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Reduction of Tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) by Chromium(II)

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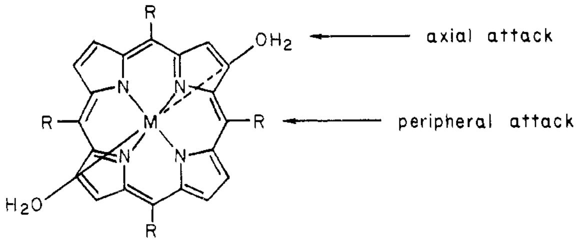
The reduction of tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) by chromium(II) has been studied. In perchlorate media ($I = 1.0$ M) the observed rate constant can be expressed as $k_{\text{obsd}} = k_0 + k_2[\text{H}^+]^{-1}$, where $k_0 = 173 \pm 10$ M^{-1} s^{-1} and $k_2 = 2.0 \pm 0.1$ s^{-1} at 25 °C. Product analyses indicate that some of the chromium(III) produced in the reaction is bound to the CoTPPS complex. The results are discussed in terms of an axial inner-sphere mechanism.

Introduction

The substitution and electron-transfer reactions of several meso-substituted metalloporphyrin complexes have been studied in an attempt to gain some insight into the redox reactions of metalloporphyrin–protein complexes in living systems.[1-9] Two modes of attack can be envisaged for reduction of these complexes as shown in I. Electron transfer could take place by reductant attack at an axial water molecule or at the periphery of the porphyrin ring. For the reduction of tetrakis(4-*N*-methylpyridyl)porphinatocobalt(III) and -iron(III) ($\text{R} = \text{C}_5\text{H}_4\text{NCH}_3^+$) by chromium(II) in perchlorate media,[4] a two-term rate law was found with the form



I

$$k_{\text{obsd}} = k + k^1[\text{H}^+]^{-1}$$

The acid-dependent pathway was attributed to reductant attack at a deprotonated axial water molecule resulting in a hydroxy-bridged transition state. The acid-independent term was thought to involve an outer-sphere mechanism in which the two metal centers are separated by two water molecules. Both terms apparently involved attack of chromium(II) at the axial positions and no evidence was found for a pathway where reduction takes place through the porphyrin ring system.

However, Fleischer and Cheung[10] have recently reported that the reduction of tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) ($\text{R} = \text{C}_6\text{H}_4\text{SO}_3^-$) and tetrakis(*p*-carboxyphenyl)porphinatocobalt(III) ($\text{R} = \text{C}_6\text{H}_4\text{CO}_2\text{H}$) by chromium(II) proceeds by attack at the sulfonatophenyl and carboxyphenyl substituents, respectively, with electron transfer subsequently occurring via the porphyrin π cloud. Their conclusions were based on cation-exchange experiments using radioactive chromium tracer techniques. We report our own results on the chromium(II) reduction of tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) which are substantially different from those above and lead to a different interpretation.

Experimental Section

Materials. All chemicals were reagent grade unless otherwise specified. Sodium porphinetetrakis(*p*-benzenesulfonate), Na_4TPPS_4, was purchased from Strem Chemicals, Inc., Danvers, Mass. Tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III), $\text{Na}_3[\text{CoTPPS}(\text{H}_2\text{O})_2]$, was prepared as described in the literature except that the source of cobalt was $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. In 0.1 M HClO_4 ($I = 1.0$ M, LiClO_4) the visible absorption spectrum showed peak maxima at 424 nm (ϵ 2.5×10^5 M^{-1} cm^{-1}) and 537 nm (ϵ 1.2×10^4 M^{-1} cm^{-1}), in reasonable agreement with reported values.[6,10] Chromium(II) perchlorate solutions were prepared by reduction of chromium(III) perchlorate with amalgamated zinc and by dissolving high-purity chromium metal in standard HClO_4. All solutions were handled using standard syringe techniques under an argon atmosphere.

Kinetic Measurements. The reduction was followed using a Durrum stopped-flow spectrophotometer by observing the change in absorbance at 542 nm. All reactions were carried out under pseudo-first-order conditions.

