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Relationship between Porphyrin Basicity and Thiocyanate Anation Rates of Cobalt(III) Porphyrins in Neutral Detergent Solutions

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Mechanistic kinetic studies on porphyrin and metalloporphyrin systems are usually done in aqueous solution using synthetic porphyrins made water soluble by virtue of *N*-methylpyridinium, sulfonic acid, or carboxylic acid functions.[1] While these peripheral charge-type variations modify porphyrin reactivity, such charge effects can never be clearly separated from the basicity effects of the central porphyrin nitrogen atoms, since charge and basicity often parallel one another. Uncharged water-insoluble disubstituted deuteroporphyrin esters and related natural porphyrins offer a wide range of nitrogen basicities and can be conveniently studied in aqueous detergent solutions.[2,3] We report (a) a comparison of equilibrium and kinetic parameters for the complexation of thiocyanate by synthetic water-soluble cobalt(III) porphyrins both in the presence and in the absence of a neutral detergent and (b) anation studies of water-insoluble cobalt(III) porphyrins of varying basicity in the same detergent media.

Experimental Section

The cobalt(II) porphyrins were purified chromatographically and air-oxidized to their Co(III) forms. The Co(II) disubstituted deuteroporphyrin esters have their Soret bands at ca. 412 nm, while those of Co(III) are at ca. 427 nm. Cobalt(III) uroporphyrin I, prepared either by air-oxidation under acidic conditions in detergent, in aqueous basic solution, or with DDQ (2,3-dichloro-5,6-dicyanobenzoquinone) in benzene, gave identical kinetic results.

Table I. Effect of the Neutral Detergent Triton X-100 on the Cobalt(III)–Porphyrin–SCN Formation Constant and Anation Rate[a]

	k_f, M^{-1} s^{-1}		$10^{-3}K$, M^{-1}	
porphyrin[b]	H_2O	detergent	H_2O	detergent
TMpyP(4)	2.1[c]	3.0	6.4[c]	7.8
TMpyP(3)	2.8[d]	3.7	3.4[d]	28.0
$TPPS_4$	157[e]	200	11.0[e]	24.3

[a] 25 °C, pH 1.5, $\mu = 0.5$ $NaClO_4/HClO_4$, H_2O or 2% Triton X-100. [b] TMpyP is tetrakis(4(or 3)-*N*-methylpyridyl)porphyrin; $TPPS_4$ is tetrakis(4-sulfonatophenyl)porphyrins. [c] Pasternack, R.; Cobb, M. *J. Inorg. Nucl. Chem.*, **1973**, 35, 4327; Ashley, K.; Berggren, M; Cheng, M. *J. Am. Chem. Soc.*, 1975, 97, 1422. [d] Williams, G. N; Hambright, P. *Bioinorg. Chem.*, 1977, 7, 267. [e] Our data on Co^{III}-$TPPS_4$ in water is in reasonable agreement with that of Ashley, K; Au-Young, S. *Inorg. Chem.*, **1976**, 15, 1937.

Table II. Thiocyanate Formation Constants and Anation Rates of Cobalt(III) Porphyrins in 2% Triton X-100[a]

porphyrin[b]	pK_3	k_f, M^{-1} s^{-1}	$10^{-3}K$, M^{-1}	peripheral charge
$TPPCOO^-$	6.1	450[c]	3	−4
MPDME	5.9	333	114	0
DPDME	5.6	238	36	0
$TPPS_4$	4.9	200	24	−4
Uro I	3.4	26.4	16	0
Br_2DPDME	3.0	22.7	114	0
TPPCOOH	2.9	20.1	143	0
TMpyP(3)	2.0	3.7	28	+4
TMpyP(4)	1.6	3.0	8	+4

[a] 25 °C, pH 1.5, $\mu = 0.5$ $NaClO_4/HClO_4$. [b] TPPCOOH, tetrakis(4-carboxyphenyl)porphyrin; MPDME, mesoporphyrin IX dimethyl ester (DME); DPDME, deuteroporphyrin IX DME; $TPPS_4$, tetrakis(4-sulfonatophenyl)porphyrin; Uro I, uroporphyrin I; Br_2DPDME, 2,4-dibromodeuteroporphyrin IX DME; TMpyP(X), tetrakis(4(or 3)-*N*-methylpyridyl)porphyrin. [c] k_f and K in H_2O; data from Pasternack, R; Parr, G. *Inorg. Chem.*, **1976**, 15, 3087.

