times 10^6\ M^{-2}\,s^{-1}$. Finally, for the chromium(II) reduction of Co^{III}-TPyP, $k_1' = 49\ M^{-1}\,s^{-1}$, $k_1^* = 0.4\ s^{-1}$, $k_2 = 2.3 \times 10^3\ M^{-2}\,s^{-1}$, and $k_2' = 1.8 \times 10^5\ M^{-2}\,s^{-1}$. Since the electron-transfer reactions were always faster than the axial ligand substitution of the cobaltic porphines, the axial inner-sphere pathway was precluded. The reduction products were analyzed with cation-exchange columns. Using radioactive chromium tracer techniques, the chromium was observed to be bound to the Co^{II}-TPPS and Co^{II}-TCPP after the reductions. Since the axial ligands of cobaltic porphyrins are labile, this experimental result firmly establishes the peripheral inner-sphere pathway with attack at the para substituents. Consequently, the path of the electron transfer is via the porphyrin π cloud and not via the metalloporphyrin axial ligand positions. For the chromium(II) reduction of Co^{III}-TPyP, steric and electrostatic effects precluded the peripheral inner-sphere pathway. Finally the inverse acid term is assigned to be due to the deprotonation of the para substituents. The halide and thiocyanate catalysis is attributed to nonbridging ligand effects.

Metalloporphyrins participate in the electron-transfer steps of many essential metabolic processes. However, the metalloporphyrin electron-transfer reaction mechanism remains to be confirmed unambiguously. The aim of this paper is to systematically investigate the possible paths of electron-transfer reactions involving metalloporphyrins and to establish the mechanisms operative in these systems.[1-18] Theoretically, the electron-transfer mechanisms involving metalloporphyrins can be classified into axial inner-sphere, peripheral inner-sphere, axial outer-sphere, and peripheral outer-sphere pathways. In this paper we employ the reducing agents hexaaquochromium (II), hexaaquovanadium (II), and hexaammineruthenium(II) to probe the metalloporphyrin redox reactions.

Experimental Section

Chromium(III) Perchlorate Solutions. The chromium(III) perchlorate solutions were prepared by appropriate dilutions of a 1 M chromium(III) solution obtained by following the method of Zwickel.[19]

Dinitrogen Gas. Dinitrogen gas purchased from Air Carbonic was 99.9996% pure. Any dioxygen impurities were removed by passing the dinitrogen gas through two 500-ml chromous scrubbing towers and finally through a 0.01 N sodium hydroxide solution. Minimum lengths of tubing were used to connect the scrubbing towers to minimize the possibility of contamination by dioxygen diffusion.

Zinc Amalgam. Analytical grade mossy zinc from Mallinckrodt was washed several times with distilled water and was then allowed to stand in 1 M HCl for about 3 min. The acid was removed by repeated washing of the zinc with distilled water. Then the zinc was amalgamated with an acidic solution of saturated mercuric chloride solution (76 g of $HgCl_2$ in 1 l. of 0.1 M H_2SO_4) for 10 min. Any excess of the mercuric solution was then thoroughly removed by repeated washing of the zinc amalgam with large amounts of distilled water.

Hexaammineruthenium Chloride. The $Ru(NH_3)_6Cl_3$, containing 37.0% Ru, was purchased from Matthey Bishop Inc. and was used without further purification. The solutions of $Cr(H_2O)_6^{2+}$, $V(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$ were prepared by zinc amalgam reduction of aliquots of the corresponding chromium(III) perchlorate, vanadyl sulfate, and ruthenium(III) hexaammine stock solutions. The solutions were always deoxygenated with scrubbed dinitrogen before addition of the zinc amalgam. The solutions were freshly prepared before each kinetic run and analyzed with potassium permanganate solutions. The reducing agent determination was repeated at least three times and the results were within 4% of each other. The extinction coefficient of the permanganate solution at 545 nm of 2340 M^{-1} cm^{-1} was employed in our calculations. Radioactive chromium was ^{51}Cr purchased from ICN, Irvine, Calif., in the form of $CrCl_3$ in HCl. These solutions were diluted and were used as tracers in the product studies of the chromous reductions of the cobaltic porphyrins. The ion exchange resins employed in this study were treated according to the procedure used by Deutsch.[20]

Tetraphenylporphine. *meso*-Tetraphenylporphine was synthesized according to the procedure of Adler[21] and made chlorin free by refluxing in dimethyl sulfoxide.[22]

Sodium Tetra(*p*-sulfonatophenyl)porphine, H_2TPPS. Sodium tetra(*p*-sulfonatophenyl)porphine was prepared from H_2TPP by the reaction with concentrated sulfuric acid.[23] The purity of the H_2TPPS was demonstrated by comparison of extinction coefficients with literature values, by single spot on thin layer chromatography, and by the chemical analysis. Anal. Calcd for $Na_4TPPS\cdot 10H_2O$ [$C_{44}H_{36}O_{22}N_4S_4Na_4$]: C, 44.3; H, 3.0; N, 4.7; S, 10.7. Found: C, 44.9; H, 2.8: N, 4.0; S, 9.8. Mole ratio S/N calcd 1.0, found 1.07. Absorption spectrum of H_2TPPS in water:[24] 411 (493), 515 (17), 552 (7.1), 580 (6.3), 633 (3.3).