Cation Exchange Chromatography of Reaction Mixtures. Reaction mixtures were subjected to cation exchange chromatography on Dowex 50W-X12. Reactions were carried out with a ratio of Cr^{II} to Co^{III}TPPS of 1:1 at hydrogen ion concentrations of 5.0×10^{-3} and 0.10 M. Other experiments were carried out using up to four redox cycles as follows. After the first reduction (1:1 ratio of Cr^{II}:Co^{III}TPPS), the solution was aerated to oxidize Co(II) produced in the reaction to Co(III), and the solution was charged onto the cation exchange column and the eluant collected. This eluant which apparently contained most of the Co^{III}TPPS was degassed and again reduced with Cr(II) (1:1 ratio of Cr(II) to Co(III)). The eluant after each cycle was analyzed for Cr(III). The amount of Cr(III) left on the column was also determined. The concentration of Co^{III}TPPS was maintained between 10^{-4} and 10^{-5} M since at higher concentrations the porphyrin forms polymeric species and the ion-exchange results are different. Due to the low concentrations used, quantitative estimation of Cr(III) was difficult and our results probably reflect order of magnitude values. Each experiment was repeated at least five times, giving a consistent pattern. The ionic strength of the reaction mixtures was maintained at both 1.0 and 0.25 M with LiClO_4. Blank experiments with Co^{III}TPPS, which exists as the trianion at all pHs studied, showed that the complex was not held by the ion exchange resin.

Physical Measurements. Electronic spectra were obtained using a Beckman Acta CIII spectrophotometer.

Results

The Co^{III}TPPS complex follows Beer's law over the range of concentrations of complex ($(2\text{–}5) \times 10^{-5}$ M) and hydrogen ion (0.5–0.005 M) used in this study. Upon addition of Cr(II), the Soret band maximum shifts from 424 to 411 nm while the peak at 537 nm is shifted to 528 nm. Both peaks decreased in intensity. Upon aeration, the original spectrum is rapidly restored although the intensities of the peaks are slightly less than those in the original Co(III) spectrum. The shift of the visible peaks to lower wavelength in porphyrin complexes upon reduction has been noted[4,11] and commented on[12] previously. Furthermore, if the electron were added to the π system of the porphyrin ring, a shift of the Soret band to longer wavelength would be expected if the radical complex were stable.[13] The observed shift then indicates that the metal center is being reduced rather than the π system of the porphyrin ring.

Kinetic Studies. The data for the reduction of Co^{III}TPPS by chromium(II) are given in Table I. The data obey eq 1,

$$k_{\text{obsd}} = (k_0 + k_2/[\text{H}^+])[\text{Cr}^{2+}] \qquad (1)$$

where $k_0 = 170 \pm 10$ M^{-1} s^{-1} and $k_2 = 2.1 \pm 0.1$ s^{-1}.

The reduction kinetics were also studied after one redox cycle (after 1:1 Cr^{II}/Co^{III}TPPS reduction, the reaction mixture

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Table I. Kinetic Data for the Reduction of Tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) by Chromium(II)^{a,b}

[Cr(II)], M	[H$^+$], M	k_{obsd}/[Cr^{2+}], M^{-1} s^{-1}	[Cr(II)], M	[H$^+$], M	k_{obsd}/[Cr^{2+}], M^{-1} s^{-1}
0.020	0.50	163	0.020	0.0080	426
0.020	0.30	181	0.020	0.0050	580
0.020	0.10	202, 190	0.010	0.0050	610
0.020	0.030	226	0.020	0.0050	590
0.020	0.014	310	0.040	0.0050	616
0.020	0.010	377			

^{a} Temperature = 25.0 ± 0.1 °C. Ionic strength = 1.0 M, maintained with LiClO$_4$. The rate constants are averages of at least four separate determinations. ^{b} [Co^{III}TPPS] = 5.0 × 10^{-5}.

Table II. Reduction of Tetrakis(*p*-sulfonatophenyl)porphinatocobalt(III) by Chromium(II) after One Redox Cycle^{a,b}

[Cr(II)], M	[H$^+$], M	k_{obsd}/[Cr^{2+}], M^{-1} s^{-1}	[Cr(II)], M	[H$^+$], M	k_{obsd}/[Cr^{2+}], M^{-1} s^{-1}
0.020	0.30	670, 640	0.020	0.015	740
0.020	0.15	682	0.020	0.010	800, 770
0.020	0.075	685	0.020	0.005	860, 850

^{a} The solution which was reduced was treated in the following manner. First Co^{III}TPPS was reduced with a stoichiometric amount of chromium(II) at pH 4. After aeration to regenerate Co^{III}, the solution was passed through a cation exchange column in the Li ion form. This solution was used to prepare solutions for kinetic runs. ^{b} The ionic strength was approximately 0.4 M maintained with LiClO$_4$.

was aerated to give Co^{III}TPPS, followed by passage through a cation exchange column). These data are collected in Table II. The data obey eq 2.

$$k_{obsd} = (675 + 0.95/[H^+])[Cr^{2+}] \qquad (2)$$

Product Analyses. Reductions of Co^{III}TPPS solutions were carried out at pH 1 and 4, and the reaction mixtures were subjected to cation exchange chromatography. Preliminary experiments clearly showed that under stoichiometric conditions (1:1 ratio of Co^{III}TPPS to Cr^{II}) some Cr(III) was always held on the cation exchange resin at both pHs. Furthermore, significantly more Cr(III) was held on the column at the higher acidity. A quantitative estimate of Cr(III) on the column was made by elution with a solution of NaClO$_4$–HClO$_4$ and conversion of chromium to chromate. The amount of Cr(III) that passed through the column could not be estimated as chromate since the Soret band of the surviving TPPS interfered. Similar analyses were carried out after four redox cycles. For the latter experiments the Co^{III}TPPS complex passed through the cation exchange column indicating that the prophyrin species had either zero or negative charge.

