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Kinetic Study of the Reactions of *meso*-Tetrakis(*p*-sulfonato)porphinatodiaquorhodate(III) and *meso*-Tetrakis(4-*N*-methylpyridyl)porphinediaquocobalt(III) with Thiourea in Aqueous Solution

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Abstract

The reactions of *meso*-tetrakis(*p*-sulfonatophenyl)porphinatodiaquorhodate(III), $[Rh(TPPS)(H_2O)_2]^{3-}$ and *meso*-tetrakis(4-*N*-methylpyridyl)porphinediaquocobaltate(III), $[Co(TMPP)(H_2O)_2]^{5+}$ with thiourea have been studied in 0.1 M H^+ and $\mu = 1.0$ M ($NaNO_3$) at different temperatures and pressures. The kinetic parameters for the substitution of the first aquo ligand by thiourea are as follows for $[Rh(TPPS)(H_2O)_2]^{3-}$ and $[Co(TMPP)(H_2O)_2]^{5+}$ respectively: k_1 at 25 °C; 4.69×10^{-2} and 8.88×10^{-1} M^{-1} s^{-1}, $\Delta H^{\ddagger}$; 85.1 ± 1.3 and 91.4 ± 0.7 kJ mol^{-1}, $\Delta S^{\ddagger}$; 14.9 ± 4.2 and 60.6 ± 2.2 J K^{-1} mol^{-1}, $\Delta V^{\ddagger}$; 11.1 ± 0.5 and 12.6 ± 0.6 cm^3 mol^{-1}. These results were interpreted as evidence for a dissociative mechanism.

Introduction

In a series of papers, it was demonstrated that the porphyrin ligand labilizes the axial positions in octahedral complexes [1–5]. For example, the anation reactions of *trans*-$[M(TPPS)(H_2O)_2]^{3-}$ (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine) are about 10^9, 10^3 and 10^2 times faster than those of $[M(NH_3)_5(H_2O)]^{3+}$, where M = Co(III), Rh(III) and Cr(III) respectively [6].

A high-pressure kinetic study indicated that the reactions of *trans*-$[M(TPPS)(H_2O)_2]^{3-}$ with thiocyanate ions proceed via a dissociative reaction mode; a D mechanism for M = Co(III) and an Id mechanism for M = Rh(III) and Cr(III) [7]. Tanaka and coworkers also presented evidence (a high-pressure kinetic study) in favour of a dissociative mechanism for the substitution reaction between $[Co(TMPP)(H_2O)_2]^{5+}$ and NCS^- [8]. There is also other kinetic evidence, such as LFER, in favour of a dissociative reaction mode for the substitution reactions of different porphyrin complexes of Co(III), Rh(III) and Cr(III) [4, 6].

In all these cases the reactions were between a positive or negative charged complex and an anion. In this respect it is important to note that the formal charge of the complex is spread over a very large planar surface area since the negative charged sulphonato groups or positive charged pyridinium groups, are far removed from the positive metal ion centre. All these reactions may thus be considered as a reaction between an anion and a positive charged metal ion.

With this in mind, we studied the kinetics of the reactions between $[Co(TMPP)(H_2O)_2]^{5+}$ and $Rh[TPPS)(H_2O)_2]^{3-}$ and the neutral ligand thiourea.

Experimental

Analytical grade reagents and redistilled water were used throughout. Tetrasodium-*meso*-tetra(4-sulfonatophenyl)porphine and *meso*-tetra(4-*N*-methylpyridyl)porphinetetraiodide were obtained from Strem Chemicals. $[Rh(TPPS)(H_2O)_2]^{3-}$ [1] and $[Co(TMPP)(H_2O)_2]^{5+}$ [6] were prepared and characterized as described before.

The kinetics of the anation reactions were studied under pseudo-first-order conditions by monitoring the absorbance change at the Soret bands of the different complexes, *i.e.* 417 and 436 nm for the Rh(III) and Co(III) complexes respectively [1, 6]. All rate measurements and stability constant determinations were done in 0.1 M HNO_3 and at an ionic strength of $\mu = 1.0$ M controlled by the addition of $NaNO_3$. A Hitachi 150-20 spectrophotometer, equipped with a constant temperature block, was used for the atmospheric pressure measurements.

Kinetic measurements at elevated pressures were made *in situ* on a Cary Model 17H spectrophotometer. The solution samples were contained in a le

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Noble–Schlott cell [8] inside an Aminco 41-11551 optical pressure vessel which was pressurized with water from an external hydraulic system. The temperature of the pressure vessel was kept constant (±0.1 K) with a jacket fed with circulating water from a thermostat. The sample was exposed to the spectrophotometer light beam only intermittently (just long enough to make the desired absorbance readings) so as to minimize any possibility of photolysis.

The observed pseudo-first-order rate constants, k_{obs}, were obtained from plots of $\ln(A_t - A_\infty)$ *versus* t, where A_t and A_∞ are the absorbances at time t and infinity respectively. All such plots were linear for at least three half-lives.

