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Kinetics of the Reduction of Cyano Cobalt(III) Porphyrins by Dithionite

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Due to the stability of dithionite ($S_2O_4^{2-}$) in aqueous base, many electron transfer kinetic studies have been done with this reductant and base soluble trivalent metalloporphyrins. Such work includes reduction to their divalent forms of dipyridine iron (III) [1], pyridinated manganese(III) [2], aquohydroxy manganese(III) [3, 4], cobalt(III) [5] and iron(III) [1] porphyrins. As an extension of our previous work with 2,4-disubstituted deuteroporphyrin dicyano iron(III) porphyrins with dithionite [6], we report the kinetic behavior of the corresponding reductions of cyano cobalt(III) porphyrins. The cyano cobalt(III) and iron(III) porphyrins behave in a remarkably different fashion.

Experimental

The cobalt(III) porphyrin esters prepared before [7] were hydrolyzed in base and precipitated with dilute HCl. The absorption spectra of these complexes in base are similar to those found in the literature [8, 9]. For Co^{III}-protoporphyrin -IX in 0.1 *M* NaOH, 0.2 *M* NaCl, λ_{max} 418 nm ($\epsilon = 1.0 \times 10^5$ M^{-1} cm^{-1}), 536 nm (1.0×10^4), and 571 nm ($9.9_6 \times 10^3$). In 0.1 *M* NaCN, 0.1 *M* NaOH, 0.1 *M* NaCl, λ_{max} 439 nm ($\epsilon = 9.6 \times 10^4$ M^{-1} cm^{-1}), 551 nm (1.2×10^4) and 548 nm, sh, ($5.7_5 \times 10^3$). After reduction by dithionite in deaerated solutions (N_2 scrubbed with Cr^{2+}), the cyano Co^{II}-protoporphyrin shows λ_{max} 439 nm (4.1×10^4 M^{-1} cm^{-1}) and 560 nm (1.0×10^4). Isosbestic points are found at 584, 538, and 474 nm, as the cyano Co^{III} complex is transformed into the Co^{II} form. The kinetics of the dithionite reductions were run at I = 0.3, 25 °C, and followed spectrophotometrically at 512 nm under pseudo first order conditions with an excess of $Na_2S_2O_4$ and total cyanide to total porphyrin (*ca.* 10^{-5}*M*). Dithionite concentrations were analyzed by titration against ferricyanide [10].

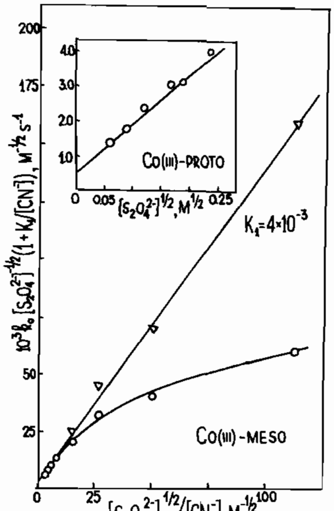

Fig. 1. Kinetic results for the reduction of cyano-cobalt(III) porphyrins by dithionite. Insert is a plot of $k_0/(S_2O_4^{2-})^{1/2}$ vs. $(S_2O_4^{2-})^{1/2}$ for Co^{III}–protoporphyrin, (CN^-) = 0.1 *M*, pH 13. The lower curve is a plot of $k_0/(S_2O_4^{2-})^{1/2}$ *vs.* $(S_2O_4^{2-})^{1/2}/(CN^-)$ for Co^{III}–mesoporphyrin, and the upper curve assumes $K_1 = 4 \times 10^{-3}$ for eqn. 3.

Results

The cobalt(III) porphyrins were mixed with 10^{-3} *M* cyanide, and allowed to equilibrate under N_2 for one hour before addition of dithionite. The reactions were found to be cleanly first order in porphyrin over three half-lives, and at constant cyanide and dithionite concentration the observed rate constant, k_0, was independent of pH from pH 11.5 to 13.0. At the high and constant cyanide concentration of 0.1 *M*, the insert in Fig. 1 for Co^{III}–protoporphyrin shows the linear relationship between $k_0/(S_2O_4^{2-})^{1/2}$ and $(S_2O_4^{2-})^{1/2}$, over a twenty five fold range in dithionite concentration. For all of the porphyrins, the intercept, found by least squares analysis was small but real. At constant dithionite levels, as the cyanide concentration decreased, the k_0 values increased and approached a limiting value. For the Co^{III}–mesoporphyrin, Fig. 1 itself shows the observed curvature of plots of $k_0/(S_2O_4^{2-})^{1/2}$ *vs.* $[(S_2O_4^{2-})^{1/2}/(CN^-)]$. For each porphyrin, a value of K_1 was chosen to give the best least-squares linear plots of $[k_0/(S_2O_4^{2-})^{1/2}$ $(1 + K_1/(CN^-))]$ *vs.* $[(S_2O_4^{2-})^{1/2}/(CN^-)]$, as noted for Co^{III}–mesoporphyrin ($K_1 = 4 \times 10^{-8}$) in Fig. 1. The empirical rate law is thus

$$k_0/(S_2O_4^{2-})^{1/2}(1 + K_1/(CN^-)) = A + B[(S_2O_4^{2-})^{1/2}/(CN^-)] \quad (1)$$

