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Kinetic and Equilibrium Study of the Reaction of [*meso*-Tetrakis(*p*-sulfonatophenyl)porphinato]diaquachromate(III) with Pyridine in Aqueous Solution

KENNETH R. ASHLEY* and IDALIA TRENT

East Texas State University, Chemistry Department, Commerce, TX 75428 (U.S.A.)

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Abstract

The reaction of pyridine (py) in aqueous solution with [*meso*-tetrakis(*p*-sulfonatophenyl)porphinato]diaquachromate(III) ($CrTPPS(H_2O)_2{}^{3-}$) has been studied at 15, 25 and 35 °C in $\mu = 1.00$ M ($NaClO_4$) from pH = 5.00 to 1.00 M NaOH. The free py concentration, [py], was varied from 1×10^{-4} to 1.00 M. The species $CrTPPS(H_2O)_2{}^{3-}$, $CrTPPS(OH)(H_2O)^{4-}$, $CrTPPS(OH)_2{}^{5-}$, $CrTPPS(py)(H_2O)^{3-}$, $CrTPPS(OH)py^{4-}$ and $CrTPPS(py)_2{}^{3-}$ were all observed. However, the ligation reactions of $CrTPPS(H_2O)_2{}^{3-}$, $CrTPPS(OH)(H_2O)^{4-}$ and $CrTPPS(py)(H_2O)^{3-}$ were the only kinetically important ones observed. The values of the various stability constants, rate constants and activation parameters are reported. The porphyrin ligands labilize the Cr(III) to axial substitution and the OH^- ligand labilizes it even more. But, there are no apparent trends reflected in the values of the activation parameters of the various paths. A comparison to reactions with NCS^- and imidazole imply that the reactions are dissociatively activated.

Introduction

The continued interest in the ligation reactions of metalloporphyrins in aqueous solution [1–23] has led to the investigation of the reaction of pyridine (py) with [*meso*-tetrakis(*p*-sulfonatophenyl)porphinato]aquachromate(III) ($CrTPPS)(H_2O)_2{}^{3-}$). Fleischer and Krishnamurthy [15, 16] have reported the results of a study of this reaction. This is a report of the results of a more extensive study of this reaction between pH 5.0 and 1.00 M OH^-, at an ionic strength $\mu = 1.00$ M ($NaClO_4$), and at 15, 25 and 35 °C.

The axial ligation reactions of metalloporphyrin ions in aqueous solution are characterized by the labilization of the metal ion. The extent of this labilization is dependent upon the particular metal ion and the *trans* ligand. In general, the reactions of Co(III) [1–14] are more labile than Cr(III) [14–21] or Rh(III) [14, 22, 23]. This labilization is greater than 10^9 times for Co(III), about 10^3 times for Cr(III) and from 10^3 to 10^7 for Rh(III). The presence of a *trans* OH^- ligand enhances the lability, compared to H_2O, of Co(III) toward py substitution by about 10^3 [11] and of Cr(III) toward imidazole (im) by about 50 times [17, 21].

However, the mode of both labilization effects is still uncertain. Although, it appears that the mechanisms of the reactions of Co(III) are dissociative or interchange dissociative [24], the data for Rh(III) and Cr(III) are contradictory in nature. The values of ΔH^* and ΔS^* are such that no clear mechanistic assignment can be made [18, 19]. But, the values of ΔV^* imply that the reactions are dissociatively activated [14]. This report is part of the continuing investigation of these types of ligation reactions and the attempts to ascertain the reaction mechanisms for them.

Experimental

Reagents

The general reagents used have been described previously [5]. The reagent grade pyridine was distilled and the fraction boiling at 114–115 °C was collected. The aqueous stock solutions of py were prepared by mass, stored in the dark and used within 2 weeks. The $NaClO_4$ solutions were prepared and standardized as previously reported [25]. The buffering reagents were used as received. $Cr(CO)_6$ was purchased from Alfa Products, Thiokol/Ventron Division, Danvers, MA; Na_4TPPS was supplied by Midcentury, Posen, IL; and $Na_3[CrTPPS(H_2O)_2]$ was prepared as described previously [18].

Equilibrium Constants

The acid dissociation constants, ${}^{pyH}K_a$, of the pyridinium ion (pyH^+) were determined by potentiometric titration of a 0.100 M solution of py in 1.00 M $NaClO_4$ with 0.100 M $HClO_4$ in 0.900 M $NaClO_4$ at 25.0 ± 0.10 °C. The calomel reference electrode, as in all measurements, contained 4.0 M

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*Author to whom correspondence should be addressed.

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NaCl instead of saturated KCl solution in order to prevent precipitation of $KClO_4$ at the junction. It was assumed that $pH = -\log[H^+]$ for the calculations of ${}^{pyH}K_a$.