Tetra(*p*-carboxyphenyl)porphine, H_2TCPP. The tetra(*p*-carboxyphenyl)porphine free base was synthesized and purified by literature methods.[16] Absorption spectrum of pure H_2TCPP in pyridine: 422 (350), 517 (16.8), 552 (9.8), 591 (6.5), 649 (4.7).

Tetra(4-pyridyl)porphine, H_2TPyP. The tetra(4-pyridyl)porphine free base was prepared and purified by a literatue method.[25] Absorption spectrum of H_2TPyP in water: 518 (13.1), 553 (5.2), 585 (6.7), 638 (1.7).

Tetra(*p*-sulfanotophenyl)porphinatocobalt(III), Co^{III}-TPPS. Cobaltous acetate, 0.3 g, was added to 1.0 g of H_2TPPS in 50 ml of refluxing methanol. The product, Co^{III}-TPPS, has an absorption at 426 nm in its visible spectrum. If any of the 417-nm peak of Co^{II}-TPPS is observed, a few drops of H_2O_2 is added to oxidize the metalloporphyrin to the cobaltic state. The solvent was removed on a steam bath and the residue was dissolved in water and passed through a sodium form of a cation exchange resin. The cobaltic porphine was purified by Soxhlet extraction with methanol followed by acetone precipitation. The purified product was dried in an oven at 100 °C for 2 h. The visible absorption spectrum of the Co^{III}-TPPS is: 427 (230), 543 (15). This compares favorably with a pure analyzed Co^{III}-TPPS sample.[26,27]

Tetra(*p*-carboxyphenyl)porphinatocobalt(III). When cobaltous acetate was added to H_2TCPP in refluxing glacial acetic acid, a brown precipitaate formed immediately. This precipitate gave a typical cobaltic porphyrin spectrum when dissolved in 0.2 N NaOH. This porphyrin was purified by two reprecipitations from methanol solutions with hydrochloric acid. Finally, the Co^{III}-TCPP was recrystallized from chloroform and dried in vacuo overnight. The visible absorption spectrum of the Co^{III}-TCPP in 5% Na_2CO_3 is 430 (230), 547 (13.1), and 586 (5.8) which compares well with the literature values.[28]

Tetra(4-pyridyl)porphinatocobalt(III). The Co^{III}-TPyP was synthesized by refluxing a twofold excess of cobaltous acetate with H_2TPyP in glacial acetic acid.[25] The Co^{II}-TPyP was purified on an activated alumina column using 5% methanol–chloroform to elute the Co^{II}-TPyP after the unreacted TPyP was eluted off with pure chloroform. The Co^{II}-TPyP was oxidized to Co^{III}-TPyP with ferricyanide; the oxidant was removed with a Biorad A61-X8 anion exchange column.

Apparatus and Techniques. All the visible spectra reported in this paper were recorded on a Beckman ACTA III UV-visible spectrophotometer. A Beckman Holmium Oxide filter was used to check the wavelength accuracy of the spectrophotometer. The pH measurements were made at room temperature with a Beckman Century SS pH meter. The rates of the reactions were measured with a Durram-Gibson stopped-flow spectrophotometer. The usual 20-mm path length, with a 1 mm slit width, was used to observe the disappearance of the cobalt(III) porphines or appearance of the formation of the cobalt(II) porphines. Solutions for the kinetic runs were equilibrated in a Haake temperature regulating bath for at least 10 min before each run. Syringe techniques were employed to handle the air-sensitive solutions with carefully rinsed stainless steel needles. The ionic strength, unless otherwise stated, was maintained at 0.25 M for all runs ($NaClO_4$ + NaCl + NaSCN). The *maximum* ionic strength contribution from the cobaltic porphyrins and reducing agents is 0.01 N and was neglected in the calculation of total ionic strength. The reactions were all carried out under pseudo-first-order conditions with the reducing agent always in excess. The slopes of plots of ln ($OD_\infty - OD_t$) vs. time are linear and were extracted from the data by least-squares analysis and are equal to the k_{obsd} for each run. The plots were linear over at least 3 half-lives and in general the kinetics were very well behaved. The products of the kinetic runs were determined by observing the absorption spectra after the reducing agents were added. The rate constants were reproducible within 5% of each other and individual runs gave a correlation coefficient for the least-squares analysis of 0.99 or higher.

The radioactivities of the ^{51}Cr were measured with a Tracerlab Versamatic II scaler with a NaI well-type Gamma Counter or with a Beckman Biogamma Counter. In the former method, clean 15 × 125 mm Pyrex test tubes closed with parafilm were used as containers while in the latter counter the supplied capped 15 × 55 mm polyester containers were used.

Reduction of Co^{III}-P with Various Reducing Agents. The reduction of all the cobaltic porphyrins used in this study [Co^{III}-TPPS, Co^{III}-TCPP, and Co^{III}-TPyP] with the various reducing agents [$Cr(H_2O)_6^{2+}$, and $Ru(NH_3)_6^{2+}$][29] has a rate law

$$-\frac{d[Co^{III}\text{-}P]}{dt} = k_{obsd}[Co^{III}\text{-}P] = k[R^{II}]\,[Co^{III}\text{-}P]$$

where k stands for the slope of the plot of k_{obsd} vs. R(II) concentrations. In this study the $k_{obsd}/[Ru^{II}]$ is constant over a 6- to 20-fold variation in R(II) concentrations. Finally, the rate of the reactions depends upon the variation of experimental constraints such as pH and change in added ligand concentration such as halide and thiocyanates. In cases where a straight line is obtained in plots of k vs. [L], the reaction rate law becomes

$$-\frac{d[Co^{III}\text{-}P]}{dt} = [k_1 + k_2(L)][R^{II}][Co^{III}\text{-}P]$$

where k_1 is the y intercept and k_2 is the slope of the plot of k vs. [L]. Note k_1 can have the following form $k_1' + k_1^*/[H^+]$.

