Short Communication

Kinetics of the reaction of cyanide with ruthenium phthalocyanine complexes

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Abstract

Kinetic studies of the reaction of cyanide with (CO)(DMF)RuPc and $(DMSO)_2RuPc$ in DMF are reported. In the presence of a large excess of cyanide, the $(CN)_2RuPc$ complex is formed by pseudo first order kinetics. The reaction is first order in both cyanide and phthalocyanine, with specific rate constants of 5.2×10^{-2} and 7.2×10^{-2} M^{-1} s^{-1} for reactions of cyanide with (CO)(DMF)RuPc and $(DMSO)_2RuPc$, respectively. The rate constants correspond to the coordination of the second cyanide ligand to the ruthenium phthalocyanine species.

Introduction

Phthalocyanine (Pc) complexes are structurally similar to the porphyrins, hence phthalocyanines may be used to model the naturally occurring porphyrin systems which are difficult to study directly. Because of the presence of iron porphyrin complexes in nature, iron phthalocyanine (FePc) has been widely studied as a model compound for the porphyrin complexes. Studies of the properties of ruthenium phthalocyanine (RuPc) are very important since otherwise reactive intermediates are expected to be more stable for Ru than for Fe complexes [1].

There is also a need to develop drugs that will act against the toxic effects of cyanide. To this effect, there have been several investigations on the kinetics of cyanide coordination to several porphyrin complexes [2–7]. Both Ru(II) and Ru(III) porphyrin complexes are known to bind cyanide [2]. Cyano complexes of RuPc have been reported [8, 9], but there has been no study on the kinetics of the displacement of axial ligands in $(L)_2RuPc$ complexes by cyanide ligands.

Studies [10–14] on axial ligand exchanges in FePc complexes have shown that ligand substitution in $(L)_2FePc$ complexes is a stepwise process shown by reactions (1) and (2)

$$(L)_2FePc+X \rightleftharpoons (L)(X)FePc+L \qquad (1)$$

$$(L)(X)FePc+X \rightleftharpoons (X)_2FePc+L \qquad (2)$$

where L is the leaving ligand and X is the entering ligand. It has been shown that the exchange of the first DMSO ligand in $(DMSO)_2FePc$ by pyridine or imidazole [10, 11] occurs very fast and causes only minor spectral changes. We present in this work the kinetics of the replacement of axial ligands in $(DMSO)_2RuPc$ and (CO)(DMF)RuPc by cyanide. The results are compared with the kinetic data for axial ligand exchange in FePc and metalloporphyrin complexes.

Experimental

$(DMSO)_2RuPc\cdot 2DMSO$ and (CO)(DMF)RuPc were prepared and purified according to the method of Dolphin *et al.* [15]. The preparation of $K_2[(CN)_2Ru(II)Pc]$ has been reported before [8]. (CO)(DMF)Ru(II)Pc: $\nu(CO)=1950$ cm^{-1}, λ(Q band) = 642 nm, $\epsilon_{642}=148\,000$ l mol^{-1} cm^{-1}; $(DMSO)_2RuPc\cdot 2DMSO$: λ(Q band) = 640 nm, $\epsilon_{640}=88\,000$ l mol^{-1} cm^{-1} and $K_2[(CN)_2Ru(II)Pc]$: $\nu(CN^-)=2075$ cm^{-1}, λ(Q band) = 620 nm, $\epsilon_{620}=60\,000$ l mol^{-1} cm^{-1}. Absorbances and extinction coefficients are reported for DMF solutions. Dimethyl sulfoxide (DMSO, Merck) and dimethyl formamide (DMF, BDH) were stirred in alumina and distilled under reduced pressure.

Kinetic runs were performed at 25 °C and monitored with a Beckman UV 5240 spectrophotometer. Typically, a known volume of the DMF solutions of $(DMSO)_2RuPc$ or (CO)(DMF)RuPc in the concentration range 10^{-5}–10^{-6} M, was added to the spectrophotometric cell of 1 cm path length; accurate values of the phthalocyanine concentrations were obtained from the Q band absorption using the extinction coefficients reported above. Then, a known volume of a DMF solution of potassium cyanide was added to the spectrophotometer cell and the absorption spectra monitored with time. Pseudo first order conditions were adopted since the concentration of cyanide was, in all experiments, at least 50 times higher than the concentration of the

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RuPc complexes. The cyanide concentration was determined by titration with silver nitrate.

IR spectra (KBr disks) were collected with a Perkin-Elmer model 180 IR spectrophotometer.

Results

Like all (CO)(L)RuPc complexes [15], (CO)(DMF)RuPc exhibits a characteristically sharp Q band, while the Q band for $(DMSO)_2RuPc$ is broader. The kinetics for cyanide addition to both (CO)(DMF)RuPc and $(DMSO)_2RuPc$ were followed by monitoring either the decrease in intensity of the Q band of the original species or the increase in intensity of the Q band of the cyano complex formed at 620 nm. The experiments were performed by keeping the phthalocyanine concentration constant and changing the cyanide concentration.

Figure 1 shows spectral changes observed when solutions of potassium cyanide in DMF were added to DMF solutions of (CO)(DMF)RuPc (Fig. 1(a)) and $(DMSO)_2RuPc$ (Fig. 1(b)). The Q band at 642 and 640 nm, for (CO)(DMF)RuPc and $(DMSO)_2RuPc$, respectively, decreases in intensity and a new band is formed at 620 nm. The presence of an isosbestic point shows that only two species are involved in the reaction. Figure 2 shows a plot of log[(CO)(DMF)RuPc] against time. Similar plots were obtained for the $(DMSO)_2RuPc$ complex. The results shown in Fig. 2, show that the reaction is first order in phthalocyanine. The observed rate constant, k_{obs}, was found to vary linearly with cyanide concentration, Fig. 3, showing that the reaction is first order in cyanide. The least-squares analysis gave second order rate constants of 0.052±0.003 M^{-1} s^{-1} for the (CO)(DMF)RuPc complex and 0.072±0.005 M^{-1} s^{-1} for $(DMSO)_2RuPc$.