The $CrTPPS(H_2O)_2{}^{3-}$–py stability constants were determined spectrophotometrically on a Beckman DU-8a instrument with the temperature maintained at 25.0 ± 0.1 °C [5]. The pH was adjusted to that desired by adding $HClO_4$ or NaOH, the solutions were 0.010 M in buffer, the ionic strength, μ, was maintained at 1.00 M ($NaClO_4$), and $[CrTPPS(H_2O)_2{}^{3-}] = 5.1 \times 10^{-5}$ M. The buffers used and the pH ranges were: $H_2PO_4^-$ (5.00–7.50); H_3BO_3 (8.00–9.50); and $HPO_4{}^{2-}$ (10.00–11.50). The pH was checked both before and after the measurements to insure constancy of the pH. Experiments were performed at both pH = 5.00 and 6.00 for $CrTPPS(H_2O)py^{3-}$ and $CrTPPS(py)_2{}^{3-}$ and at $\lambda = 444$ and 464 nm, respectively. At pH 10.23, $CrTPPS(OH)py^{4-}$ was studied at $\lambda = 436$ nm. In 0.100 M OH^-, $CrTPPS(OH)py^{4-}$ and possibly $CrTPPS(py)_2{}^{3-}$ were studied at $\lambda = 435$ nm.

Kinetics

The kinetic studies of the ligation reactions were spectrophotometrically performed on a Beckman DU-8a instrument, an Amminco-Morrow stopped-flow spectrophotometer, or an electronically renovated Beckman DU-2 spectrophotometer fitted with a Hi-Tech Scientific Ltd. rapid kinetics accessory. This latter system was interfaced to an Apple II+ computer via an Interactive Microware data acquisition system. The temperature was maintained constant to within ±0.1 °C of that desired and $\mu = 1.00$ M ($NaClO_4$). The change in absorbance A was recorded at $\lambda = 435$, 436, 444 or 464 nm. The pseudo-first order rate constants were calculated in the usual manner by plotting $\ln(A - A_\infty)$ versus t, where t is the time and A_∞ is the absorbance measured at the end of the reaction. In some cases, two consecutive rate processes were present. The steps had to be resolved and the rate constants determined as previously reported [26, 27].

The pH was adjusted as in the equilibrium studies and was checked both before and after a kinetic run to insure constancy of the pH. The pH was read directly from the pH meter between pH 5.00 and 10.00 and it was assumed that $pH = -\log[H^+]$. From pH 10.00 to 11.50, a calibration procedure was used. Various solutions of known [NaOH] were prepared with $\mu = 1.00$ M ($NaClO_4$) and the pH measured (pH_{det}) with a pH meter. The relationship between pH_{det} and pH was established by a linear least-squares fit [29] of eight points to eqn. (1). The value of A is 1.11 ± 0.03. Above pH_{det}

$$pH = A(pH_{det} - 8.00) + 8.00 \qquad (1)$$

of 11.50, the NaOH served as the buffer and eqn. (2) was used to calculate the pH, a concentration pH. This method gave an empirical relation between

$$pH = pK_w + \log[OH^-] \qquad (2)$$

pH and actual $[OH^-]$. The values of pK_w were taken as 14.13, 13.79 and 13.45 at 15, 25 and 35 °C, respectively [28]. The values at 15 and 35 °C were calculated from the reported $\Delta H°$ and $\Delta S°$ values.

Results and Discussion

Equilibrium

The data from the potentiometric titration of py were fit by a non-linear least-squares program [29] to eqn. (3), where $[H^+] = 10^{-pH}$, V_a is the volume

$$[H^+] = {}^{pyH}K_a(V_a/(V_t - V_a)) \qquad (3)$$

of $HClO_4$ added, V_t is the volume required to reach the endpoint, and ${}^{pyH}K_a$ is the acid dissociation constant for pyH^+. The value of ${}^{pyH}K_a$ at 25 °C is $(2.6 \pm 0.1) \times 10^{-6}$ M. This uncertainty, and all others reported, are the estimated one standard deviation of the measurement. This value compares with a $p^{py}K_a$ value of 5.39 ± 0.02 previously reported [30]. Thus, the values of $p^{pyH}K_a$ of 5.7 ± 0.3 and 5.5 ± 0.3 at 15 and 35 °C, calculated from the reported value of $\Delta H°$ and $p^{pyH}K_a$ at 25 °C, were used [30]. These values of ${}^{pyH}K_a$ were used to calculate the [py] and $[pyH^+]$ present in the solutions at the various temperatures. The term [py] is used to refer to free py. The total py was varied as the pH was changed in order to give the desired [py].