Reductions of Co^{III}-TPPS with Cr(II).[30] The dependence of the reduction of Co^{III}-TPPS with Cr(II) is given in Table I and Figure 1. The reaction was followed at both 427 nm (decrease in Co^{III}-TPPS) and 411 nm (increase in Co^{II}-TPPS). The two wavelengths yielded rates constant within 2–3% of each other.

The Co^{III}-TPPS reduction was determined as a function of pH. The pH recorded in Table II is that of the product solution collected from the exhaust of the stopped-flow apparatus. The pH above 3.5 was

Table I. Rate Measurements for the Chromous Reduction of Co^{III}-TPPS at 30.0 °C, pH 2.55, and $\mu = 0.25$ N

$[Cr^{II}]$ $\times 10^{-3}$	k_{obsd}, s^{-1} 427 nm	k_{obsd}, s^{-1} 411 nm	k, $M^{-1} s^{-1}$ [a] 427	k, $M^{-1} s^{-1}$ [a] 411
5.42	12.5	12.7	2310	2340
3.34	7.32	7.95	2190	2380
2.29	5.26	5.56	2300	2430
1.67	3.29	3.74	1970	2240
1.41	3.16	3.20	2241	2270
0.90	1.98		2200	
0.71	1.44	1.38	2230	1940
0.70	1.48	1.46	2110	2090
0.34	0.68	0.63	2000	1850
			$2170^b \pm 120$	$2190^b \pm 200$

[a] $k = k_{obsd}/[Cr^{II}]$. [b] Average ± standard deviation.

Table II. Results of the Rate Measurements of the Chromous Reduction of Co^{III}-TPPS at 30.0 °C and $\mu = 0.25$ N

pH	k, $M^{-1} s^{-1}$ [a]	pH	k, $M^{-1} s^{-1}$ [a]
1.40	132	3.61	18 000
2.20	631	3.67	21 000
2.30	780	3.87[b]	31 400
2.48	1 400	4.10[b]	67 700
2.60	2 170	4.34[b]	127 000
2.75	2 780	4.53[b]	190 000
3.00	5 000	4.63[b]	211 000
3.50[b]	14 800	4.83[b]	367 000
3.51	15 500	4.99[b]	471 000
3.54	18 425	5.22	585 000

[a] Average of rates determined at 427 and 411 nm. $k = k_{obsd}/[Cr^{II}]$. [b] Acetate buffer. [c] From least-squares of k vs. $1/[H^+]$ we obtain $k_1^* = 4.9/[H^+]$.

controlled with acetate buffers. The rates with and without buffer at the same pH were the same within the errors of the measurement indicating that the acetate buffer did not affect the reaction system. A plot of the data in Table II of log k vs. pH is a straight line with least-squares slope = 0.99. A least-squares plot of k vs. $1/[H^+]$ yields a slope of 4.9 with a correlation coefficient of 0.995.

Thus within the errors of the experiment, the data can be expressed as $k_1^* = (4.9 \pm 0.6)/[H^+]$ s^{-1} over the pH range of 1.0 to 5.0.

The variation of the Co^{III}-TPPS reduction rate was determined as a function of added halides or thiocyanates. Within experimental error the catalytic effect was independent of whether the anions were added to the reductant or oxidant solutions. Table III gives the data for these reactions. It should be noted that in the SCN case the errors in the measurement are larger than usual due to the fact that the rates are very fast and they are near the limit of the instrument.

A comparison of the various anion catalysts for the Cr(II) reduction of Co^{III}-TPPS is given in Table IV which yields the increasing order of catalysis of

$$Cl < I^- < Br^- < N_3^- \sim SCN^-$$

Reductions of Co^{III}-TPPS with V(II) and Ru(II). In the study of the rate dependence of V(II) concentrations the reductant concentration ranged from 1.1×10^{-4} to 1.2×10^{-2} M. There was a linear relationship between the observed rate constant and reductant concentration yielding a rate constant of 1330 $M^{-1} s^{-1}$ which was independent of pH between pH 2.2 and 3.6. The data for this system are given in Table V. The rate constant k_1' for the reduction of Co^{III}-TPPS with Ru(II) at 30.0 °C and $\mu = 0.25$ is 5820 $M^{-1} s^{-1}$.

Reduction of Co^{III}-TCPP with Cr(II). Since it is known that the TCPP system is not as well behaved as TPPS in terms of aggregation[31] a limited set of kinetics was carried out on the Co^{III}-TCPP. The data for the reductions under various conditions are gven in Table VI. Assuming the previous pathway is followed the rate is given by

$$k_1^* = 3.0/[H^+]\ s^{-1}$$

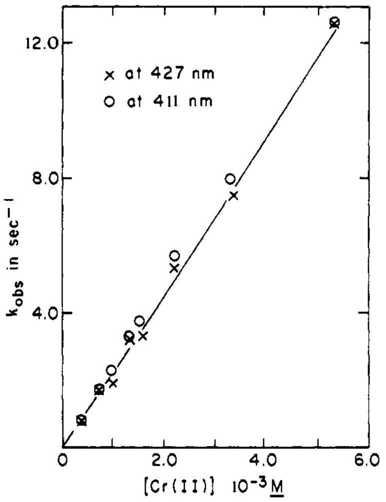


Figure 1

Table III. Rate Measurements of Chromous Reduction of Co^{III}-TPPS at 30.0 °C, pH 2.55, and $\mu = 0.25$ (ClO_4^-) with added Cl^- or SCN^-