Results and Discussion

The substitution kinetics of $[Co(TMPP)(H_2O)_2]^{5+}$ and $[Rh(TPPS)(H_2O)_2]^{3-}$ with a number of entering ligands have been studied in detail before [1, 5]. The overall reaction scheme is complicated due to the partition of the diaquo, aquohydroxo and dihydroxo complex species. In this study the systems were simplified by working in 0.1 mol dm^{-3} HNO_3 where only the diaquo species exist in solution.

In the spectrophotometric determination of the stability constants, the concentration of the thiourea was varied from 1.0×10^{-5} to 0.4 mol dm^{-3}. Plots of absorbance *versus* [thiourea] revealed that only one axial water ligand was replaced by the incoming thiourea ligand in the case of $[Rh(TPPS)(H_2O)_2]^{3-}$ and that both water ligands can be replaced in the case of $[Co(TMPP)(H_2O)_2]^{5+}$, Figs. 1 and 2. The overall reactions can therefore be represented by reactions (1)–(3).

$$[Rh(TPPS)(H_2O)_2]^{3-} + T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Rh(TPPS)(H_2O)(T)]^{3-} + H_2O \qquad (1)$$

$$[Co(TMPP)(H_2O)_2]^{5+} + T \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(TMPP)(H_2O)(T)]^{5+} + H_2O \qquad (2)$$

$$[Co(TMPP)(H_2O)(T)]^{5+} + T \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Co(TMPP)(T)_2]^{5+} + H_2O \qquad (3)$$

From Beer's law, the mass balance and the definitions of K, eqn. (4), can be derived.

$$A = \frac{A_r + A_p K[T]}{1 + K[T]} \qquad (4)$$

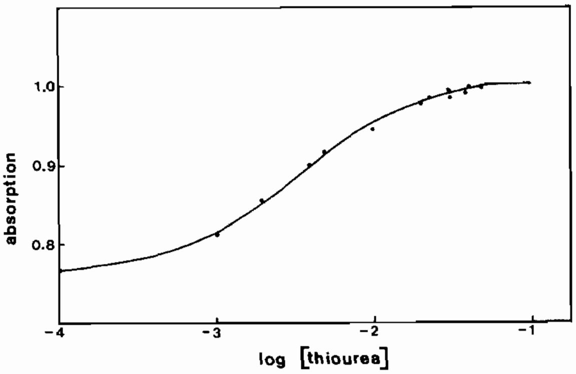

Fig. 1. Plot of absorbance *vs.* log[thiourea] for the reaction of $[Rh(TPPS)(H_2O)_2]^{3-}$ at 35 °C. $[H^+] = 0.10$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3}, $[Rh(TPPS)(H_2O)_2]^{3-} = 6.1 \times 10^{-5}$ mol dm^{-3} and $\lambda = 434$ nm.

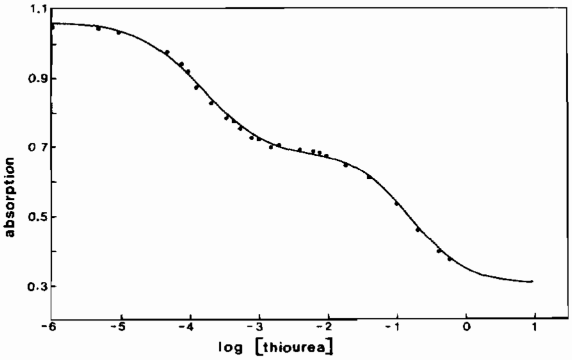

Fig. 2. Plot of absorbance *vs.* log[thiourea] for the reaction of $[Co(TMPP)(H_2O)_2]^{5+}$ at 35 °C. $[H^+] = 0.10$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3}, $[Co(TMPP)(H_2O)_2]^{5+} = 5.5 \times 10^{-6}$ mol dm^{-3} and $\lambda = 436$ nm.

A_r, A_p and A are the absorbances of the reactant, product and solution at a particular concentration of thiourea [T] and K is either K_1 or K_2. The A *versus* [T] data were fitted to eqn. (4) by using a nonlinear least-squares program to obtain the equilibrium constants at 35 °C: $K_1(Rh) = 311 \pm 48$, $K_1(Co) = (6.75 \pm 0.9) \times 10^3$ and $K_2(Co) = 7.5 \pm 0.8$ M^{-1}. The value of $K_1(Rh)$ was also determined kinetically at 34.7 °C where the thiourea concentration was varied from 0.005 to 0.04 M. The values of k_1 and k_{-1} were determined as $(1.48 \pm 0.07) \times 10^{-1}$ M^{-1} s^{-1} and $(4.47 \pm 0.18) \times 10^{-4}$ s^{-1} respectively yielding $K_1(Rh) = k_1/k_{-1} = 331$ M^{-1}.