Figure 1 shows the spectra of $CrTPPS(H_2O)_2{}^{3-}$ and py between 400 and 500 nm as the [py] is varied at pH = 6.00. Similar spectral changes were obtained at pH 5.00. The appearance of isosbestic points in these spectral sets at low and then again at high [py] at low pH was taken to imply that

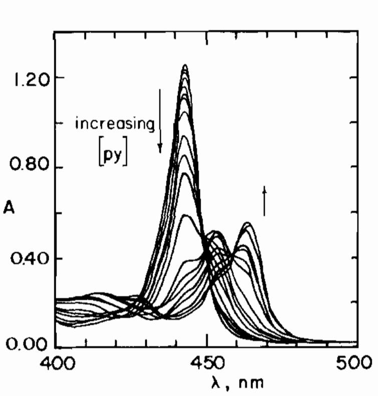
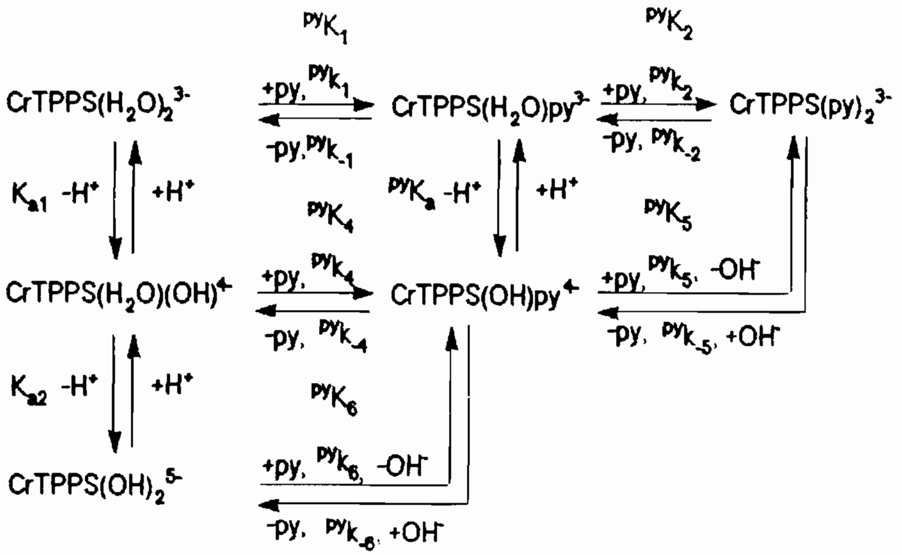


Fig. 1. Spectral changes at pH 6.00, 25 °C, $\mu = 1.00$ M ($NaClO_4$), 0.0100 M phosphate buffer, and [py] = 0.00–3.00 × 10^{-1} M. Arrows indicate the direction of absorbance change with increasing [py].



Scheme 1.

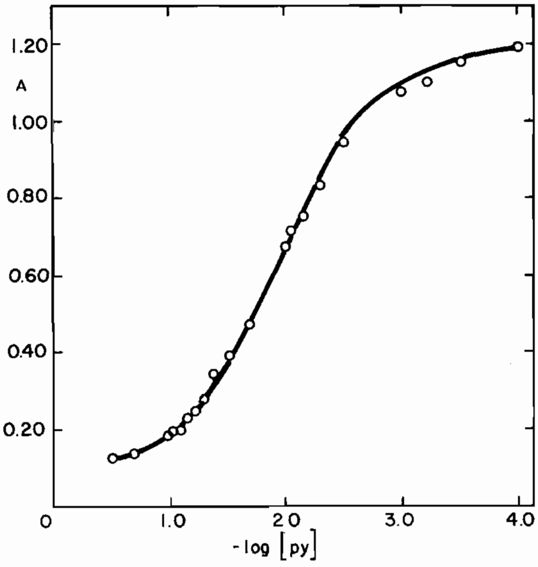


Fig. 2. Absorbance as a function of [py] at pH = 6.00, 25 °C, $\mu = 1.00$ M ($NaClO_4$), 1.00×10^{-2} M phosphate buffer, $\lambda = 444$ nm, and [py] = 1.00×10^{-4}–3.00×10^{-1} M. The line is the calculated one.

the stepwise formation of the mono- and bi(pyridine) species occurred. At pH 10.23 and 0.100 M OH^-, only one maxima was observed and hence, only the monopyridine species is formed to any extent. Scheme 1 adequately describes the system under investigation. The rate constant for a reaction will be used to label that path. The values of K_{a1} and K_{a2} at 25 °C are $(2.33 \pm 0.07) \times 10^{-8}$ and $(3.53 \pm 0.17) \times 10^{-12}$ M [18].

Equation (4) can be derived from a consideration of Beer's law, the mass balance, and the definitions

$$A = \frac{A_0 + A_1{}^{py}K_i[py] + A_2{}^{py}K_i{}^{py}K_j[py]^2}{1 + {}^{py}K_i[py] + {}^{py}K_i{}^{py}K_j[py]^2} \qquad (4)$$

of the stability constants implicit in Scheme 1. A is the absorbance at a particular [py]; A_0, A_1 and A_2 are the absorbance of solutions of Cr(III) containing zero, one and two py ligands, respectively; and ${}^{py}K_i$ and ${}^{py}K_j$ are the stepwise stability constants. If a single step only is being considered, a similar equation is derived by setting $K_j = 0$.