$[Cr^{II}]$ $\times 10^{-3}$ M	Cl^-, M	k_{obsd}, s^{-1}	k, $M^{-1} s^{-1}$
1.10	0.00	2.39	2 170
1.75	0.063	6.79	3 920
1.18	0.125	4.94	5 900
1.41	0.187	10.5	7 450
1.59	0.250	15.2	9 560[a]
	SCN^-		
1.0	0.00	2.31	2 310
1.0	0.006	10.4	10 400
1.0	0.010	16.0	16 000
1.0	0.025	32.5	32 500

[a] Least-squares fit to data for equation $k = k_1 + k_2[L]$ yields for the Cl^- case $k = 2130 + 2.9 \times 10^4[Cl^-]$ with a correlation coefficient of 0.999 while for the SCN^- case $k = 3000 + 1.1 \times 10^6[SCN^-]$ with a correlation coefficient of 0.998.

Table IV. Measurements for Chromous Reduction of Co^{III}-TPPS at 30.0 °C, pH 2.2, $[Cr^{II}] = 1.23 \times 10^{-3}$ M, $\mu = 0.25$ N for Various Anions

Anion	k_2, $M^{-2} s^{-1}$
Cl^-	2.9×10^4
Br^-	3.5×10^5
I^-	1.2×10^5
SCN^-	1.1×10^6
N_3^-	1.2×10^6

The Co^{III}-TCPP reductions with Cr(II) were catalyzed by both Cl^- and SCN^- with resulting k_2 of 4.4×10^4 and 1.3×10^6 $M^{-2} s^{-1}$, respectively. Each of the above k_2's was determined from six independent anion concentrations at 30.0 °C and $\mu = 0.25$ M.

Reduction of Co^{III}-TCPP with V(II). The reduction of Co^{III}-TCPP with V(II) is first order in V(II) and the rate constant determined from a least-squares analysis of the data taken at 30.0 °C and $\mu = 0.25$ M is 1420 ± 60 $M^{-1} s^{-1}$. The V(II) concentration ranged from 0.003 to 0.02 M.

Reduction of Co^{III}-TPyP with Cr(II). The data for the Co^{III}-TPyP reduction with chromous ion are given in Table VII.

The analysis of the data gives $k = 49\ M^{-1} s^{-1} + 0.4/[H^+]\ s^{-1}$. There is only a very small acid-dependent term. The anion effects were measured at 30.0 °C and $\mu = 0.25$ M for both Cl^- and SCN^- with resulting k_2's of 2.3×10^3 and 1.8×10^5 $M^{-1} s^{-1}$, respectively. The

Table V. Results of Rate Measurements of Vanadous Reductions of Co^{III}-TPPS at 30.0 °C and $\mu = 0.25$ N ($Cl^- + ClO_4^- + SCN^-$)

$[V^{II}]$ $\times 10^{-2}$ M	pH	$[Cl^-]$, M	k_{obsd}, s^{-1}	k, M^{-1} $s^{-1\,a}$
1.24	2.7		16.8	1350
0.69	2.7		8.9	1290
0.12	2.7		1.7	1420
1.2	2.7		15.8	1320
1.2	2.7	0.13	16.7	1390
1.2	2.7	0.16	16.2	1350
1.2	2.7	0.25	16.4	1370
0.69	3.6		8.8	1280
1.15	2.1		15.6	1360
1.15	2.1	0.25 $SCN^{-\,b}$	14.1	1230
1.15	2.1	0.25 $SCN^{-\,c}$	12.3	1070
				Av 1310 ± 100

[a] $k = k_{obsd}/[V^{II}]$. [b] SCN^- in V(II) solution. [c] SCN^- in Co^{III}-TPPS solution.

Table VI. Results of the Rate Measurements of the Chromous Reduction of Co^{III}-TCPP at 30.0 °C, pH 4.1, and $\mu = 0.25$ M

$[Cr^{II}]$ $\times 10^{-3}$ M	k_{obsd}, s^{-1}	k,[a] $\times 10^4$ M^{-1} s^{-1}
5.0	180	3.6
3.3	126	3.8
2.7	96	3.6
1.7	59	3.5
0.59	20	3.4
		Av 3.6

[a] $k = k_{obsd}/[Cr^{II}]$.

Table VII. Results of Rate Measurements of Chromous Reduction of Co^{III}-TPyP at 30.0 °C and $\mu = 0.25$ M

$[Cr^{II}]$ in M	$[H^+]$	k_{obsd}, s^{-1}	k,[a] $M^{-1}s^{-1}$	k_{calcd}
0.080	0.25	3.68	47	51
0.041	0.25	2.20	54	51
0.020	0.25	1.04	52	51
0.004	0.25	0.20	50	51
0.0112	0.24	0.55	50	51
0.0125	0.25	0.65	52	51
0.0125	0.15	0.66	53	52
0.0112	0.10	0.60	53	53
0.0112	0.075	0.60	53	54
0.0125	0.063	0.62	56	55
0.0112	0.063	0.57	56	55

[a] $k = k_{obsd}/[Cr^{II}] = 49 + 0.4/[H^+]$.