In all cases the concentration of Co^{III}TPPS was kept in the range where polymerization did not occur. The concentrations used account for the rather large uncertainty in the results. The data, given in Table III, indicate that at pH 4 approximately 50% of the chromium(III) produced from the reduction reaction is bound to CoTPPS and passes through the cation exchange column. At pH 1 it appears that less than 25% of the chromium(III) is bound to CoTPPS.

The Co(III) product of one redox cycle carried out at pH 4 was also examined spectrophotometrically. In the pH range 1.5–4.5 the maximum at 539 nm decreased with increasing pH as did a peak at 572 nm. This latter peak was not present in the spectrum of Co^{III}TPPS alone. In this pH range an isosbestic point was observed at 494 nm. The next spectrum taken at pH 5.75 did not go through the isosbestic point at 494 nm. Further spectra taken in the range pH 5.75–11.8 showed new isosbestic points at 514 and 544 nm. This behavior indicates that at about a pH of 4.5–5.7 a species is produced which is independent of that produced at lower pH. The changes observed on going from acidic to alkaline media were not reversible.

Table III. Product Analyses for Reduction of Co^{III}TPPS by Chromium(II)^{a,b}

amt of Co^{III}TPPS, mol × 10^{-5}	amt of Cr^{II}, mol × 10^{-5}	pH	amt of Cr^{III} eluted from column, mol × 10^{-5}	% Cr^{III} "bound" to CoTPPS (passed through column)
0.50	0.50	1	0.37	26
0.50	0.50	1	0.50	0
0.50	0.50	4	0.21	58
0.50	0.50	4	0.27^c	46
0.50	0.50	4	0.20	60
0.50	0.50	4	0.29	42
0.50	2.0^d	1	1.49	26
0.50	2.0^d	4	1.15	43

^{a} In all cases the initial concentration of Co^{III}TPPS was 5 × 10^{-4} M. The final volume of the reaciton mixture was 10 mL. ^{b} Chromium was estimated spectrophotometrically as chromate; ϵ = 4815 M^{-1} cm^{-1} at 372 nm. ^{c} After reduction at pH 4, the pH was changed to 1 and then the solution charged on the cation exchange column. ^{d} Four redox cycles with 0.50 × 10^{-5} mol of Cr(II) for each cycle.

Discussion

Our results for the reduction of Co^{III}TPPS by chromium(II) are similar to those reported by Pasternack and Sutin[4] for the reduction of tetrakis(4-*N*-methylpyridyl)porphinatocobalt(III), Co^{III}TMepyP, by chromium(II). The rate law is consistent with two parallel paths for reduction, and a reasonable scheme is shown in (3) and (4). For the inverse hydrogen ion term

$$\mathrm{Co^{III}TPPS(OH_2)_2^{3-} + Cr^{2+} \xrightarrow{k_0}} \qquad (3)$$

$$\mathrm{Co^{III}TPPS(OH_2)(OH)^{4-} + Cr^{2+} \xrightarrow{k^1}} \qquad (4)$$

$k_2 = K_{a_1}k^1$, where K_{a_1} is the acid dissociation constant for the first axial water molecule. For Co^{III}TPPS at 25 °C and I = 1.0 M (NaClO$_4$) K_{a_1} = 1.90 × 10^{-6} M.[6] This gives a value of 1.1 × 10^6 M^{-1} s^{-1} for k^1 in the above scheme.

For the k_0 term three detailed paths can be considered. Chromium(II) can attack at the axial water molecule. This would be expected to be an outer-sphere reaction since water is not predicted to be a good bridging ligand.[14,15] Alternatively, the reductant could attack at the edge or periphery of the porphyrin ring system in either an inner- or outer-sphere mechanism. For the peripheral inner-sphere path the transition state can be represented as [Co^{III}TPPSO$_3$Cr^{II}]‡. Whether this latter path is possible depends on the electron-mediating properties of SO$_3^-$ and its ability to form the precursor complex (vide supra).

The k^1 path probably involves the transition state [Co^{III}OHCr^{II}]‡. This is supported by the large ratio of k^1 to k_0 observed.[16] Furthermore, since the Co^{III}TPPS complex appears to exist exclusively as the trianion [CoTPPS(OH$_2$)$_2$]$^{3-}$, even at [H$^+$] = 0.100 M,[6] it does not seem reasonable that a kinetically significant amount of SO$_3$H can provide the necessary inverse hydrogen ion term.