The absorbance–[py] data at various wavelengths were fit to eqn. (4), or a similar equation, using a non-linear least-squares program [29]. Figure 2 is a plot of the absorbance A versus py concentration for the ligation reaction at pH = 6.00 and a wavelength of 444 nm. The solid line is the calculated fit of the data with the derived values of ${}^{py}K_1 = (1.07 \pm 0.06) \times 10^2$ and ${}^{py}K_2 = (2.2 \pm 0.2) \times 10$ M^{-1}. A similar plot was obtained at pH 10.23 and $\lambda = 436$ nm with ${}^{py}k_4 = (1.02 \pm 0.02) \times 10$ M^{-1}. The previously reported values of ${}^{py}K_1$ and ${}^{py}K_2$ of 49 ± 4 and 5.4 ± 0.6 M^{-1} at pH 7 are similar to those reported here [16]. No value for ${}^{py}k_4$ was reported.

The successful fit of the data at 0.100 M OH^- could not be effected. Attempts to fit the data at 0.100 M OH^- considering one step and two steps were unsuccessful. A fit, albeit a poor one, could be effected by fixing the value of A_0 at the observed one, arbitrarily fixing the values of A_1 and A_2, and considering a two step situation or by fixing A_0 and A_1 and assuming only one step. However, in both cases the fit was not good. The two step case gave constants of 1.0 ± 0.2 and 2.0 ± 0.3 M^{-1} for the first and the second steps, respectively. The single step case gave a value of 1.4 ± 0.4 M^{-1}. If this is for the ${}^{py}K_6$ path, then this is the value of ${}^{py}K_6/[OH^-]$ or 0.14 ± 0.04 for ${}^{py}K_6$. The calculated value of $^{py}K_6$ ($^{py}K_4K_w/K_{a2}$) is $4.7 \pm 0.3 \times 10^{-2}$. This agreement is not too bad. The calculated value of $^{py}K_5$ ($^{py}K_2K_w/^{py}K_a]$) is $(2.2 \pm 0.5) \times 10^{-4}$, which is considerably different from the value of 0.20 ± 0.03 for the second step in the two step case. The value of $^{py}K_a$ was kinetically determined, *vide infra*. Thus, this value does not seem to be associated with $^{py}K_5$. Hence, it is uncertain as to what reaction to assign to these equilibrium constants. Tentatively, the first constant is associated with $^{py}K_5$ and a possible explanation for the second step will be discussed later in the kinetic section.

The values of $^{Y}K_1$, for Y = Im, py, F^-, and NCS^- are 1×10^4, 1×10^2, 2.7×10, and 2.5 M^{-1}, respectively [16–18, 21]. This is the order of decreasing $p^{Y}K_a$ for Y, 7.13, 5.58, 2.96, and 0.90, respectively [31, 32]. The same order is noted for $^{Y}K_2$ for Im and py, 3×10^3 and 2×10 M^{-1}. For $^{Y}K_4$, for Y = Im, py, and NCS^{-1}, the values are, respectively, 2×10^3, 1×10, and 7×10^{-1} M^{-1}. Although all of these values are in the same order, the values of $^{Y}K_i$ do not reflect as great a range as $p^{Y}K_a$. The order of these values, with the exception of F^-, is also the same order as the π electron donating ability of the ligands. It is unclear as to which factor is the more important, if either is. The larger values for Im might reflect the better π electron donating ability of Im [33].

It is interesting to note that these values of $^{Y}K_i$ are similar to those for the CrTPPClL–Y system in toluene [34]. In this system, where the leaving ligand, L, is PPh_3, $P(OPr)_3$, $P(C_2H_4CN)_3$ or py; and the entering ligand, Y, is MeIm, py and PPh_3, the values of $^{Y}K_i$ range from about 1 to 10^5 M^{-1}*. When L is PPh_3, the value of ^{Y}K is about 10^2 times larger for Y = MeIm than for py. The value of $^{Im}K/^{py}K$ for $CrTPPCl(PPh_3)$ is 1.6×10^2 compared to 9.6 for the equivalent quantity for $CrTPPS(H_2O)_2^{3-}$. These values are surprisingly similar in view of the large differences in the solvents, in the porphyrins, and in the *trans* ligands. The similarity of these values in very different solvents might reflect the inherent affinity of the Cr(III) for these ligands.

The comparison of the values of $^{Y}K_1$ for other chromium(III) porphyrins, where the porphyrin is TPPS, TMPP or TAPP, can only be made for NCS^- [18–20]. It appears that neither the charge on the complex (porphyrin) nor the electron donating ability of the porphyrin affects the value of $^{NCS}K_1$, even though it has been reported that the *para* substitutes have substantial effect on the electron density available at the pyrrole nitrogens [35].

