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Pentacyanocobaltate(II) Reductions of Dicyano(porphyrinato)iron(III) Complexes

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Redox reactions of iron(II) and iron(III) porphyrins are of interest since the results of such studies may help to elucidate electron transfer behavior in hemoprotein chemistry [1]. Inner sphere pathways have been suggested [2] in the reduction of (H_2O/OH^-)–Fe^{III}–porphyrins with Cr^{2+}, while outer sphere mechanisms have been found with $Ru(NH_3)_6^{2+}$ as the reductant [3]. We report a study of the reduction to their divalent forms of a series of dicyano(porphyrinato)iron(III) complexes with pentacyanocobalate(II), a reagent for which both inner and outer sphere components can be delineated [4].

Experimental

The iron(III) porphyrins were obtained from Man-Win Chemicals, Washington, DC. The reactions were run at 25 °C, I = 0.5 ($NaOH/NaCN/NaClO_4$), and the solutions deareated with chromous scrubbed N_2. Spectrophotometric titrations in the Soret region indicated that the $(NC)_2Fe^{III}$–P adducts were fully formed above 10^{-2} *M* cyanide concentration at pH = 12. Reduction of these cyano ferric porphyrins under such conditions with either dithionite ($S_2O_4^{2-}$) or $Co(CN)_5^{3-}$ formed the corresponding $(NC)_2Fe^{II}$–P derivatives, whose peak maxima were in the same positions as found for the pyridine hemochromes [5]. The kinetics were studied on a Gibson-Durrum stopped flow apparatus, under pseudo first order conditions with an excess of Co^{2+} to total porphyrin (*ca.* 10^{-6} *M*). The Co^{2+} in one syringe at pH 5 was mixed with $(NC)_2Fe^{III}$–P from a second syringe containing total cyanide high enough to saturate the porphyrin, and leave (CN^-) greater than 10^{-2} *M*, after the formation of $Co(CN)_5^{3-}$. The reactions went to completion, and were first order in porphyrin and cobalt.

Results and Discussion

The observed rate law for the reduction of $(NC)_2Fe^{III}$–P by $Co(CN)_5^{3-}$ was of the form:

$$k_{obs}/[Co^{2+}] = k_1 + k_2(CN^-) \quad (1)$$

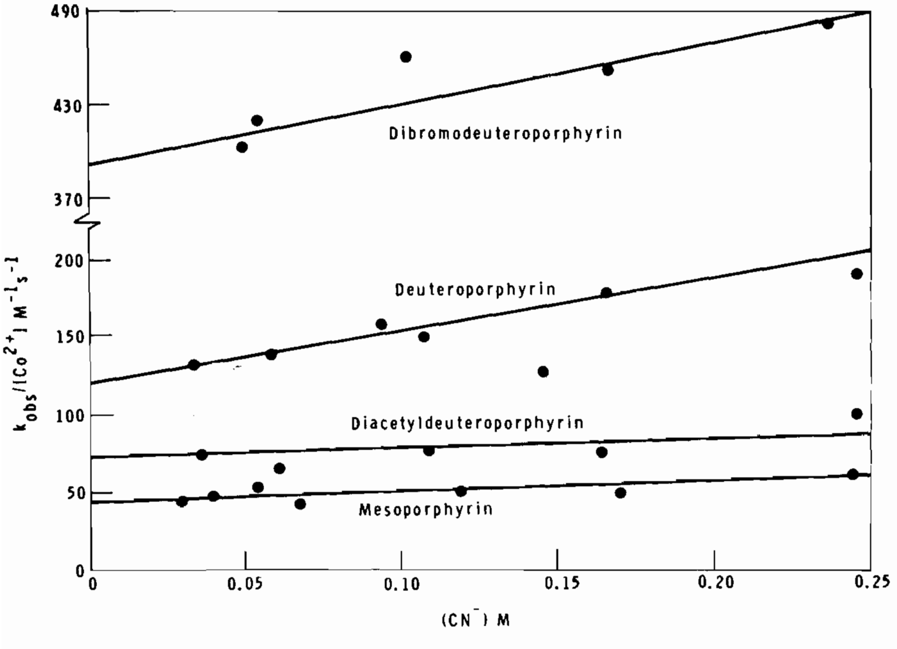

Fig. 1. Plot of the specific rates of the $Co(CN)_5^{3-}/(NC)_2Fe^{III}$–porphyrin reactions *vs.* (CN^-).

