

9-iodo-12-(chloromethyl)-*o*-carborane are formed but are easily removed by a single crystallization.

Experimental Section

Iodination of *o*-Carborane in CCl₄. A solution of 3.3 g of I₂, 2.1 g of *o*-carborane, and 0.3 g of AlCl₃ in 80 mL of CCl₄ was refluxed under N₂ for 3 h. The mixture was poured into 100 mL of distilled water and the organic layer separated and dried over MgSO₄. The filtered solution was concentrated at the water pump to give a residue that was analyzed by gas chromatography on a 6 ft × 1/4 in. 15% OV 101 on Gaschrom Q 60/80 column at 200 °C. Preparative gas chromatography gave known compounds **1**, **2**, **3**, and **5** as well as the unknown **4** (mp 163–164 °C). Precise mass for B₁₀C₂ClH₁₀I: calcd, 306.0448; found, 306.0442 ± 0.003.

Iodination of *o*-Carborane in CH₂Cl₂. A mixture of 10.35 g of *o*-carborane and 18.2 g of I₂ was refluxed in 250 mL of CH₂Cl₂ with a catalytic amount of AlCl₃ for 16.5 h. The clear yellow solution was poured into distilled water and the organic layer separated. The water was extracted once with 100 mL of ether, and the combined organic layers were dried over MgSO₄. The filtered solvent was removed at the water pump and the residue recrystallized from hexane to give 18 g of **1** (93%; mp 125–126 °C, lit.^{7b,10} mp 122–123 °C).

Registry No. **1**, 17830-03-4; **2**, 19513-12-3; **3**, 98330-58-6; **4**, 98330-59-7; **5**, 17702-35-1; *o*-carborane, 16872-09-6.

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Kinetics of Reduction of Cobalt(III) Porphyrins by Fe^{II}-EDTA²⁻

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Kinetics studies on the mechanisms of reduction of cobalt(III) porphyrins to their divalent states have employed chromium(II),¹⁻³ vanadium(II),² dithionite,^{4,5} hexaammineruthenium(II),^{2,6} radiolysis-produced radicals,⁷ superoxide,⁸ cobalt(II) porphyrins,⁹ and metalloporphyrin anion radicals.⁷ In contrast to many of these reagents, iron(II) ethylenediaminetetraacetate (Fe^{II}-EDTA²⁻) is a weak reductant that will attack only the coordinated metal ion and not reduce the metalloporphyrin ring system itself. We report the kinetics of reduction of five water-soluble positively and negatively charged cobalt(III) porphyrins with Fe^{II}-EDTA²⁻. The observed rate laws are a function of the porphyrin charge type, and the corresponding Co^{III/II}-porphyrin self-exchange rate constants are calculated.

Experimental Section

The cobalt(III) forms of tetrakis(4-sulfonatophenyl)porphyrin (TPPS), tetrakis(*N,N,N*-trimethylanilinium)porphyrin (TAP), and tetrakis(*N*-methyl-4-, -3-, or -2-pyridinium)porphyrin (TMPyP(X)) were prepared and purified by literature methods.¹⁵⁻¹⁷ Iron(II) in the form

Table I. Kinetic Data for Co^{III}-P/Fe-EDTA²⁻ Reactions^a

compd	E ^{ox} , V ^b	pK ₃	k _D , M ⁻¹ s ⁻¹ ^c	K, M ⁻¹ ^c	k _C , s ⁻¹
Co ^{III} -TPPS ³⁻	+1.06	4.6	2.0 × 10 ³	<10	
Co ^{III} -TAP ⁵⁺	+1.17	3.6	7.3 × 10 ³	460	1.6 × 10
Co ^{III} -TMPyP(3) ⁵⁺	+1.19	1.8	7.8 × 10 ⁴	530	1.5 × 10 ²
Co ^{III} -TMPyP(4) ⁵⁺	+1.19	1.4	8.7 × 10 ⁴	470	1.8 × 10 ²
Co ^{III} -TMPyP(2) ⁵⁺		-0.9	1.4 × 10 ⁵	770	1.8 × 10 ²

^a Conditions: I = 0.5 (NaCl/HCl); pH 5; 25 °C. ^b Potential for the Co^{III}-P/Co^{II}-P⁺ oxidation vs. NHE. ^c k_D = A, K = B, and k_C = A/B from eq 1.