According to reactions (1)–(3) the value of k_{obs} is given by eqn. (5) under pseudo-first-order conditions (reaction (2) represents the rate determining step in the case of the Co(III) complex).

$$k_{obs} = k_{-1} + k_1[T] \qquad (5)$$

The equilibrium constants, K_1, and the [T] used in the high-pressure study, are such that the reactions go to completion and eqn. (5) can be simplified to

TABLE I. k_1 as a Function of Pressure for the Anation of $[Rh(TPPS)(H_2O)_2]^{3-}$ and $[Co(TMPP)(H_2O)_2]^{5+}$ by Thiourea[a]

Complex	P (bar)	k_1[b] (M^{-1} s^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})
$[Rh(TPPS)(H_2O)_2]^{3-}$	400	2.29×10^{-2}	11.1 ± 0.5
	700	1.97×10^{-2}	
	1000	1.71×10^{-2}	
	1400	1.46×10^{-2}	
$[Co(TMPP)(H_2O)_2]^{5+}$	200	4.21×10^{-1}	12.6 ± 0.6
	400	3.87×10^{-1}	
	700	3.17×10^{-1}	
	1000	2.69×10^{-1}	
	1400	2.34×10^{-1}	

[a] $T = 21.9 \pm 0.1$ °C, $[Rh(III)] = 2.3 \times 10^{-5}$ mol dm^{-3}, $[Co(III)] = 5.5 \times 10^{-6}$ mol dm^{-3}, $[H^+] = 0.10$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} ($NaNO_3$). [b] Mean value of between two and three kinetic runs.

TABLE II. Kinetic Data for the Anation of $[Rh(TPPS)(H_2O)_2]^{3-}$ and $[Co(TMPP)(H_2O)_2]^{5+}$ by Thiourea at 25 °C

Complex	k_1 (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	$\Delta V^{\ddagger}$ (cm^3 mol^{-1})
$[Rh(TPPS)(H_2O)_2]^{3-}$	4.69×10^{-2}	85.1 ± 1.3	14.9 ± 4.2	11.1 ± 0.5
$[Co(TMPP)(H_2O)_2]^{5+}$	8.88×10^{-1}	91.4 ± 0.7	60.6 ± 2.2	12.6 ± 0.6

Other parameters as specified in Table I.

$$k_{obs} = k_1[T] \qquad (6)$$

The pressure dependence of k_1 was therefore calculated from the pressure dependence of k_{obs} at an excess thiourea concentration. Plots of $\ln k_1$ *versus* pressure, were linear and the volumes of activation $\Delta V^{\ddagger}_{exp}$ were calculated from the slope of these lines and represented in Table I. The values of k_1 were determined from the slopes of the curves of k_{obs} *versus* [T] at different temperatures. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by means of a nonlinear least-squares fit of the temperature *versus* k_1 data to the Eyring–Polanyi equation and are reported in Table II.

The values of $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ for the reaction of $[Rh(TPPS)(H_2O)_2]^{3-}$ with thiourea are significantly higher than the values for the reaction with NCS^-, $\Delta S^{\ddagger}(NCS^-) = -43.1 \pm 2.5$ J mol^{-1} K^{-1} and $\Delta V^{\ddagger}(NCS^-) = 8.8 \pm 0.4$ cm^3 mol [7]. This may be interpreted that the negative charged NCS^- ligand is more likely to react via an Id mechanism due to possible ion-pair formation with the positive charged Rh(III) centre than the neutral thiourea ligand.

The large positive $\Delta V^{\ddagger}$ values can be interpreted as evidence for a dissociative mechanism. The suggested mechanism is outlined in reactions (7) and (8).

$$[MP(H_2O)_2] \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [MP(H_2O)] + H_2O \qquad (7)$$

$$[MP(H_2O)] + T \xrightarrow{k_4} [MP(H_2O)(T)] \qquad (8)$$

(M = Co(III) for P = TMPP and M = Rh(III) for P = TPPS, charges omitted.)
For this reaction scheme

$$k_{obs} = \frac{k_3 k_4[T]}{k_{-3} + k_4[T]} \qquad (9)$$

which can be simplified to

$$k_{obs} = k_3 k_4[T]/k_{-3} \qquad (10)$$

since it was observed that plots of k_{obs} *versus* [T] were linear indicating that $k_{-3} \gg k_4[T]$.

From eqns. (6) and (10) it follows that $\Delta V^{\ddagger}(k_1) = \Delta V^{\ddagger}(k_3) + \Delta V^{\ddagger}(k_4) - \Delta V^{\ddagger}(k_{-3})$. $\Delta V^{\ddagger}(k_4)$ and $\Delta V^{\ddagger}(k_{-3})$ are both expected to be negative since they involve bond formation. It may also be assumed that $/\Delta V^{\ddagger}(k_4)/ > /\Delta V^{\ddagger}(k_{-3})/$ since the volume of activation is expected to depend on the molar volume of the entering ligand which is about 54 and 18 cm^3 mol^{-1} for thiourea and water, respectively. This means that $\Delta V^{\ddagger}(k_3)$ is at least as large as $\Delta V^{\ddagger}(k_1)$ and points to a dissociative mechanism for the reaction of thiourea with both complexes.

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