Kinetics

The ligation reactions were studied between pH 5.00 and 13.79 (1.00 M OH^-). At pH 5.00 and 6.00 and below 0.0200 M py, only a single step was observed. Above this py concentration, a second step was observed. Both steps followed first order rate expressions and the pseudo-first order rate constants (k'_{obs} and k''_{obs}) for the two consecutive steps were resolved as reported [21, 27]. The data was consistent with the second step being the addition of the second py. At pH 10.23 and above, only one step was observed at 0.0500 M py. The absorbance changes in the reactions ranged from 0.70 to 0.060, with the ΔA decreasing at the higher $[OH^-]$. At constant pH or $[OH^-]$ and variable py, eqn. (5) was observed to be applicable for both steps

$$k_{obs} = a + b[\text{py}] \tag{5}$$

An examination of the pseudo-first order rate constant, k'_{obs}, for the first step as a function of pH at [py] = 0.050 M revealed complex dependence. Figure 3 is a plot of the k'_{obs}–pH data for this step. An examination of Scheme 1 indicated that all of the chromium(III) species are potential reactants over the pH range. Assuming that they all are reactants and that all three paths are operative, eqn. (6) can be derived.

$$k'_{obs} = \frac{\{^{py}k_1[H^+]^2 + {}^{py}k_4K_{a1}[H^+] + {}^{py}k_6K_{a1}K_{a2}\}[\text{py}]}{\{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}\}} + \frac{\{^{py}k_{-4} + {}^{py}k_{-6}[OH^-]\}^{py}K_a + {}^{py}k_{-1}[H^+]}{\{[H^+] + {}^{py}K_a\}} \tag{6}$$

An attempt to fit the data for pH 5.00 to 12.50 to eqn. (6) was unsuccessful [29]. The algorithm of the program would not give convergent values for the parameters, or parameters in the numerator and denominator would simultaneously become very, very large. Hence, the data were fitted by noting that the $^{py}k_1$ and $^{py}k_6$ paths were not operative over the same pH range. Equations (7) and (8) can be constructed. Note that eqns. (7) and (8)

$$k'_{obs} = \frac{\{^{py}k_1[H^+] + {}^{py}k_4K_{a1}\}[\text{py}]}{\{[H^+] + K_{a1}\}} + \frac{^{py}k_{-4}{}^{py}K_a + {}^{py}k_{-1}[H^+]}{\{[H^+] + {}^{py}K_a\}} \tag{7}$$

$$k'_{obs} = \frac{\{^{py}k_4[H^+] + {}^{py}k_6K_{a2}\}[\text{py}]}{\{[H^+] + K_{a2}\}} + {}^{py}k_{-4} + \frac{^{py}k_{-6}K_w}{[H^+]} \tag{8}$$

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*Abbreviations: TPPS = *meso*-tetra(*p*-sulfonatophenyl)porphine; TAPP = *meso*-tetrakis(trimethylammoniophenyl)porphine; TMPP = *meso*-tetrakis(*N*-methyl-4-pyridyl)porphine; TPP = tetraphenylporphine; py = pyridine; Im = imidazole; PPh_3 = triphenylphosphine; $P(OPr)_3$ = triisopropyl phosphite; $P(C_2H_4CN)_3$ = tris(2-cyanoethyl)phosphine; MeIm = *N*-methylimidazole.

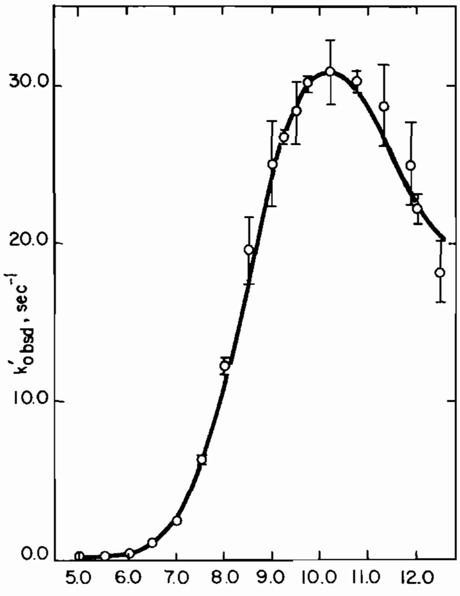

Fig. 3. Value of k'_{obs} (first ligation reaction) as a function of pH at 25 °C, 1.00×10^{-2} M borate or phosphate buffer, $\mu = 1.00$ M ($NaClO_4$), and [py] = 5.00×10^{-2} M.