Table VIII. Product Studies of Co^{III}-TPPS + $^{51}Cr^{II}$

Reactants	Net counts[c]/10 min	% Cr[d]
Cr^{II} + air	3460 ± 110[a]	5
	160 ± 88[b]	
Cr^{III} + Na_4TPPS	3560 ± 111[a]	8
	280 ± 90[b]	
Cr^{II} + Co^{III}-TPPS	3260 ± 100[a]	83 ± 5
(1:1)[e]	2860 ± 103[b]	
Cr^{II} + Co^{III}-TPPS	6560 ± 120[a]	91 ± 6
(2:1)	3160 ± 150[b]	
Cr^{II} + Co^{III}-TPPS	9360 ± 130[a]	94 ± 6
(3:1)	3260 ± 105[b]	

[a] Before passage through column. [b] After passage through column. [c] All counts corrected for background. [d] % ^{51}Cr that passed through column. [e] Stochiometric ratio of Cr^{II}/Co^{III}-TPPS.

Table IX. Results of Co^{III}-TPPS + Cr^{II} Reduction and Cycling through Oxidation–Reduction

Condition	Counts	Cr^{III}/Co-TPPS
Blank	248 ± 30	
Cr(II)[a]	50 810 ± 220	
Cr(III)[b]	400 ± 20	
C1[b]	49 900 ± 220	1
C2[b]	99 000 ± 310	2
C3[b]	149 000 ± 390	3

[a] Before passage through column. [b] After passage through column.

reduction of Co^{III}-TPyP with V(II) yields rate constants k_1' of 1400 s^{-1} at 30.0 °C, $[H^+] = 0.1$ M, and $\mu = 0.25$ M. The rate of substitution of SCN^- into the Co^{III}-TPyP fifth and sixth position follows the rate law

$$k_{obsd} = 1.6[SCN^-]/\{0.26 + [SCN^-]\}\ s^{-1}$$

at $[H^+] = 0.026$ M, 30.0 °C, and $\mu = 0.25$ M. Thus the half-life of substitution in the Co(III) site at 0.050 M SCN^- is about 2 s while the redox reaction is about 7 ms. Thus when the SCN^- is placed in the Cr(II) reactant, the electron transfer is much faster than the substitution reaction on Co(III).

Chromium Product Study of Co^{III}-TPPS Reduction. A 6 in. × 1 in. cation exchange column of Dowex 50W-X8 resin was employed in the product studies of the Co^{III}-TPPS reductions with chromous solutions.

The radioactive chromium solution from ICN was 2.6×10^{-3} M in $CrCl_3$ and 10^{-3} M in HCl. It was mixed with a nonradioactive Cr(III) solution to form a stock solution 1.2×10^{-3} M Cr(III), 1.0×10^{-3} M $HClO_4$, and 2.4×10^{-4} M HCl. The resultant solution was then reduced to Cr(II) with zinc amalgam and the concentration of the solution was verified with the permanganate method.

The Co^{III}-TPPS employed in this study was a 10^{-4} M solution in water at a pH of 4. When 10 ml of the Co^{III}-TPPS solution was passed through the column, the major portion of the cobaltic porphyrin was collected in the first 18 ml of eluent. The negatively charged porphyrin would, of course, be expected to pass directly throughthe cation column. Various controls were run which demonstrated that less than 5% of the Cr(III) passed through the column under the conditions of the experiment. Then the Co^{III}-TPPS reduction with Cr(II) was carried out with varying amounts of Cr(II) from a stoichiometric amount to a threefold excess. These solutions were then passed through the cation column with results shown in Table VIII. In each case *one* and only one Cr(III) passed through the column with the Co^{II}-TPPS. It is also known that a mixture of Co^{III}-TPPS with Cr(III) when passed through the column has no chromium getting through the column. Thus the only way ^{51}Cr is not held on the cation column is via the redox reaction.

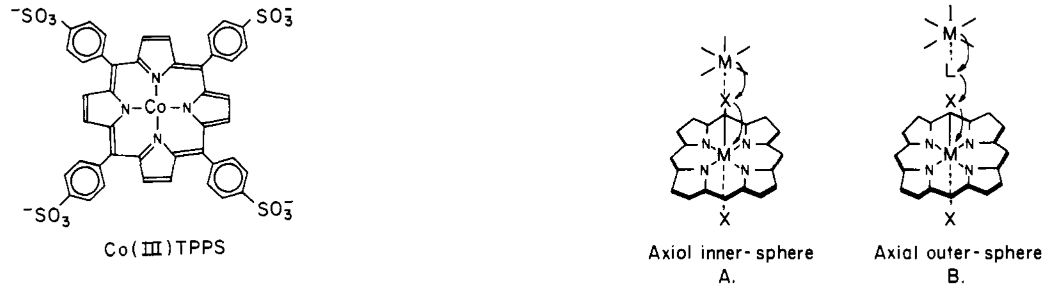
Product Studies of Formation of $Cr^{III}{}_n$-Co^{II}-TPPS. Three 10-ml solutions of 10^{-3} M Co^{III}-TPPS were deoxygenated in serum-capped flasks. A radioactive 7×10^{-2} M Cr(II) solution, 0.15 ml, was added to each of the Co^{III}-TPPS solutions. Visible spectra of diluted samples of the product solutions showed that the Co^{III}-TPPS was totally reduced to Co^{II}-TPPS. Then the solutions were all exposed to air until the Co^{III}-TPPS formed. One of the solutions was labeled C1. The other two solutions were deoxygenated once more and an additional 0.15 ml of Cr(II) solution was added to each. The second solution C2 was set aside while the last solution was recycled as above and after Cr(II) reduction was labeled C3. All three solutions were passed down the cation exchange column, and the resulting radioactivities are shown in Table IX.

