

Kinetics of Anation Reactions of a Water-Soluble Rh(III)-Porphyrin

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*Synthesis and characterization of sodium tetra-*p*-sulfonatophenylporphinatorrhodium(III) (Rh(III)-TPPS) is reported. Equilibrium constants for the reactions $Rh(III)TPPS + SCN^- = [Rh(III)TPPS(SCN)]$, and $Rh(III)-TPPS + CN^- = [Rh(III)TPPS(CN)]$ have been determined to be $39M^{-1}$ and $1880M^{-1}$ respectively. Rates and activation parameters of these anation reactions have also been determined. Possible mechanisms are discussed.*

Introduction

Recently several labile substitution reactions of cobalt(III)-porphyrins have been reported in literature [1, 2]. A detailed investigation [3] of imidazole binding to a chromium(III)-porphyrin failed to reveal any unusual labilisation due to porphyrin ligand. Considering the easily available lower oxidation state for cobalt porphyrins and unavailability of such a configuration for chromium porphyrins, the observed labilization could be electronic in origin. To further explore the cause of the labilization we have synthesized the water-soluble tetra-*p*-sulfonatophenylporphinatorrhodium(III) complex, (Rh-TPPS), Figure 1, and investigated the equilibrium and kinetic properties of it. This report summarizes our results.

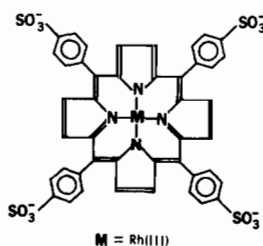


Figure 1. Tetra-*p*-sulfophenylporphinatorrhodium(III).

Experimental

Reagent grade chemicals were used without further purification. A Beckman Century 35 model pH meter was used for titrations and adjusting pH. A Beckman Acta III spectrophotometer equipped

with an automatic sample changer was used for equilibrium and kinetic studies. For faster reactions, a Durrum-Gibson stopped-flow spectrophotometer was used. The thermostated cell compartment was maintained at $30.0 \pm 0.1^\circ C$ for all the studies. The details of equilibrium and kinetic studies were the same as described elsewhere [4].

Synthesis of sodium tetra-*p*-sulfonatophenylporphine: tetraphenylporphine (TPP) was synthesized by the method of Adler *et al.* [5]. In a mortar 10g of TPP was ground with 40 ml of conc. sulfuric acid and the paste was transferred into a 250 ml Erlenmeyer flask. Another 20 ml of conc. sulfuric acid was used to rinse the mortar and transfer the porphyrin as completely as possible. The paste was heated on a steam-bath for 4-5 hours and then left aside overnight. Next day 20 ml of ice-cold water was added to the mixture in the flask. The porphyrin mixture which is green in color was neutralised with sodium hydroxide solution with constant cooling in a one liter beaker. When neutralisation is complete the color turns red. This red solution was evaporated until the solution becomes saturated with sodium sulfate as noted by the crust formation on the surface of the solution. Then the solution is cooled and filtered. The sodium sulfate crystals were washed with methanol till the filtrate became colorless. The filtrate was evaporated to dryness on a steam bath. The solid residue was Soxhlet-extracted with methanol. After removing the methanol on a rotary evaporator, the purified Na_4TPPS was dried in an oven at $100^\circ C$. An extinction analysis indicated the sample to be as pure as that obtained by the literature methods [6, 7].

Synthesis of Rh(III)-TPPS

In a 250ml round-bottom flask, a stoichiometric amount of $(Rh(CO)_2Cl)_2$ was mixed with a luke-warm methanolic solution of Na_4TPPS (1 gm 100 ml) and stirred continuously. Addition of 0.1g of sodium acetate ensured the completion of the reaction. When the spectrum of the reaction flux indicated the absence of free base, the reaction mixture was allowed to cool to room temperature. About two ml of 3% H_2O_2 was added dropwise with stirring. The yellowish solution turned red in about 5 minutes.

Then the solution was heated to decompose the excess peroxide and the solvent was pulled off in a rotary evaporator. The solid residue was dissolved in water and the solution was passed through a column of cation-exchange resin in sodium form. Using dilute sulfuric acid, the pH of the effluent was adjusted to about 2.5 to 3.0. The solution was evaporated to dryness on a steam bath. The residue was Soxhlet-extracted with methanol. The extract was reduced in volume by evaporation and pure Rh(III)-TPPS was precipitated with acetone, filtered and dried in an oven at 100 °C.