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TABLE I. Pentacyanocobaltate(II) Reductions of Dicyano(porphyrinato)iron(III) Complexes.

$(NC)_2Fe^{III}$–P	k_1 $(M^{-1}\ s^{-1})^a$	k_2 $(M^{-2}\ s^{-1})^a$	E^{red} (Volts)^b	k $(M^{-1}\ s^{-1})$ $(SO_2^-/(NC)_2Fe^{III}$–P)
Mesoporphyrin	40	70	−0.22	8.0×10^7
Deuteroporphyrin	120	340	−0.21	9.0×10^7
Protoporphyrin	80	480	−0.18	1.5×10^8
3,8-dibromodeuteroporphyrin	390	390	−0.15	1.8×10^8
ms-Tetra(4-sulfonatophenyl)porphyrin^c	400	<70	−0.14	–
3,8-diacetyldeuteroporphyrin	72	60	−0.12	2.6×10^8

^{a}25 °C, I = 0.5 ($NaOH/NaCN/NaClO_4$), pH = 12. ^{b}Reduction potential at pH = 9 for $(NC)_2Fe^{III}$–P + e^- = $(NC)_2Fe^{II}$–P (*vs.* NHE). ^{c}Data from Ph.D. thesis of V. Taniguchi, Univ. of California, Irvine, 1978.

where $(CN^-) = [Cn^-] - 5\ [Co^{2+}]$. Representative results are shown in Fig. 1. A reasonable mechanism is:

$$Co(CN)_5^{3-} + CN^- = Co(CN)_6^{4-} \qquad K \tag{2}$$

$$Co(CN)_5^{3-} + (NC)_2Fe^{III}\text{–P} \rightarrow \text{Products} \qquad k_I \tag{3}$$

$$Co(CN)_6^{4-} + (NC)_2Fe^{III}\text{–P} \rightarrow \text{Products} \qquad k_O \tag{4}$$

The derived rate law would be of the form:

$$k_{obs}/[Co^{2+}] = k_I + k_O K(CN^-)/[1 + K(CN^-)] \tag{5}$$

Since the value of the equilibrium constant K could be [4] from 10^{-1} to 10^{-4} M^{-1}, the term $[1 + K(CN^-)] \simeq 1$, and thus $k_1 = k_I$, and $k_2 = k_O K$. The k_I and k_2 values are found in Table I.

The results show that from 10^{-2} to 0.5 *M* CN^-, the observed specific rate constant increases by no more than a factor of six for the different complexes. Such a marginal observed cyanide effect is partially due to the small value of K. Hence for the porphyrins in general, the outer sphere rate constants, k_O, could be between 10^3 to 10^6 $M^{-1}\ s^{-1}$, greater than the inner sphere terms, k_I. This might be due to the smaller amount of reorganizational free energy expected for an outer sphere pathway, in contrast to the inner sphere pathway, where substitution, reorganization or dissociation might be rate limiting.

In previous work, with over one hundred free base porphyrins under identical conditions [6, 7], we have measured in DMF the parameter $E^r_{1/2}$ (1), the first reduction potential of the metal free porphyrin H_2–P forming the radical anion H_2–P^-. $E^r_{1/2}$ (1) has been found to correlate a wide range of porphyrin and metalloporphyrin equilibrium and kinetic data. In particular, there is a linear relationship between the reported [8] reduction potentials for the process

$$(NC)_2Fe^{III}\text{–P} + e^- = (NC)_2Fe^{II}\text{–P} \qquad E^{red} \tag{6}$$

at pH = 9 (*vs.* NHE), and $E^r_{1/2}(1)$, (*vs.* Ag/Ag^+ (0.10 *M*) in DMF) of the form

$$E^{red} = 0.38 + 0.33\ E^r_{1/2}\ (1) \tag{7}$$

Using this equation, the reduction potentials of the iron porphyrins studied are shown in the Table. An increase in the electron withdrawing capacity of the peripheral porphyrin substituents increases the reduction potentials of the $(NC)_2Fe^{III}$–porphyrins. Dithionite reductions of the bis-ligated Fe(III), Co(III) and Mn(III) porphyrins, which involve SO_2^- as the reductant are presumably outer sphere in character. For a given metal [9, 10], the reduction rates parallel the porphyrin and metalloporphyrin reduction potentials, as shown in the Table for the $S_2O_4^{2-}/(NC)_2$-Fe^{III}–P system.