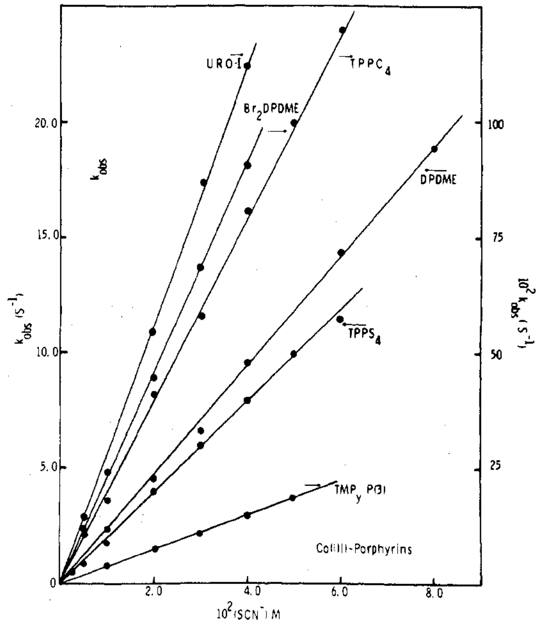

Figure 1. Plots of k_{obsd} vs. $[SCN^-]_0$ for the anation of cobalt(III) porphyrins in 2% Triton X-100 at 25 °C, pH 1.5, $\mu = 0.5$ $(HClO_4/NaClO_4)$. The porphyrin abbreviations are listed in Table II.

Spectroscopic grade Triton X-100, a neutral detergent, was added (2%) in some kinetic runs but not in others. All experiments were maintained at 25 °C, pH 1.5, and ionic strength 0.5 $(HClO_4/NaClO_4)$. The basicity parameters, pK_3, for the monocation–free base porphyrin equilibrium $(H_3\text{-}P)^+/(H_2\text{-}P)$ were measured in 2.5% sodium dodecyl sulfate and obtained from the literature.[2,4]

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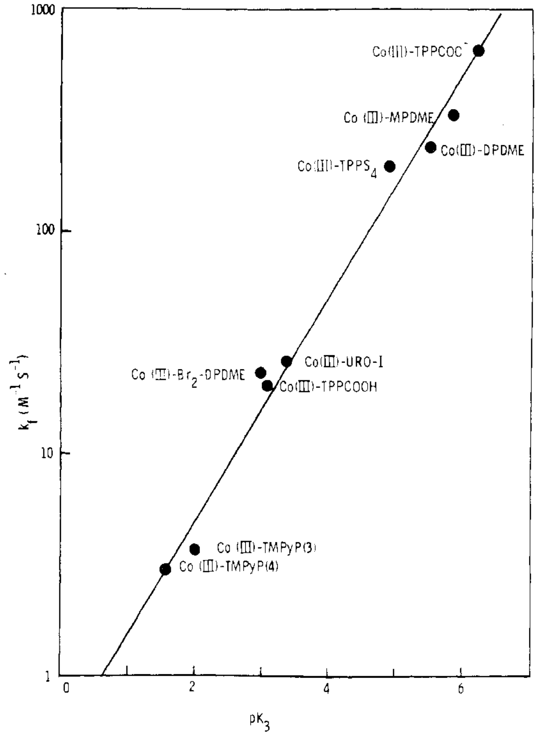

Figure 2. Plot of the forward anation rate constant k_F (semilog plot) vs. the free base porphyrin basicity parameter, pK_3.