Analysis of Rh-TPPS

Rhodium was analyzed by neutron activation as ^{104}Rh . The other analyses were done by Chemalytics Inc., Tempe, Arizona.

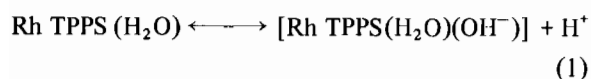
Anal.	C	H	N	S	Rh
Calcd. for $\text{Na}_3\text{C}_{44}\text{H}_{56}\text{N}_4\text{S}_4\text{O}_{28}\text{Rh}$:	38.04	4.15	4.01	9.16	7.38
Found	37.89	2.44	4.08	8.86	7.09

The compound did not show any C–O stretch and was diamagnetic, indicating that the oxidation state of rhodium is three in this complex.

The visible spectrum of Rh(III)-TPPS and the cyano and thiocyanato complexes are presented in Figure 2. A pHmetric titration of Rh(III)-TPPS indicated only one inflection in the pH range of 6.5 to 8.5, the approximate pK_a (pH at half-neutralization point) being 7.5. A plot of absorbance against pH at 415 and 418 nm also showed only one inflection in the pH range 6.0–9.0. A plot of log

$$\frac{A - A_\infty}{A_0 - A}$$

versus pH was found to be straight line with a slope of 0.9 and an intercept of 7.60 ± 0.05 .



Spectrophotometric titrations were carried out in the Soret region (400–450 nm) with SCN^- at pH 4.7 (phthalate buffer) and $\mu = 0.5 \text{ F}$ ($\text{KSCN} + \text{KNO}_3$) and with CN^- at pH 10.50 (Borate buffer) and $\mu = 0.5 \text{ F}$ ($\text{NaCN} + \text{NaClO}_4$). Plots of log

$$\frac{A - A_\infty}{A_0 - A}$$

versus $-\log(\text{ligand})$ in the case of SCN^- and CN^- at 431 and 429 nm were straight lines with a slope of 1.20 and 1.11 respectively. The equilibrium constants for the following reactions were extracted from the data.

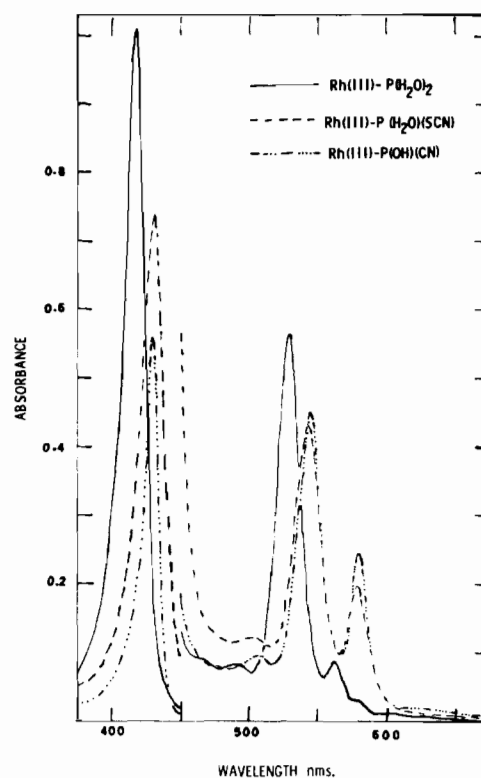
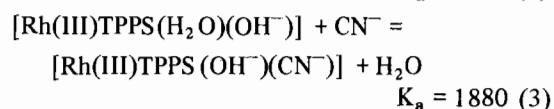
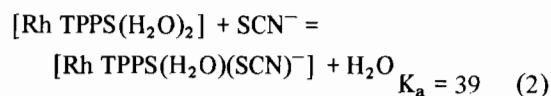


Figure 2. Visible spectrum of rhodium-porphine complexes in solution (absorbance below 450 nm, Soret region, is 30 times the rest of the spectra for aquo and thiocyanato complexes; 60 times for cyano complex).