Thus we favor an axial outer-sphere mechanism for the k_0 term and an axial inner-sphere mechanism for the k^1 term.

However, a study of the same system at I = 0.25 M (NaClO$_4$), pH 1.40–5.22, and 30 °C gave different results, and a different interpretation was advanced.[10] In this[10] study

^{51}Cr was used in conjunction with cation exchange in an attempt to indicate the position of attack of the chromium(II). After reduction with ^{51}Cr(II), the solution was passed through a cation exchange column and the radioactivity of the eluant was measured. It was shown that 1 mol of chromium(III) was eluted along with 1 mol of CoTPPS after one redox cycle whereas 2 and 3 mol of chromium(III)/mol of CoTPPS were eluted after two and three redox cycles, respectively. In all cases elution was effected by simply charging on the column followed by washing with water. These results were explained by postulating a peripheral inner-sphere mechanism where Cr(II) attacks at the SO_3 groups on the edge of the porphyrin ring. The results after two and three redox cycles appear questionable since the product species postulated would have overall charges of 3+ and 6+ and it is highly unlikely that they would be easily removed from the cation exchange column.[17]

The above report prompted us to carry out our own cation exchange experiments. The results confirm that the Co^{III}TPPS species produced after one, two, three, or four redox cycles does indeed come off the cation exchange column upon charging followed by elution with water. However, we find the same amount of Cr(III) bound to Co^{III}TPPS no matter how many redox cycles are carried out. The discrepancy between our results and those reported in ref 10 may be due to the fact that the previous workers used high Co^{III}TPPS concentrations (1×10^{-4} M) where the species is known to polymerize. At pH 1 the same results were obtained except that the amount of Cr(III) bound to Co^{III}TPPS was much less. Consequently, at least at $I = 1.0$ M ($LiClO_4$), it appears that Cr(III) remains bonded to CoTPPS presumably at an axial site and can be eluted from the cation exchange column. In light of the lability of the fifth and sixth positions in cobalt(III) and chromium(III) porphyrin complexes this is astonishing; however, we can offer no reasonable alternatives.

The Cr(II) reduction of the resulting complex formed after one redox cycle was carried out in an attempt to use the rate law to infer the position of attack. Our expectation was that the inverse hydrogen ion term would disappear if the mechanism were axial inner sphere and would be larger if the mechanism were peripheral inner sphere. Although the inverse hydrogen ion term did shrink, the fact that we have at least two Co(III) species present and have lowered the ionic strength does not allow us to make any quantitative predictions. However, the results do suggest that it is the axial path that operates since the $[H^+]^{-1}$ term decreased even though the ionic strength was lower.[18] It appears that the ionic strength of the medium is extremely important in determining the rate law and thus the product analyses give a more reliable guide to mechanism.

Fleischer and Cheung[10] have also studied the chromium(II) reduction of the tetrakis(*p*-carboxyphenyl)- and tetrakis(4-pyridyl)porphinatocobalt(III) complexes. The former complex is claimed to react via the peripheral path whereas the latter is claimed to react by the axial path. Considering the three substituents used, *p*-sulfonatophenyl, *p*-carboxyphenyl, and 4-pyridyl, some conclusions can be drawn as to their relative ability to act as electron-transfer lead-in groups toward chromium(II) from reduction studies of simpler complexes. The reduction of $(NH_3)_5CoO_2CC_6H_4SO_3^+$ by chromium(II) occurs by attack at the adjacent carbonyl rather than at the remote SO_3 group. At least in this system, SO_3 does not appear to be an effective lead-in group when compared to coordinated carboxylate.[19,20] For the nitrile complexes $(NH_3)_5CoNCC_6H_4COOH$[21] and $(NH_3)_5CoNCC_5H_4N$[22] reduction by chromium(II) does occur by reductant attack at the remote COOH and pyridyl groups, respectively. However, attack at the COOH group occurs only slowly. These facts suggest that in an inner-sphere reaction the COOH and SO_3^- groups may be poor lead-in groups. For pyridyl, the effectiveness as a lead-in group appears to depend on whether other sites are available for reductant attack and we can make no firm prediction.[23,24]

In summary, this work tends to negate the suggestion that Co^{III}TPPS is reduced by Cr(II) via attack at the peripheral SO_3 groups. First, the observed hydrogen ion dependence in the rate law does not correspond to that resulting from deprotonation of the SO_3H groups but is consistent with deprotonation of an axial water molecule. Second, early work on simpler systems indicates that the SO_3 group is devoid of lead-in properties for electron transfer. Finally, the ion-exchange results are not consistent with attack at the peripheral SO_3 groups but are more reasonably interpreted with an axial inner-sphere mechanism.

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