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TABLE I. Rate Data for the Dithionite Reductions of Cyano Cobalt(III) Porphyrins, 25 °C, I = 0.3.

Cobalt(III) Porphyrins	$E^r_{1/2}(1)$ (volts)[a]	K_1[b]	k_1 (M^{-1} s^{-1}) $SO_2^-/(NC)_2-Co^{III}-P$	k_2 (M^{-1} s^{-1}) $S_2O_4^{2-}/(NC)-Co^{III}-P-OH_2$
Mesoporphyrin-IX	−1.82	4×10^{-3}	160	3.5×10^{-1}
Deuteroporphyrin-IX	−1.77	6×10^{-3}	100	2.3×10^{-1}
Protoporphyrin-IX	−1.71	10×10^{-3}	40	1.8×10^{-1}
2,4-dibromodeuteroporphyrin	−1.57	25×10^{-3}	30	5.0×10^{-2}

[a] One electron reduction potentials of the metal free porphyrin esters to the mono-anions in DMF *vs.* $Ag/AgNO_3$ (0.10 *M* in DMF). See Refs. 19 and 20. [b] K_1 for the reaction $H_2O + (NC)_2-Co^{III}-P = (NC)-Co^{III}-P-OH_2 + CN^-$, pH 12.

In the absence of cyanide at pH 13, the reduction of Co^{III}–mesoporphyrin by dithionite was probed by stopped flow methods. The reactions were found to be biphasic, with approximate half-times in the 0.6 second range. The reactions appeared to be independent of dithionite concentration from 5×10^{-2} to 1×10^{-3} *M*.

Discussion

One possible reaction scheme for the cobalt(III) porphyrin reductions is as follows:

$$S_2O_4^{2-} \overset{K_0}{\rightleftharpoons} 2SO_2^- \qquad (2)$$

$$H_2O + (NC)_2-Co^{III}-P \overset{K_1}{\rightleftharpoons} (NC)-Co^{III}-P-OH_2 + CN^- \qquad (3)$$

$$SO_2^- + (NC)_2-Co^{III}-P \xrightarrow{k_1} \text{Products} \qquad (4)$$

$$S_2O_4^{2-} + (NC)-Co^{III}-P-OH_2 \xrightarrow{k_2} \text{Products} \qquad (5)$$

With K_0 and K_1 rapid preequilibria, the derived rate law is

$$k_0/(S_2O_4^{2-})^{1/2}(1 + K_1/(CN^-) = k_1K_0^{1/2} + k_2K_1[S_2O_4^{2-})^{1/2}/(CN^-)] \qquad (6)$$

By comparison to eqn. 1, $K_1 = K_1$, $A = k_1K_0^{1/2}$ and $B = k_2K_1$. Using $K_0 = 1.4 \times 10^{-9}$ *M*, for the dithionite equilibria [11], the derived K_1, k_1 and k_2 values are listed in Table I.

The reduction of the four Co^{III} porphyrins in basic cyanide solutions by dithionite gives evidence for an equilibrium between $(NC)_2-Co^{III}-P$ and $(NC)-Co^{III}-P-OH_2$, each of which reacts with a different form of dithionite. Such results would have been more reassuring if spectral evidence leading to an independent evaluation of K_1 could have been obtained. In the region of the calculated K_1 values, however, the spectral changes with cyanide were small, and insufficient for equilibrium calculations, as might be expected for a mono to di-cyano ligation. In basic solution a mono-hydroxy/mono-cyano cobalt porphyrin might be expected to exist. Nevertheless, the reduction kinetics were definitely independent of pH from 11.5 to 13.

Cobalt(III) porphyrins themselves in hydroxide media are presumably mixtures of monomers, dimers and polymers, as evidenced by axial ligation studies [12], as well as the biphasic dithionite independent reduction kinetics mentioned earlier, and such behavior has been known for over forty years [8]. Most negatively charged carboxylic acid porphyrins are dimeric in base [13], and apparently cobalt(III) complexation will monomerize some of these initially dimeric species [14]. A dicyano cobalt(III) complex of etioporphyrin has been isolated [15], while other workers have obtained only mono-aquo/mono-cyano adducts [16].