A similar set of experiments were carried out with Cr^{II} + Co^{III}-TCPP with a 1:1 Cr^{III}-Co^{II}-TCPP complex being eluted through the column after the redox reaction.

Table X. Summary of Results of Reductions of Various Cobaltic Metalloporphyrins[a] at 30.0 °C and μ = 0.25 M

Porphyrin	Reducing agent	Anion	k_1', M^{-1} s	k_1^*, s^{-1}	k_2, $M^{-2}\,s^{-1}$
Co^{III}-TPPS	Cr^{II}		0	4.9	
		Cl^-			2.9×10^4
		SCN^-			1.1×10^6
		N_3^-			1.2×10^6
		Br^-			3.5×10^5
		I^-			1.2×10^5
	Ru^{II}		5820	0	0
	V^{II}		1330	0	0
Co^{III}-TCPP	Cr^{II}		0	3.0	
		Cl^-			4.4×10^4
		SCN^-			1.3×10^6
	V^{II}		1420	0	0
Co^{III}-TPyP	Cr^{II}		49	0.4	
		Cl^-			2.3×10^3
		SCN^-			1.8×10^5
	V^{II}		1400	0	0

[a] General rate law: rate = $\{k_1' + k_1^*/[H^+] + k_2[L]\}\,[R^{II}][Co^{III}\text{-}P]$.



Co(III)TPPS

Axiol inner-sphere
A.

Axial outer-sphere
B.

Figure 2.

Discussion

This paper reports on the kinetics and product studies of the reduction of cobaltic meso tetrasubstituted porphines. Figure 2 is the formula for the Co^{III}-TPPS; the octahedral coordination sites are completed with two waters in the fifth and sixth positions of the metalloporphyrin.[32] The tetracarboxy (Co^{III}-TPCC) and the tetrapyridyl (Co^{III}-TPyP) substituted porphines are also employed in our study.

The stoichiometry of all the reactions followed has been established as

$$Co^{III}\text{-}P + R^{II} \rightarrow Co^{II}P + Ox^{III}$$

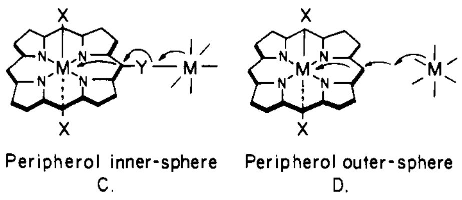
The general rate law for these reductions is established as

$$\{k_1' + k_1^*/[H^+] + k_2[L]\}\,[R^{II}][Co^{III}\text{-}P]$$

where the k's for the various porphyrins and reducing agents studied in this paper are listed in Table X.

The various classes of redox pathways available to metalloporphyrins are outlined in Figure 3. We will refer to these possible pathways in our discussions of the results of this study.

We will initially focus our attention on the outer-sphere pathways B and D since they are simpler. The reducing agents $R(NH_3)_6^{2+}$ and $V(H_2O)_6^{2+}$ can act as outer-sphere reducing agents.[33] The Ru(II) always acts as an outer-sphere reducing agent, while V(II) can act either as an inner- or outer-sphere reducing agent. The rate of water exchange for the $V(H_2O)_6^{2+}$ is 100 s^{-1}.[33] This relatively slow rate of ligand exchange will be employed to assign an outer-sphere mechanism when the electron transfer is faster than the water exchange rate.



Peripherol inner-sphere
C.

Peripherol outer-sphere
D.

Figure 3.

In a correlation of the rates of reduction of various Co(III) complexes Gould[34] demonstrated that for outer-sphere reduction by Ru(II) and V(II) there is a free energy relationship in the form

$$\log k_{Ru} = 1.05 \log k_V + 0.48$$

Since the $Ru(NH_3)_6^{2+}$ must react with an outer-sphere mechanism, then the inner-sphere component of the $V(H_2O)_6^{2+}$ reduction can be calculated. The excess of k_V over that predicted from the above equation is ascribed to the inner-sphere pathway.

For Co^{III}-TPPS reduction with Ru(II) and V(II), the rate constants are 5820 $M^{-1}\,s^{-1}$ and 1330 $M^{-1}\,s^{-1}$, respectively. Using the linear correlation equation the rate constant predicted for the outer-sphere reduction is 1342 $M^{-1}\,s^{-1}$ in very good agreement with the observed values. This gives clear-cut evidence for the outer-sphere reduction of Co^{III}-TPPS by both reducing agents. There are two other points that should be made about these outer-sphere reductions: One is that they are relatively anion independent. Second, the V(II) rates of reduction are quite similar for various porphyrins reduced: Co^{III}-TPPS, 1330 M^{-1} s; Co^{III}-TCPP, 1430 $M^{-1}\,s^{-1}$; and Co^{III}-TPyP, 1400 $M^{-1}\,s^{-1}$. Although there is no direct experiment to distinguish between the two outer-sphere pathways (Figures 3B and 3D), there is some indirect evidence that the peripheral outer-sphere pathway may be operative in these reductions. The relatively small effect of an anion on the rates leads us to suspect that the axial outer-sphere mechanism is not the preferred one. On the other hand, with the present experiments the two pathways cannot be distinguished. The rates are also surprisingly independent of the porphyrin charge. This might indicate the following is the mechanism for the reduction of the metalloporphyrin with the second step being very fast. A similar type of mechanism has been recently proposed for the oxidation of metalloporphyrins.[35]