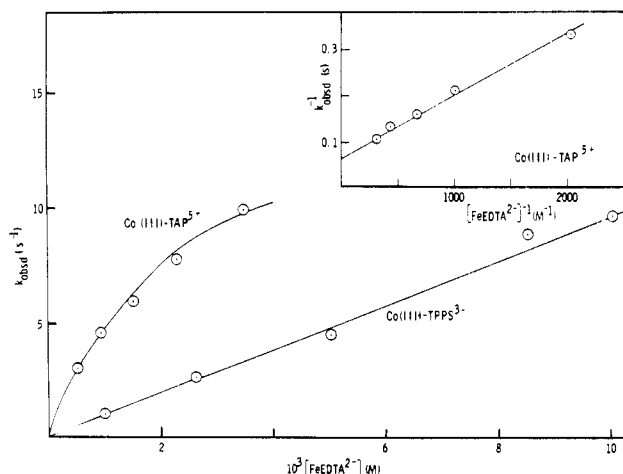


Figure 1. Graphs of k_{obs} vs. Fe-EDTA²⁻ for the Co^{III}-P/Fe-EDTA²⁻ reactions at 25 °C (Co^{III}-TPPS³⁻ data at I = 0.1, Co^{III}-TAP⁵⁺ data at I = 0.5). The insert is a plot of k_{obs} vs. [Fe-EDTA²⁻]⁻¹.

FeCl₂·4H₂O or Fe(NH₄)₂(SO₄)₂·6H₂O (both gave the same kinetic results) was dissolved in deaerated solutions and analyzed spectrophotometrically with *o*-phenanthroline.¹⁸ A stoichiometric amount of standardized deaerated EDTA was added to produce the air-sensitive Fe-EDTA²⁻. All reagents were handled in Hamilton glass syringes. The reactions were run under chromous scrubbed argon at 25 °C and followed on a Durrum-Gibson stopped-flow apparatus. The ionic strength (I) was maintained with NaCl/HCl, and 10⁻² M HOAc/NaOAc was the buffer. Ac and cyclic voltammetry¹⁹ using a polished glassy-carbon electrode and SCE was done on N₂-deaerated solutions at pH 4.5 (I = 0.1 M HCl/KCl, 0.01 M HOAc/NaOAc).

Results

While other groups have reported reduction potentials in aqueous solution for Co^{III/II} porphyrins with TMPyP(4) (E° = +0.42 V vs. NHE²⁰), TPPS (-0.41 V²¹), TAP (+0.38 V²²), we found only broad, ill-defined peaks in the expected potential ranges using slow-sweep ac voltammetry. However, one-electron-oxidation waves assigned to the ligand oxidation process Co^{III}-P = Co^{III}-P⁺ + e⁻ were readily observed under the same conditions, and such E^{ox} values are listed in Table I. Cyclic voltammetry studies gave one-electron-reduction potentials of 0.00 V for Mn^{III/II}-TMPyP(4) and -0.21 V for Mn^{III/II}-TPPS at pH 4.5.

The kinetics were followed at the Soret bands for the cobalt porphyrins. Under pseudo-first-order conditions with at least a 50-fold excess of Fe-EDTA²⁻ to Co(III)-P (ca. 10⁻⁶ M), the reactions were all first order in porphyrin for over 90% of the reaction, with an observed rate constant k_{obs} . For Co(III)-TPPS³⁻