Anation reactions 2 and 3 were studied at 419 and 429 nm respectively under pseudo first order conditions. The pseudo-first order macroscopic rate constants, k_{obs} , were extracted from the plots of $\ln(A_t - A)$ versus time, which were straight lines over several half-lives. In Figure 3 and 4 the rate constants, k_{obs} , were plotted against the ligand concentration for SCN^- and CN^- respectively. The reactions were studied over a tenfold variation in concentration for SCN^- and fifteenfold variation for CN^- . The entropy and enthalpy of activation at 303 °K are respectively $89.3 \pm 9.1 \text{ kJ}$ and $-1.1 + 14.3 \text{ J}$ for SCN^- reaction and $59.6 \pm 2.1 \text{ kJ}$ and $-77.8 \pm 39.1 \text{ J}$ for CN^- reaction.

Discussion

Recently several studies on the anation reactions of Rh(III) complexes have been reported in the

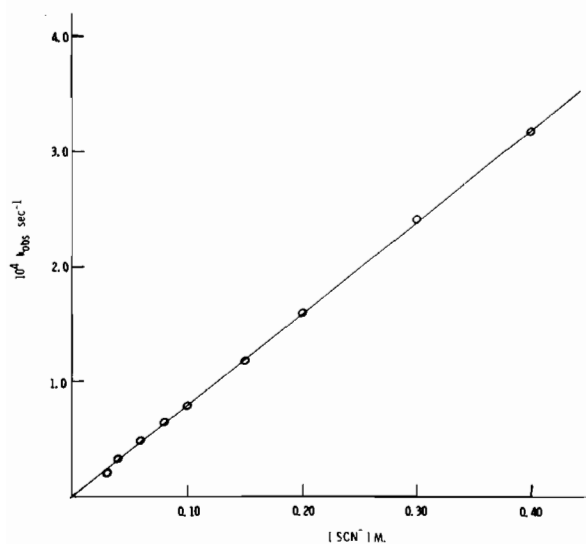


Figure 3. Dependence of pseudo-first order rate constants on the concentration of thiocyanate ion.

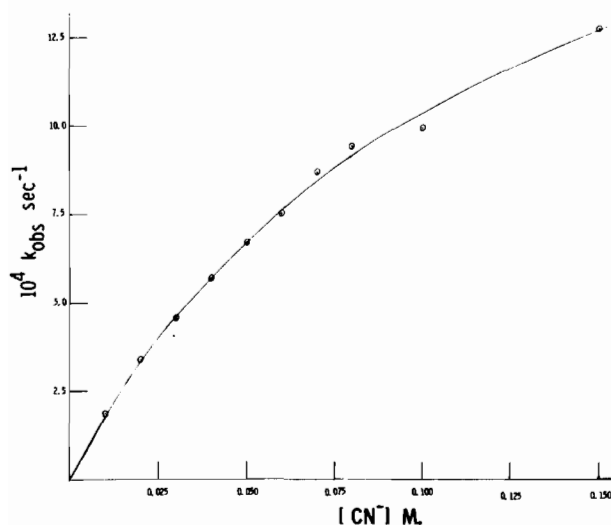


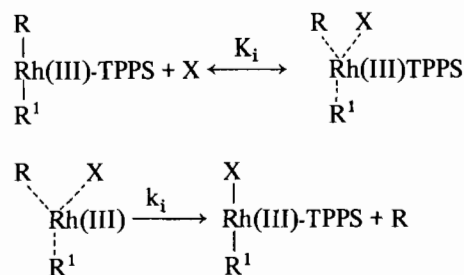
Figure 4. Dependence of pseudo-first order rate constants on the concentration of cyanide ion.

literature [8–17]. In general, they all favor an I_a or S_N2 type mechanism [18] for these reactions. Monacelli and Viel [8] studied the water exchange reaction of $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})^{3+}$ by ^{18}O tracer technique and proposed a predominantly nucleophilic attack path basing their arguments on observed activation parameters. The activation entropy of this reaction is found to be -3.0 e.u. While for the corresponding reaction of Co^{3+} , where the mechanism was proposed to be S_N1 on the basis of the effect of pressure, it was found to be $+6.7$ e.u. In furtherance of this study Monacelli [9] also investigated the anation by Cl^- , Br^- , and SO_4^{2-} of the complex ion $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})^{3+}$. These reactions were shown to follow

an interchange process on the basis of ion-pair formation constants and the kinetic data. Independently Poë and co-workers [10] reported their results on these and some other anation reactions of Rh(III), and proposed a S_N2 or I_a mechanism for these reactions.