SCN^- adds to aquo cobalt(III) porphyrins in distinct steps [7], with the first formation constant for the porphyrins used in this study *ca.* 10^5 M^{-1}. The less basic cobalt(III)–tetra(4-carboxyphenyl)porphyrin [12] has $K_1^f = 2.9 \times 10^3$ M^{-1}, with the second formation constant, $K_2^f = 7.4$ M^{-1}. With cyanide, our $K_2^f (= K_1^{-1})$ values range from 40 M^{-1} to 250 M^{-1}, and thus the large K_1^f and smaller K_2^f values demanded by our interpretations of the cyano cobalt(III) reactions may not be inconsistent with those measured for SCN^-. The five-coordinated behavior [7] of cobalt(II) porphyrins with nitrogenous bases might suggest that $(NC)-Co^{II}-P$ is the product in these reactions, although a six-coordinated $(NC)-Co^{II}-P-OH_2$ cannot be excluded.

SO_2^- is found to be the primary reductant with $(py)_x-Mn(III)$ [2], $(NC)_2-Fe(III)$ [6], $(py)_2-Fe(III)$ [1], $(py)_2-Co(III)$ [2, 5], and now $(NC)_2-Co(III)$ porphyrins. The relative rates for the mesoporphyrin ligand are $(NC)_2-Fe^{III}(8 \times 10^7 M^{-1}$ $s^{-1}) > (py)_2-Fe^{III}(4 \times 10^7 M^{-1}$ $s^{-1}) > (py)_x-Mn^{III}(7 \times 10^5 M^{-1}$ $s^{-1}) > (py)_2-Co^{III}(4 \times 10^3$ M^{-1} $s^{-1}) > (NC)_2-Co^{III}(1.6 \times 10^2$ M^{-1} $s^{-1})$. The reactions are outer sphere in character, and the relative rates are not unreasonable. Thus the self exchange rates for low spin Fe^{II}/Fe^{III} porphyrins [6, 18] are $\geqslant 10^9$ M^{-1} s^{-1}, and *ca.* 20 M^{-1} s^{-1} for Co^{II}/Co^{III} porphyrins [19]. The low-spin d^5 to d^6 transformation leads to crystal field stabilization effects for iron porphyrin reductions, and is disfavored for the low-spin d^6 to d^7 process for cobalt porphyrins. It is usually found [2, 6] that the SO_2^- reduction rates increase with a decrease in free-base porphyrin basicity, where this basicity is measured by $E^{I}_{1/2}(1)$, the first reduction potential of the free base porphyrin to its monoanion [20, 21]. $E^{I}_{1/2}$ (1) values generally parallel the metalloporphyrin reduction potentials [22, 23]. and the best oxidizing agent metalloporphyrins are found to be reduced the fastest. The present $(NC)_2$–Co^{III} and (NC)–Co^{III}–P–OH_2 porphyrins show the opposite trend, where k_1 and k_2 are directly proportional to $E^{I}_{1/2}(1)$, that is, the presumed least powerful oxidant is reduced the fastest. Electron donation by the porphyrin might favor a product containing a sigma donor (H_2O) and pi acceptor(CN^-), and such product stability might rationalize the rate dependence on porphyrin basicity for both the SO_2^- and $S_2O_4^{2-}$ pathways. In this connection, little dependence of the reduction rate on the nature of the porphyrin was found in the (Co-$(CN)_5^{3-}$/$(NC)_2$–Fe^{III})porphyrin reactions [23].

While the dicyano cobalt(III) porphyrins react with SO_2^-, the mono-cyano cobalt(III) form prefers $S_2O_4^{2-}$ as the reductant. Related work has shown that hydroxy/aquo cobalt(III) porphyrins [5] react with both SO_2^- and $S_2O_4^{2-}$, whereas the bispyridine and di-aquo forms favor SO_2^-. Pinnell and Jordan [24] have shown that for several $(NH_3)_5Co^{III}$–X complexes, the nature of -X determines the reactant, with SO_2^- as outer sphere, and $S_2O_4^{2-}$ as a postulated bridged inner-sphere species. Mehrotra and Wilkins have studied dithionite reductions [25] of a number of chelated Co^{3+}, Fe^{3+} and Mn^{3+} complexes, with similar results. At present, neither the structure nor the oxidation potential of the metal complex allows a prediction of its preference for SO_2^- or $S_2O_4^{2-}$ as the favored reductant. It is clear, however, that the presence of cyanide in the coordination sphere of these cobalt(III) porphyrins stabilizes the cobalt center towards reduction by dithionite.

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