have the same form as eqn. (5) if the [H^+] is constant. The values of the derived parameters from the non-linear least-squares fit to eqn. (7) for pH = 5.00–9.50 were: ${}^{py}k_1 = (7.0 \pm 0.6) \times 10^{-1}$ (M s)$^{-1}$, ${}^{py}k_4 = (2.40 \pm 0.06) \times 10^2$ (M s)$^{-1}$, ${}^{py}k_{-1} = (4.9 \pm 2.9) \times 10^{-3}$ s^{-1}, and ${}^{py}k_{-4} = (2.02 \pm 0.01) \times 10$ s^{-1}. The values of K_{a1} and ${}^{py}K_a$ were fixed at 2.33×10^{-8} and 1.63×10^{-9} M, *vide infra*. The data between pH 9.50 and 12.50 could best be fitted to eqn. (8) if it were assumed that the ${}^{py}k_6$ path were negligible. This gave values of ${}^{py}k_4$ and ${}^{py}k_{-4}$ of $(2.4 \pm 0.2) \times 10^2$ (M s)$^{-1}$ and $(1.92 \pm 0.07) \times 10$ s^{-1} when the value of K_{a2} was fixed at 3.53×10^{-12} M. The solid line in Fig. 3 is calculated from these data.

An inspection of Fig. 3, the values of the parameters derived from eqns. (7) and (8), and the values of K_{a1} and K_{a2} clearly imply that the ${}^{py}k_4$ path is the predominant one over the entire pH range. The kinetics of the addition of the first py at pH = 10.31 were studied at [py] = $(1.00–10.0) \times 10^{-2}$ M and at 15, 25 and 35 °C. The data were fitted by the non-linear least-squares program to eqn. (5) and the values of ${}^{py}k_4$ (*b*) and ${}^{py}k_{-4}$ (*a*) are reported in Table 1. The activation parameters were determined from a fit of the data to the Erying–Polanyi equation and are reported in Table 1.

The kinetics of the first step of the ligation reaction was studied also between pH 11.8 and 13.8 (1.00 M OH^-) and [py] = 0.100–1.00 M. The data at [py] = 0.60 M could not be fitted to eqn. (8) unless the ${}^{py}k_6$ path was assumed to be negligible. This fit at 25 °C resulted in values of ${}^{py}k_4 = (2.7 \pm 0.2) \times 10^2$ (M s)$^{-1}$ and ${}^{py}k_{-4} = 3.4 \pm 0.3$ s^{-1}. While the value of ${}^{py}k_4$ is close to the previously determined one at lower [py] and pH, the value of ${}^{py}k_{-4}$ is substantially smaller. The reaction was studied also at pH 12.79 (0.100 M OH^-), at 15, 25 and 35 °C, and [py] = 0.100–1.00 M. The data were fitted to eqn. (5) with the value of *b* ascribed to ${}^{py}k_4$ and *a* to ${}^{py}k_{-4}$. The results along with the activation parameters are reported in Table 1.

The values of ${}^{py}k_4$ determined at both pH values are consistent with each other. However, the values of ${}^{py}k_{-4}$ differ by a factor of two, a significant amount. This seems to be too large to ascribe to medium effects. Different attempts to fit the data to a rate law which contained a complex term, including one inverse in [py], for the ${}^{py}k_{-4}$ path were unsuccessful. A possible scheme involving the complex formation of [$CrTPPS(OH)py^{4-}$]·py seems most likely [36]. However, the necessary kinetic data needed below 0.200 M py cannot be determined with sufficient accuracy to test adequately this scheme. These kinetic anomalies, along with the unresolved stability constant problems, imply that the system at higher pH is not as simple as first thought. At this time no other explanations are offered.

The values of the parameters determined from eqns. (7) and (8) and of α_0 and α_1, the fractions of $(Cr(III))_{total}$ in the form of $CrTPPS(H_2O)_2^{3-}$ and $CrTPPS(OH)H_2O^{4-}$, respectively, indicated that the ${}^{py}k_4$ path provides the predominant kinetic route to $CrTPPS(py)H_2O^{3-}$ formation at all accessible pH values. At pH 5.00 the values of α_0 and α_1 are 9.98×10^{-1} and 2.00×10^{-3} at 25 °C, but the ${}^{py}k_4$ path provides 85.7, 30.7 and 11.4% of the reaction pathway at 15, 25 and 35 °C, respectively. This means that the values of ${}^{py}k_1$ and ${}^{py}k_{-1}$ are very dependent upon the values of K_{a1} and ${}^{py}K_a$, and, hence, they have a large propagated uncertainty associated with them. The values for the ${}^{py}k_1$ path determined at pH = 5.00 and [py] = 4.00×10^{-3}–1.00×10^{-1} M are reported in Table 1. The accuracy was too poor to ascertain a reliable estimate of the activation parameters.