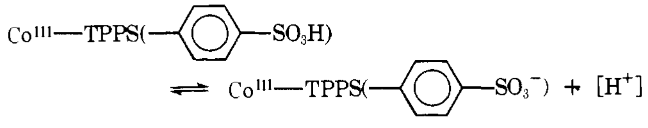
$$\mathrm{Co^{III}\text{-}P + R^{II} \rightarrow Co^{III}\text{-}P\cdot^{-} + Ox^{III}}$$

$$\mathrm{Co^{III}\text{-}P\cdot^{-} \rightarrow Co^{II}\text{-}P}$$

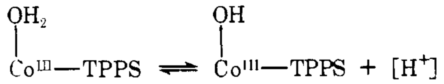
Although axial inner-sphere mechanisms have been demonstrated to occur with $\mathrm{Fe^{III}}$-TPPCl reductions,[14] in all the cases discussed here this pathway can be ruled out.

The substitution reactions on the cobaltic porphyrins fifth and sixth positions, although considerably labilized oer the usual cobaltic complexes, are still quite slow compared with the electron-transfer reaction studied here. Thus when $\mathrm{SCN^-}$ is placed in the Cr(II) side of the stopped-flow, the reduction of $\mathrm{Co^{III}}$-TPPS is highly $\mathrm{SCN^-}$ catalyzed even though the redox reaction is much faster than the substitution reaction. The k_2 is always large for $\mathrm{SCN^-}$ in the Cr(II) reductions of cobaltic porphyrins. This argument thus rules out the axial inner-sphere mechanism (Figure 3A) and the axial outer-sphere mechanism (Figure 3B). Our reductions of $\mathrm{Co^{III}}$-TPyP with Cr(II) are in reasonable agreement with the study of Pasternack and Sutin[17] on the $\mathrm{Co^{III}}$-TMPyP (a similar but not identical system). They get rate constants at 25 °C and $\mu = 0.5$ M (our data are at 30 °C and $\mu = 0.25$ M) of $k_1' = 16\ \mathrm{M^{-1}\ s^{-1}}$ and $k_1{}^* = 1.6\ \mathrm{s^{-1}}$ while we get $k_1' = 49\ \mathrm{M^{-1}\ s^{-1}}$ and $k_1{}^* = 0.4\ \mathrm{s^{-1}}$. We find a smaller acid-dependent term. The quarternization of the pyridyl groups as well as the large change in ionic strength would be expected to have some effect.

In the Cr(II) reduction of $\mathrm{Co^{III}}$-TPPS and $\mathrm{Co^{III}}$-TCPP the rate is inversely proportional to the $[\mathrm{H^+}]$ with a zero intercept ($k_1' = 0$).[39] The most likely source of the inverse $[\mathrm{H^+}]$ dependence is an equilibrium involving the sulfonate and carboxyl groups on the porphyrin periphery and not the loss of a proton from either the Co(III) or Cr(II) forming a hydroxyl species



and not



$$\mathrm{Co^{III}(OH_2)\text{—}TPPS \rightleftharpoons Co^{III}(OH)\text{—}TPPS + [H^+]}$$

In the $\mathrm{Co^{III}}$-TPyP where the species is already protonated on the pyridyl groups the small $[\mathrm{H^+}]$ dependence could even be a medium effect. There is certainly an ambiguity about the origin of the hydrogen ion dependence and no further comments will be made concerning it.

Arguments can be made concerning the amount of inner-sphere pathway a reductant follows based on the free-energy relationship referred to previously. The relationship established at 0.01 $[\mathrm{H^+}]$ for the Co(III) reductions[34] is

$$1.05 \log k_{\mathrm{Cr}} + 1.82 = 1.05 \log_{\mathrm{V}}$$

and

$$\log k_{\mathrm{Ru}} = 1.05 \log k_{\mathrm{Cr}} + 2.30$$

For both the $\mathrm{Co^{III}}$-TPPS and $\mathrm{Co^{III}}$-TCPP using the above equations we find less than 5% of the reaction proceeds via an outer-sphere reaction. Thus this analysis demonstrates that the path of these Cr(II) reductions is inner-sphere. Interestingly enough, for the $\mathrm{Co^{III}}$-TPyP case where there is a large zero intercept term k_1' of 49 $\mathrm{M^{-1}\ s^{-1}}$ the analysis leads to the pathway being at least half outer-sphere. The positively charged protonated pyridyl group of the $\mathrm{Co^{III}}$-TPyP does not give a good binding site for the Cr(II) as do the sulfonate and carboxyl groups of the TPPS and TCPP porphyrins. Thus this indirect line of evidence leads to the conclusion that will be supported by other evidence that the chromous reductions of $\mathrm{Co^{III}}$-TPPS and $\mathrm{Co^{III}}$-TCPP proceed via an inner-sphere mechanism.