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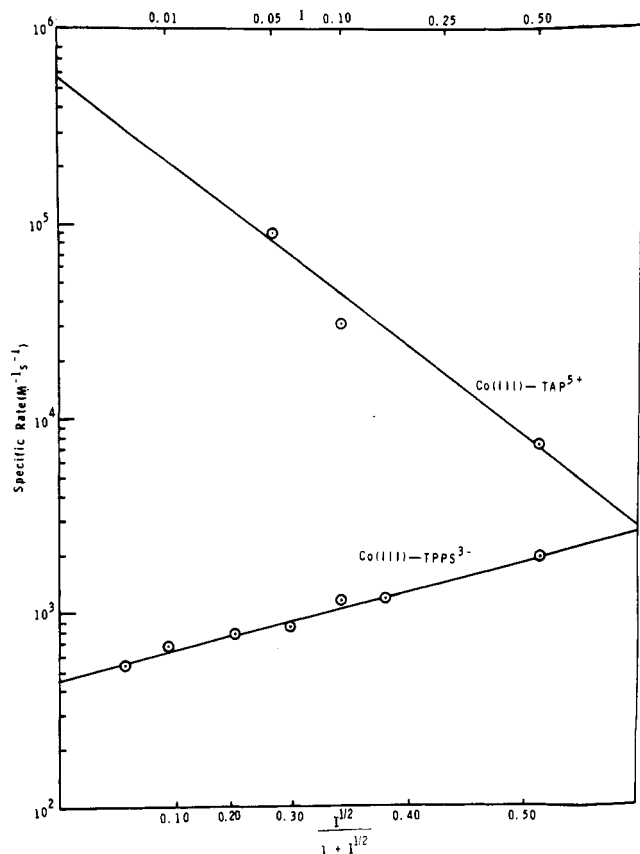


Figure 2. Plot of $\log k_D$ vs. $I^{1/2}/(1 + I^{1/2})$ for Fe-EDTA²⁻ reactions with Co^{III}-TPPS³⁻ and Co^{III}-TAP⁵⁺.

at pH 4.5 ($I = 0.1$), Figure 1 shows the reaction to be first order in Fe-EDTA²⁻ (1.0×10^{-2} – 5.0×10^{-4} M). The specific rate constant of $(1.02 \pm 0.02) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ was independent of pH in the range of 4.4–5.5, and a 5-fold excess of EDTA to Fe(II) did not alter the specific rate. Most of the reactions of the positive porphyrins were rather fast at $I = 0.1$ and were more conveniently followed at $I = 0.5$. A Co^{III}-TPPS³⁻ specific rate constant of $2.0 \times 10^3 \text{ m}^{-1} \text{ s}^{-1}$ was found under these conditions.

With all of the positively charged cobalt (III) porphyrins at $I = 0.5$, pH 4.5, plots of k_{obsd} vs. [Fe-EDTA²⁻] became less than first order in Fe-EDTA²⁻ as its concentration increased, as shown in Figure 1. The observed rate law was of the form

$$k_{\text{obsd}} = A[\text{Fe-EDTA}^{2-}]/(1 + B[\text{Fe-EDTA}^{2-}]) \quad (1)$$

Thus plots of $1/k_{\text{obsd}}$ vs. $1/[\text{Fe-EDTA}^{2-}]$ were linear (Figure 1) and the resulting A and B constants are listed in Table I. A comparison of the observed specific rates and those calculated by using eq 1 are in Table II.

Discussion

The one-electron ring oxidation potentials^{23a} for several metal-TMPyP(4) compounds are 0.32 ± 0.02 V more positive than

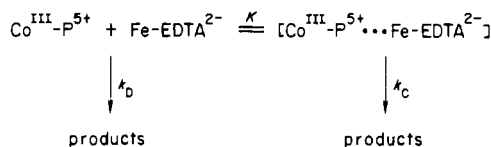
Table II. Observed and Calculated k_{obsd} Values^a

compd	[Fe-EDTA ²⁻], M	k_{obsd} , s ⁻¹	
		obsd	calcd ^b
Co ^{III} -TMPyP(2)	6.8×10^{-4}	90	62
	4.1×10^{-4}	45	44
	1.0×10^{-4}	13	13
	7.0×10^{-5}	9.2	9.3
	3.4×10^{-5}	4.7	4.6
Co ^{III} -TMPyP(3)	6.3×10^{-3}	120	110
	4.3×10^{-3}	110	100
	2.3×10^{-3}	77	79
	1.0×10^{-3}	44	52
	7.9×10^{-4}	40	43
Co ^{III} -TMPyP(4)	4.1×10^{-4}	28	26
	4.2×10^{-3}	130	120
	2.1×10^{-3}	90	92
	1.9×10^{-3}	91	88
	8.7×10^{-4}	51	54
Co ^{III} -TAP	8.2×10^{-4}	52	50
	4.0×10^{-4}	27	29
	3.3×10^{-3}	9.9	9.6
	2.3×10^{-3}	7.7	8.2
	1.5×10^{-3}	6.0	6.5
	9.9×10^{-4}	4.6	5.0
	4.9×10^{-4}	3.0	3.0