In the present pentacyanocobaltate(II) case, however, while there appears to be a trend of slightly higher k_I and k_O values with increasing E^{red}, the diacetyl derivative, having the highest thermodynamic potential to be reduced, is in fact reduced at a rate similar to that found for the weakest oxidizing agent in this series, mesoporphyrin, which has basically saturated substituents around the porphyrin ring. This may be an indication that the high k_I values found for the tetrasulfonated and dibromo complexes involve inner sphere activated complexes such as $[(NC)_5Co^{II}\text{–Br–P–}Fe^{III}\text{–}(CN)_2]^{\ddagger}$, with electron transfer through groups attached to the beta pyrrole (–Br) or meso (^-O_3S–C_6H_4–) positions of the porphyrin nucleus. In this connection, it is noted that chromium has been demonstrated to bind to the sulfonato groups of cobalt tetrasulfonated porphyrins, subsequent to chromous reduction [11]. Such peripheral pathways possibly occur along with axia axial pathways, as $[(NC)_5Co^{II}{-}NC{-}Fe^{III}{-}P]^{\ddagger}$, where the initial $(NC)_5Co^{III}{-}(NC)$ product isomerizes into the more stable $Co(CN)_6^{3-}$ species, as demonstrated in the $Co(CN)_5^{3-}/(NH_3)_5Co(CN)^{2+}$ reaction [12].

For the cobalt ammine complexes, reactants of the same charge were found [4] to have similar outer sphere rates with $Co(CN)_6^{4-}$. While $Co(NH_3)_6^{3+}$ reacts primarily through an outer sphere pathway ($k_I \leqslant 4 \times 10^2$ M^{-1} s^{-1}, $k_2 = 8 \times 10^4$ M^{-2} s^{-1}), the species $(NH_3)_5CoCN^{2+}$ utilizes both pathways, ($k_I = 2.9 \times 10^2$ M^{-1} s^{-1}, $k_2 = 4.5 \times 10^3$ M^{-2} s^{-1}), as is found in the present $(NC)_2Fe^{III}{-}P$ case. Work is in progress to further probe the postulated axial–peripheral pathways in metalloporphyrin reductions.

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References

1 C. Castro, in 'The Porphyrins', D. Dolphin, ed., Academic Press, New York, NY, 1978, Vol. 5, Part C, Chap. 1.
2 J. Reid and P. Hambright, *Inorg. Chem., 17,* 2329 (1978).
3 R. Pasternack and E. Spiro, *J. Amer. Chem. Soc., 100,* 968 (1978).
4 J. Candlin, J. Halpern and S. Nakamura, *J. Amer. Chem. Soc., 85,* 2517 (1963).
5 R. DeNello and C. Chang, in Ref. 1, Vol 1, Part A, Chap. 7.
6 P. Worthington, P. Hambright, R. Williams, J. Reid, A. Shamim, J. Turay, C. Burnham, D. Bell, R. Kirkland, R. Little, N. Datta-Gupta, and B. Eisner, *J. Inorg. Biochem., 12,* 000 (1980).
7 R. Williams and P. Hambright, *Bioinorg. Chem., 9,* 537 (1978).
8 A. Martell and M. Calvin, 'Chemistry of the Metal Chelate Compounds', Prentice-Hall, Englewood, New Jersey, 1952, p. 385.
9 P. Worthington and P. Hambright, unpublished results.
10 P. Hambright and P. Chock, *Inorg. Chem., 13,* 3029 (1974).
11 E. Fleischer and C. Cheung, *J. Amer. Chem. Soc., 98,* 8381 (1976).
12 S. Nakamura, *Ph.D. Thesis,* University of Chicago, 1964.