The kinetics of the ligation reaction of $CrTPPS(py)H_2O^{3-}$ by py were studied as a function of pH from 5.00 to 11.34 and [py] = 0.05 M. Figure 4 is a plot of the results obtained. An examination of Scheme 1 predicts that eqn. (9) should be a reasonable expression for k''_{obs}. Note that eqn. (9) reduces to eqn. (5) if the [H^+] is constant.

$$k''_{obs} = \left(\frac{{}^{py}k_2[H^+] + {}^{py}k_5{}^{py}K_a}{[H^+] + {}^{py}K_a}\right)[py] + {}^{py}k_{-2}\,\frac{{}^{py}k_{-5}K_w}{[H^+]} \qquad (9)$$

TABLE 1. The kinetic parameters for the ligation reactions of py and $CrTPPS(H_2O)_2^{3-}$. The rate constants and their associated paths are defined in Scheme 1

Rate constant	Temperature (°C)			k_i/k_{-i} $(M^{-1})^e$	ΔH^* (kcal mol^{-1})	ΔS^* (cal (deg $mol)^{-1}$)
	15	25	35			
$^{py}k_1{}^a$	$(3.95 \pm 2.70) \times 10^{-2}$	1.30 ± 0.10	8.66 ± 0.38	$(8.78 \pm 5.91) \times 10^2$	26.3	+30
$^{py}k_{-1}{}^b$		$(1.48 \pm 0.99) \times 10^{-3}$				
$^{py}k_2{}^a$	$(3.26 \pm 0.35) \times 10^{-2}$	$(1.80 \pm 0.04) \times 10^{-1}$	$(5.91 \pm 0.18) \times 10^{-1}$	$(1.05 \pm 0.01) \times 10^1$	29.4 ± 3.3	$+35.8 \pm 11.0$
$^{py}k_{-2}{}^b$	$(6.92 \pm 0.22) \times 10^{-3}$	$(1.72 \pm 0.03) \times 10^{-2}$	$(8.03 \pm 0.09) \times 10^{-2}$		24.9 ± 3.6	$+17.0 \pm 12.2$
$^{py}k_4{}^{a,c}$	$(1.00 \pm 0.01) \times 10^2$	$(2.40 \pm 0.16) \times 10^2$	$(4.46 \pm 0.50) \times 10^2$	$(1.26 \pm 0.10) \times 10^1$	13.0 ± 0.08	-4.16 ± 2.65
$^{py}k_{-4}{}^{b,c}$	9.90 ± 0.11	$(1.91 \pm 0.08) \times 10$	$(4.15 \pm 0.27) \times 10$		12.0 ± 0.9	-12.2 ± 3.0
$^{py}k_4{}^{a,d}$	$(6.50 \pm 1.36) \times 10$	$(1.87 \pm 0.17) \times 10^2$	$(2.62 \pm 0.61) \times 10^2$	$(2.14 \pm 0.21) \times 10^2$	11.7 ± 2.9	-9.26 ± 9.89
$^{py}k_{-4}{}^{b,d}$	3.96 ± 0.12	8.73 ± 0.29	$(1.84 \pm 0.13) \times 10$		13.0 ± 0.1	-10.8 ± 0.1

[a] $(M\ s)^{-1}$. [b] s^{-1}. [c] pH = 10.31. [d] pH = 12.79 (0.100 M OH^-). [e] 25 °C.

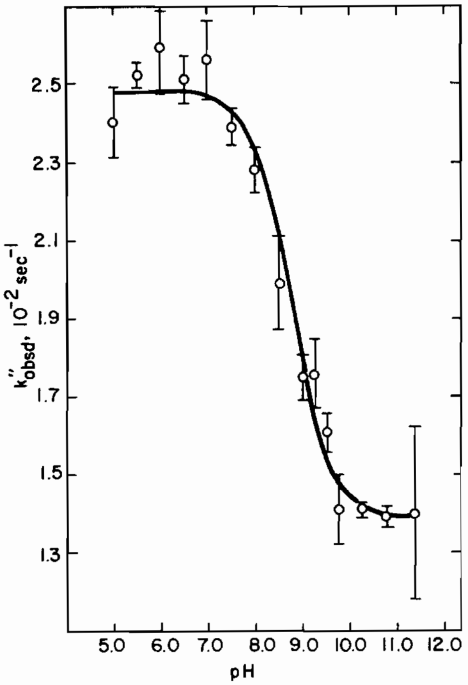

Fig. 4. Value of k''_{obs} (second ligation reaction) as a function of pH at 25 °C, 1.00×10^{-2} M borate or phosphate buffer, $\mu = 1.00$ M ($NaClO_4$), and [py] = 5.00×10^{-2} M.