^a Conditions: $I = 0.5$ (NaCl/HCl); 25 °C; pH 5.0. ^b Calculated from data in Table I.

for the corresponding TPPS complexes, and we find for the cobalt(III) porphyrins a difference of 0.37 V. Our Mn^{III/II}-porphyrin reduction potentials are essentially the same as those reported by Harriman,²⁴ with the Mn^{III}-TMPyP(4) reduced at potentials 0.21 V more positive than for Mn^{III}-TPPS. The E° value for Mn^{III/II}-TAP²⁵ is -0.15 V. Rohrbach and co-workers²⁰ used a gold minigrad electrode and the OTLE technique to determine a potential of +0.42 V for the Co^{III/II}-TMPyP(4) reaction at $I = 0.5$. We were unable to reproduce this result using a polished glassy-carbon electrode.²⁶ Nevertheless, we are going to assume the Rohrbach potential for Co^{III/II}-TMPyP(4) and use the potentials for the better behaved manganese porphyrins to calculate values for the other cobalt porphyrins. Within the manganese porphyrin series, all compounds are high spin, with the same ligation number in acid solution. Within the cobalt porphyrin series, all compounds are low spin with similar coordination numbers. We have demonstrated before^{23b} that, in DMF solutions, the reduction potentials of iron(III) and manganese(III) porphyrins parallel one another, and we are assuming this in the present series of manganese and cobalt porphyrins.

The Fe-EDTA²⁻/Co^{III}-TPPS³⁻ reaction with both reactants negatively charged was first order in oxidant and reductant in the range investigated. For the positively charged cobalt(III) porphyrins and negative Fe-EDTA²⁻, eq 1 can be rationalized by assuming complexation [Co^{III}-P⁵⁺...Fe-EDTA²⁻] between the oppositely charged reactants. Two possibilities²⁷ are usually discussed:



For the continuous-intermediate mechanism, the complex forms and electron transfer (k_C) subsequently occurs. Thus, $k_{\text{obsd}} = k_C K [\text{Fe-EDTA}^{2-}] / (1 + k [\text{Fe-EDTA}^{2-}])$, and from eq 1, $A = k_C K$ and $B = K$. In the dead-end mechanism, the complex forms as a dead-end species, and electron transfer (k_D) proceeds via the

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uncomplexed reactants. Here, $k_{\text{obsd}} = k_{\text{D}}[\text{Fe-EDTA}^{2-}]/(1 + K[\text{Fe-EDTA}^{2-}])$, and $A = k_{\text{D}}$, $B = K$. Once the preequilibrium is established, the mechanisms are kinetically indistinguishable.

We tend to prefer the dead-end mechanism on the basis of the following considerations. First, the metal ion incorporation and acid-catalyzed zinc porphyrin solvolysis reactions²⁸ for TPSP⁴⁻ and TMPyP(4)⁴⁺ follow the same rate laws. Second, assuming the self-exchange rate constants for Co^{III/II} porphyrins are similar to one another and independent of porphyrin charge, as noted earlier²⁹ in Mn^{III/II}-porphyrin systems, the relative Marcus theory for outer-sphere reactions³⁰ predicts the ratio of the Fe-EDTA²⁻ reduction rates for Co^{III}-TMPyP(4)/Co^{III}-TPPS to be 59:1 [ratio = $[10 \exp(16.9 (\Delta E^\circ))]^{1/2}$ with $\Delta E^\circ = 0.21$ V from the Mn^{III/II}-porphyrin results]. The observed k_{D} ratio at $I = 0.5$ is 44:1. Third, the self-exchange rate constant²⁰ (k_{11}) for Co^{III/II}-TMPyP(4) is $20 \text{ M}^{-1} \text{ s}^{-1}$, and that³¹ for Fe^{III/II}-EDTA ($E^\circ = -0.12$ V) is $3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The Marcus equation predicts a cross-reaction rate constant of $15 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, close to the k_{D} of $8.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ observed for Co^{III}-TMPyP(4). Finally, the SO₂⁻ reduction rates of a series of Fe(III)³² and Mn(III)³³ porphyrins increase with a decrease in porphyrin basicity ($\text{p}K_3$), and the same trend is noted here. There is a linear relationship between E° and $\text{p}K_3$ ($\text{p}K_3$ for the H₄-P²⁺/H₃-P⁺ reaction³⁴), and an equation^{34,35} of the form $\log k_{\text{D}} = 5.7 - 0.53(\text{p}K_3)$ reproduces the Co^{III}-TAP, -TMPyP(4,3), and -TPPS rate data to $\pm 30\%$. $\text{p}K_{\text{a}1}$ values for the H₂O-Co^{III}-P/HO-Co^{III}-P reactions are 7.0 for Co^{III}-TPPS,³⁶ 6.0 for Co^{III}-TMPyP(4),¹⁵ and undeterminable¹⁶ for Co^{III}-TAP. Consistent with many outer-sphere reactions,²⁷ we find little dependence of rate upon pH in the region between 4.5 and 5.5, an indication that the aquo and hydroxy forms have similar reactivities.