The product studies using $^{51}\mathrm{Cr}$ as a tracer employing cation exchange columns clearly demonstrate that a complex is formed between the Cr(III) and the Co-TPPS; this product only forms via the redox reaction. It was also demonstrated that the $\mathrm{Co^{III}}$-TPPS after Cr(II) reduction can be reoxidized and again reduced to produce $[\mathrm{Cr^{III}}]_2$-$[\mathrm{Co^{II}}$-TPPS] complex. The Cr(III) that comes through the cation column with the sulfonated porphyrin must be complexed to the porphyrin because the cation column is a very efficient scavanger of free Cr(III). A $[\mathrm{Cr^{III}}]$-$[\mathrm{Co^{II}}$-TCPP] complex was also found in the reduction of $\mathrm{Co^{III}}$-TCPP. The only reasonable position that the Cr(III) can be complexed to is via the sulfonate or carboxy groups on the periphery of the porphyrin. Thus in this case both the kinetic studies and the product studies lead to the conclusion that the mechanism of the chromous reduction of both $\mathrm{Co^{III}}$-TPPS and $\mathrm{Co^{III}}$-TCPP is by a peripheral inner-sphere pathway (Figure 3C).

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A Study of Solvent and Substituent Effects on the Redox Potentials and Electron-Transfer Rate Constants of Substituted Iron *meso*-Tetraphenylporphyrins

K. M. Kadish,*[1a] M. M. Morrison,[1a] L. A. Constant,[1b] L. Dickens,[1b] and D. G. Davis*[1b]

Contribution from the Departments of Chemistry, California State University, Fullerton, California 92634 and the University of New Orleans, New Orleans, Louisiana 70122.

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Abstract: The effect of substituents on the electrode reactions of para- and meta-substituted iron tetraphenylporphyrins was investigated by the technique of cyclic voltammetry. In all cases electron-donating substituents produce a more difficult reduction,as evidenced by a cathodic shift of the reversible polarographic half-wave potentials. For each reaction, a Hammett linear free-energy relationship was observed between the half-wave potentials, $E_{1/2}$, and the σ constants of the substituents on the four phenyl rings of Fe(p-X)TPP and Fe(m-X)TPP. Results in five nonaqueous solvent systems indicate a decrease in substituent effects on half-wave potentials with increase in solvent dielectric constant, and that an increase in the solvent complexing ability gives rise to an increased stability of the Fe(II) species relative to Fe(III). For almost all compounds investigated, the electron-transfer rate constants were larger for reactions at the porphyrin ring than those at the central metal. Electron-donating substituent were observed to increase the rate of electron transfer, suggesting that high electron density on the ring or metal is important in fast electron-transfer reactions of metalloporphyrins.

Studies of electron-transfer reactions involving iron porphyrins are of evident interest because of their importance as biological electron-transfer agents, especially in cytochromes.[2] In nonaqueous media, iron(III) porphyrins may be oxidized in two single electron-transfer steps[3-5] or reduced in three one-electron transfer steps.[6-8] The potentials and reversibility of the electrode reactions are dependent on solvent medium and axially coordinated ligands,[8,9] dimer formation,[10] and overall porphyrin basicity.[11-13] Recently, several studies have examined the effect of substituents on the chemical and physical properties of metalloporphyrins. These have included substituent effects on electronic absorption spectra,[14] equilibrium constants for addition of one or two axial ligands to the central metal of the metalloporphyrin,[15-19] and half-wave potentials of porphyrin redox reactions.[18,20-22]

In earlier papers we have quantitated the effect of substituents on the thermodynamic half-wave potentials for oxidation or reduction of +3 and +2 transition metal complexes of para-substituted tetraphenylporphyrins.[18,20] This paper concentrates on the electrode reactions of Fe(p-X)TPPCl to yield complexes of Fe(I), Fe(II), Fe(III), and Fe(IV), and includes a comparison of kinetic and thermodynamic substituent effects.

The electrode reactions described in this paper can be summarized as follows:

$$[Fe^{IV}P]^{2+} \rightleftarrows [Fe^{IV}P]^{3+} + e \qquad (1)$$

$$[Fe^{III}P]^{+} \rightleftarrows [Fe^{IV}P]^{2+} + e \qquad (2)$$

$$[Fe^{III}P]^{+} + e \rightleftarrows [Fe^{II}P]^{0} \qquad (3)$$

$$[Fe^{II}P]^{0} + e \rightleftarrows [Fe^{I}P]^{-} \qquad (4)$$

$$[Fe^{I}P]^{-} + e \rightleftarrows [Fe^{I}P]^{2-} \qquad (5)$$

P is (p-X)TPP^{2-} or (m-X)TPP^{2-}, TPP^{2-} represents tetraphenylporphyrin, and X is an electron donating or withdrawing substituent placed at the para or meta position of the four phenyl rings, as listed in Table I. The species in eq 1-5 may be expected to be coordinated with solvent and/or an anion. The existence of these complexes is assumed when the notation $[Fe^{III}P]^+$ is used in this paper.

The Hammett linear free-energy equation[23]

$$\Delta E_{1/2} = 4\sigma\rho \qquad (6)$$

describes shifts in half-wave potentials as a result of changing substituents. The value 4σ is the total of substituent constants, representing the sum of inductive and resonance effects of all substituents, and is dependent on the kind and position of the four substituents, one on each of the phenyl rings of substituted tetraphenylporphyrin complexes. The reaction constant, ρ, given in volts, measures the susceptibility of the electrode reaction to the polar effect of the substituents. Applicability of this equation in describing redox potentials of porphyrins has been discussed in previous publications.[18,20,21]

Experimental Section

The porphyrins listed in Table I were obtained from several sources.

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