Recently Swaddle and Stranks [11] reported their results on water-exchange reaction of $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})^{3+}$. These workers measured the activation parameters such as ΔV^\ddagger , ΔH^\ddagger , and ΔS^\ddagger . While the ΔH^\ddagger values reported by Swaddle and Stranks [11] agree very well with that reported by Monacelli and Viel [8] for the same reaction, the ΔS^\ddagger values differ considerably [12]. Nevertheless, the conclusion of both groups regarding the mechanism of the reaction seems to be that associative interchange is operative. From the pressure dependence of activation volume, Swaddle and Stranks conclude that I_a and I_d mechanism [19] operate competitively in this case, the former predominating at high and the latter at low pressures. They attribute this increased importance of associative mechanism for Rh(III) as compared to Co(III) complexes to the enhanced tendency of the larger central metal atom to engage in covalent bonding to the incoming nucleophile (as measured by the “class B” character [20] or “Softness [21]” of the metal) and to the reduced steric hindrance to the entry of the seventh ligand. Thus significant evidence appears to emerge in the literature [9–11] in favor of an associative mechanism for substitution reactions of Rh(III).

Our results do not distinguish between an associative interchange or a dissociative mechanism. But in conformity with the large number of Rh(III) anation reactions reported in the literature, it would appear that this reaction also proceeds by the same associative interchange mechanism. The large negative entropy of activation also seems to support this conclusion. Accordingly, the following steps are defined for the anation reactions we studied, and the constants evaluated.



When $\text{X} = \text{SCN}^-$, R and $\text{R}^1 = \text{H}_2\text{O}$; $K_i k_i = 7.90 \times 10^{-4} \text{ M}^{-1} \text{ sec}^{-1}$.

When $\text{X} = \text{CN}^-$, $\text{R} = \text{H}_2\text{O}$ and $\text{R}^1 = \text{OH}^-$; $k_i = 2.08 \times 10^{-3} \text{ sec}^{-1}$ and $K_i = 9.72 \text{ M}^{-1}$.

The pseudo-first order rate constants for the reaction of chloride [10] with $(\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O})^{3+}$ was found to be $6.4 \times 10^{-6} \text{ sec}^{-1}$ at $\mu = 1.5 \text{ F}$, $T = 35^\circ \text{C}$ and ligand concentration of 0.50 F . The water exchange rate of the pentammine complex was found to be $3.22 \times 10^{-5} \text{ sec}^{-1}$ (at $\mu = 0.12 \text{ F}$ and 35°C), and $2.2 \times 10^{-5} \text{ sec}^{-1}$ (at $\mu = 0.43 \text{ F}$ and 30°C [11]). Comparing either the chloride ion substitution rate or the water exchange rate of the pentammine complex with our data, one finds that there is at least a hundredfold labilization by the porphyrin ligand. Similarly comparing the analogous data [16] for chloride ion substitution with $\text{Rh}(\text{H}_2\text{O})_6^{3+}$ (where k_{obs} at $\text{Cl}^- = 0.50 \text{ F}$ is calculated to be $2.48 \times 10^{-6} \text{ sec}^{-1}$ at 75°C and $\mu = 2.5 \text{ F}$) with our data, one finds at least a hundredfold labilization or more. The anation reactions [13] of $(\text{RhCl}_5\text{H}_2\text{O})^{2-}$ is found to be $1.03 \times 10^{-3} \text{ sec}^{-1}$ at $\text{SCN}^- = 0.50 \text{ F}$, $\mu = 4.0 \text{ F}$ and 35°C . This rate is comparable with our data. It is not certain whether a *trans* chloride labilizes these anations or whether the assignment of rates measured pertains properly to the anation or to ion-pair formation. For in this study [13], there appear to be two consecutive reactions, of which the first faster reaction has been ascribed to anation and the second slower one to a second anion displacement. The possible *trans* labilization by chloride and hydroxide ions appears to be well documented [15–17].

In this Rh(III)-TPPS case, while available evidence does not rule out a pentacoordinate geometry, the rate constants for substitution are not appreciably dissimilar from that of normal Rh(III) complexes. This is to be expected if π -delocalization were the cause for on going from Co(III) to Rh(III) the energy of the d orbitals increases significantly rendering such a delocalization improbable. Even the labilization observed in the case of Ru porphyrins may be caused by the *trans* bound CO ligand.

Lacking a thorough knowledge about the coordination sphere of the metal in Rh-TPPS, it would be improper to ascribe the origin of the labilization to either the geometry or to the electron delocalization completely. In conclusion, the substitution reactions of Rh(III)-TPPS appear to follow an associative interchange mechanism.

Acknowledgement

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