Table I shows that K increases as the positive substituent moves closer to the metal center. Other than postulating a specific geometry involving perhaps an Fe-EDTA²⁻ group (radius ~ 4 Å) centered above one face of the porphyrin (core radius $\sim 5\%$ Å) prior to electron transfer, it is not clear at this stage why electrostatic interactions of Fe-EDTA²⁻ with positive substituents at

the periphery of the porphyrin lead to a dead-end complex. Many cases of complex formation between metalloproteins and small inorganic oxidants or reductants are known.^{37,38} The data are often considered in terms of a continuous-intermediate (CI) mechanism ($k = k_{\text{C}}K$), and lack of deviation from first-order kinetics simply implies that $K[\text{reagent}] < 1$. For Co^{III}-TPPS³⁻, $K \approx 10 \text{ M}^{-1}$ would have to be invoked. From the CI viewpoint, the three cobalt pyridylporphyrins and Co-TPPS would transfer electrons at similar rates ($k_{\text{C}} \approx 180 \text{ s}^{-1}$), which are somewhat faster than that shown for Co^{III}-TAP ($k_{\text{C}} = 16 \text{ s}^{-1}$). This seems a less productive hypothesis than the dead-end formulations advanced above.

For Fe-EDTA²⁻ reductions at $I = 0.5$, $k_{11} = 6 \text{ M}^{-1} \text{ s}^{-1}$ for Co^{III/II}-TMPyP(4) [$20 \text{ M}^{-1} \text{ s}^{-1}$ from Ru(NH₃)₆²⁺/Co^{III}-TMPyP(4) reactions²⁰], $k_{11} = 6 \text{ M}^{-1} \text{ s}^{-1}$ for Co^{III/II}-TAP with $E^\circ = +0.27$ V based upon E° for Co^{III/II}-TMPyP(4) and ΔE° from the Mn^{III/II} porphyrins [or $0.13 \text{ M}^{-1} \text{ s}^{-1}$ with use of the reported E° of $+0.38$ V²²], and $k_{11} = 4 \text{ M}^{-1} \text{ s}^{-1}$ for Co^{III/II}-TPPS³⁻ [with $E^\circ = +0.21$ V estimated in a similar fashion]. Using ¹H NMR techniques with Co^{III/II} tetraphenylporphyrins, Chapman and Fleischer⁹ find $k_{11} = 9.7 \text{ M}^{-1} \text{ s}^{-1}$ for Co^{III/II}-TPP(py)₂ and $0.13 \text{ M}^{-1} \text{ s}^{-1}$ for Co^{III}(py)₂/Co^{II}(py)-TPP in CHCl₃ solutions. While such k_{11} 's are not corrected for electrostatic work effects,¹⁰ the observed values are close to one another and appear to be independent of porphyrin charge type, at the ionic strength investigated.

A number of metalloporphyrin self-exchange rate constants have been reported: $k_{11} = 3.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (Mn^{III/II}-TPPS²⁹), $2.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (Mn^{III/II}-TAP²⁹), $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (H₂O-Fe^{III/II}-TMPyP(4)⁴¹), $> 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ((Im)₂-Fe^{III/II}-TMPyP(4)⁴¹), 10^7 - $10^8 \text{ M}^{-1} \text{ s}^{-1}$ (for various dicyano and bis(substituted imidazole) Fe^{II/III} porphyrins in Me₂SO by direct measurement⁴²), and $4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ (Ag^{III/II}-TPPS⁴³). Such metalloporphyrin k_{11} 's promise to tie together diverse observations in the porphyrin field.⁴⁴

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