The k''_{obs}–$[H^+]$ data could best be fitted if the $^{py}k_5$ path was assumed to be negligible. The solid line in Fig. 4 is the non-linear least-squares fit of the data to eqn. (9) with $^{py}k_5 = {}^{py}k_{-5} = 0$. The values of $^{py}k_2$ and $^{py}k_{-2}$ at 25 °C are $(2.2 \pm 0.1) \times 10^{-1}$ $(M\ s)^{-1}$ and $(1.39 \pm 0.03) \times 10^{-2}$ s^{-1}, respectively. The value of $^{py}K_a$ is $(1.6 \pm 0.4) \times 10^{-9}$ M at 25 °C. At pH = 6.00, eqn. (5) is applicable with $a = {}^{py}k_{-2}$ and $b = {}^{py}k_2$. These parameters were determined at 15, 25 and 35 °C and [py] = $(1.00–10.0) \times 10^{-2}$ M by a least-squares fit of the data to eqn. (5), and, along with the activation parameters, are reported in Table 1.

The labilization of $CrTPPS(H_2O)_2^{3-}$ to ligation by py is also evident in this study. However, in comparing the ligation reaction parameters for NCS^-, Im and py, one can find no trends [21]. The values of $^Yk_1$ are, respectively, 4.7×10^{-3}, 2.4, and 1.3 M s^{-1}, whereas the values of $^YK_1$ are 2.5, 1×10^4, and 1×10^2 M^{-1}. The values of ΔH^* are 17, 16 and 26 kcal/mol; and of ΔS^* are −13, −2 and +30 cal(deg $mol)^{-1}$, respectively. It must be explicitly noted again that the values of the parameters for the $^{py}k_1$ path are very uncertain. The relative values of $^Yk_1$ and $^YK_1$ imply a mechanism that is dissociatively activated [24].

An examination of the ligation parameters for NCS^-, Im and py, for the $^Yk_4$ path reveal that labilization has occurred more when the *trans* ligand is OH^- rather than H_2O [21]. The value of the rate constants are similar, 28, 98 and 240 s^{-1}, respectively; whereas the values of ${}^{Y}K_4$ are 6.9×10^{-1}, 1.9×10^3 and 1.3×10 M^{-1}. This is a labilization by a factor of 6.0×10^3, 4.1×10 and 1.9×10^2, while the stability constants change by 2.8×10^{-1}, 5.3 and 1.3×10^{-1}, respectively, for NCS^-, Im and py. Clearly, this is a kinetic and not an equilibrium effect. As for ${}^{Y}k_1$, these values imply dissociative activation for the reactions of the ${}^{Y}k_4$ paths. It is interesting to note that, for NCS^-, Im and py, the values of the ligation rate constant for the $CrTPPS^{3-}$ moiety tend toward about 10^2 M s^{-1}.

An examination of the activation parameters associated with the ${}^{Y}k_4$ paths show that the values are similar at $\Delta H^* = 15 \pm 2$ kcal mol^{-1} and $\Delta S^* = +1.0 \pm 4$ cal(deg $mol)^{-1}$. These changes in the value of ΔH^* and ΔS^* compared to the values for H_2O (${}^{Y}k_1$) are consistent with what has been observed previously for the labilization effect of the OH^- ligand [37]. These values also imply a mechanism that is dissociatively activated [24].

The value of ${}^{py}k_i$ decreases by about 7 times from $i = 1$ to 2; that is, there is no *trans* labilization by the py ligand for the addition of the second py. There is also little change in the activation parameters for the two reactions. This lack of *trans* effect was noticed also for the Im ligand [21]. The values of ${}^{Y}k_2$ and ${}^{Y}K_2$ for Y = Im and py are 0.31 and 0.18 M s^{-1} and 290 and 22 M^{-1}, respectively [21]. However, when the values of the activation parameters are examined a very bothersome observation is made. The values of ΔH^* and ΔS^* are 10 and 29 kcal mol^{-1} and -27 and $+36$ cal(deg $mol)^{-1}$ for Im and py, respectively. It is very hard to resolve these large differences in the activation parameters for two ligands that are so similar. One must conclude that the effect of Im on the $CrTPPS^{3-}$ moiety is substantially different from that of py, or that this difference might be due to ligand solvation effects.

There was no observed ${}^{py}K_5$ and ${}^{py}K_6$ paths and previously there was no observed ${}^{NCS}K_2$, ${}^{NCS}K_5$ and ${}^{NCS}K_6$ paths [18]. However, all of the available paths were observed for Im. An examination of the corresponding stability constants for the ligands reveals that the trends are such that the unobserved paths are not expected to be observed. Hence, the fact that OH^- is a poor leaving ligand in these systems is a manifestation of the equilibrium and not necessarily the kinetic properties of the chromium(III) porphyrin.

The idea that the labilization of the metal ion by the porphyrin is a result of the porphyrin donating electron density to the metal ion to make it more like a d^4 or d^7 ion has long been the rationale for the labilization effect [1, 18]. Co(III) is labilized by a factor of 10^6–10^9 whereas Cr(III) is labilized by a factor of 10^2–10^3. It is interesting to note that the rate constant for water exchange is about 7×10^9 s^{-1} for Cr(II) and for Co(II) it is about 10^5–10^6 s^{-1} [38].

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