Results

The equilibrium constants, K, for SCN$^-$ addition to the cobalt(III) porphyrins (eq 1) were determined spectrophotometrically.

$$\mathrm{Co^{III}\text{-}P + SCN^- = NCS\text{-}Co^{III}\text{-}P} \quad K,\ k_f,\ k_r \tag{1}$$

By using an excess of SCN$^-$ over total porphyrin, the anation rate law was found to be first order in porphyrin. The observed rate constant, k_{obsd}, was of the form $k_{obsd} = k_f[\mathrm{SCN^-}]$. Typical linear k_{obsd} vs. [SCN$^-$] plots are presented in Figure 1. The observed anation rate constants for cobalt(III) uroporphyrin I were independent of pH between pH 1 and 2.5. Since pK_a values for the H_2O-Co^{III}-P/HO-Co^{III}-P reactions are above 4, H_2O-Co^{III}-P is considered the reactant at pH 1.5. Co^{III}-P-(SCN)$_2$ forms at much higher SCN$^-$ concentrations than used in this study, and k_f for the first SCN$^-$ addition is orders of magnitude smaller than that for the second SCN$^-$ process.[5,6]

Table I shows a comparison of equilibrium and kinetic results measured for three water-soluble porphyrins with and without the neutral detergent. Table II is a summary of the cobalt(III)–porphyrin anation data measured in the detergent.

Discussion

Although there have been many studies of the properties of porphyrins and metalloporphyrins in detergent systems,[1-4] a comparison has never been made between the same reaction parameters in water and detergents. Such a comparison is shown in Table I between the thiocyanate equilibrium constants and anation rates with three water-soluble porphyrins in the presence and absence of the neutral detergent Triton X-100. In general, there is less than a factor of 2 increase in k_f and K when going from water to the detergent conditions, and such similarities are generally found in detergent–solvent comparisons.[7] The kinetics of copper incorporation into tetrakis(4-*N*-methylpyridyl)porphyrin in water exhibits an anion term in the rate law,[8] and a similar term was found in the Triton X-100 media.[9] We therefore have some confidence in kinetic comparisons between water-soluble and water-insoluble porphyrins, both run in this detergent.

Such comparisons are shown in Table II. The formation constants, K, are relatively insensitive to the anation rates and the basicity parameters, pK_3. It is noted, however, that k_f increases with an increase in porphyrin basicity. A plot of log k_f vs. pK_3 is linear (Figure 2) and can be described by the equation

$$\log k_f = 0.5\mathrm{p}K_3 - 0.3 \tag{2}$$

This linear free energy relationship is followed by cobalt(III) porphyrins with positive, neutral, or negative peripheral substituents. An interesting case is [tetrakis(4-carboxyphenyl)porphyrinato]cobalt(III). Under our conditions at pH 1.5, the carboxylic acid groups are protonated, and a lower pK_3 and anation rate are found in comparison to the ionized porphyrin form at pH ≥5.

Although noted before,[5,6] our data clearly show a porphyrin cis effect on the cobalt(III)–porphyrin anation rate process. The implication is that the central porphyrin nitrogen atom basicity, rather than the peripheral charge, accounts for the cis behavior. This basicity effect, in which a more basic porphyrin produces more labile Co(II) character at the cobalt center, is consistent with a dissociatively activated substitution mechanism. Such a conclusion is in agreement with studies in which, for the same cobalt(III) porphyrin, k_f is found to be relatively independent of the nature of the entering nucleophile.[10,11]

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Registry No. triton X-100, 9002-93-1; SCN$^-$, 302-04-5; H_2O-Co(III)-TMpyP(4), 67070-03-5; H_2O-Co(III)-TMpyP(3), 67070-04-6; H_2O-Co(III)-TPPS$_4$, 67113-92-2; NCS-Co(III)-TMpyP(4), 67070-05-7; NCS-Co(III)-TMpyP(3), 67070-06-8; NCS-Co(III)-TPPS$_4$, 67070-07-9; H_2O-Co(III)-MPDME, 67070-08-0; H_2O-Co(III)-DPDME, 67070-09-1; H_2O-Co(III)-UroI, 67070-10-4; H_2O-Co(III)-Br$_2$DPDME, 67070-11-5; H_2O-Co(III)-TPPCOOH, 67070-12-6; NCS-Co(III)-MPDME, 67070-13-7; NCS-Co(III)-DPDME, 67070-14-8; NCS-Co(III)-Uro I, 67070-15-9; NCS-Co(III)-Br$_2$DPDME, 67070-16-0; NCS-Co(III)-TPPCOOH, 67070-17-1.

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