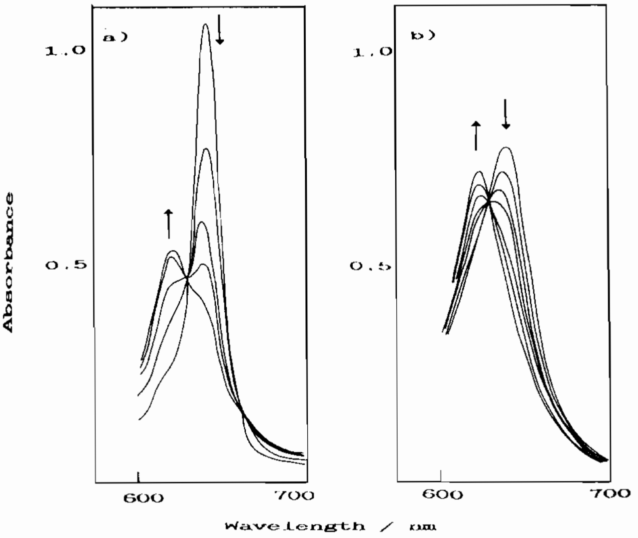

Fig. 1. Spectral changes observed after addition on cyanide to: (a) 7.2×10^{-6} M solution of (CO)(DMF)RuPc in DMF; (b) 1×10^{-6} M solution of $(DMSO)_2RuPc$ in DMF.

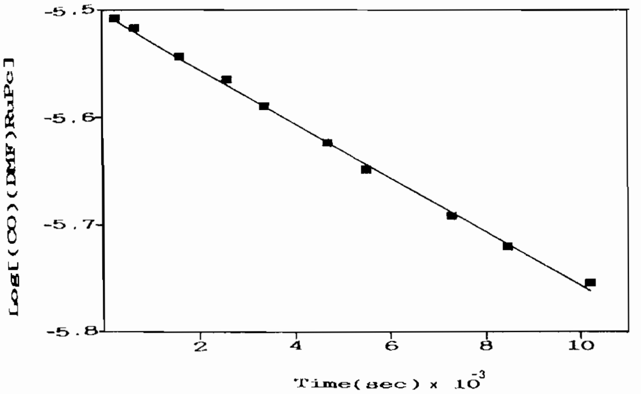

Fig. 2. Plot of log[(CO)(DMF)RuPc] vs. time. $[CN^-]=1.43\times10^{-3}$ M; $[(CO)(DMF)RuPc]=3.3\times10^{-6}$ M in DMF.

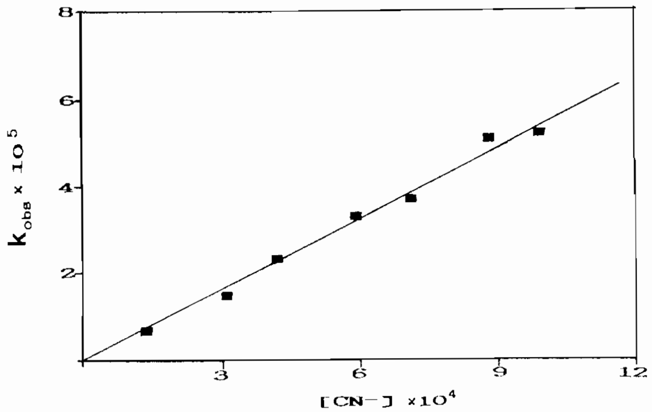

Fig. 3. Plot of K_{obs} vs. cyanide concentration for (CO)(DMF)RuPc in DMF.

Discussion

When excess cyanide was reacted with (CO)(DMF)RuPc or $(DMSO)_2RuPc$ in DMF, and the solvent evaporated to low volume, elemental analysis showed that the solid product obtained was the $K_2(CN)_2RuPc$ species [8]. The IR spectra confirm the loss of the CO ligand from the (CO)(DMF)RuPc after reaction with cyanide. The spectra at the end of the reaction of (CO)(DMF)RuPc or $(DMSO)_2RuPc$ with cyanide, Fig. 1, is identical with the spectra of $(CN)_2RuPc$ in DMF with the Q band centred at 620 nm. Thus, the final product in the reaction of DMF solutions of $(DMSO)_2RuPc$ or (CO)(DMF)RuPc with cyanide is the $(CN)_2RuPc$ complex, and hence the rate constants reported in this work correspond to the formation of this complex.

TABLE 1. Rate constants for axial ligand exchange in some phthalocyanines and porphyrin complexes

Reactant[a]	X[b]	Product	Rate constant[c]	Ref.
$CoTPPS(H_2O)_2$ (H_2O)	CN	$CoTPPS(H_2O)(CN)$	3.1×10^2	6
$CoTPPS(H_2O)(CN)$ (H_2O)	CN	$CoTPPS(CN)_2$	3.0×10^4	6
RuP(CO) (H_2O)	CN	RuP(CO)(CN)	2.3	2
RuP(CO)(CN) (H_2O)	CN	$RuP(CN)_2$	4.6×10^{-5}[d]	2
$FePc(DMSO)_2$ (DMSO)	py	FePc(DMSO)(py)	1.5×10^4	11
FePc(DMSO)(py) (DMSO)	py	$FePc(py)_2$	35.5	11
$FePc(DMSO)_2$ (DMSO)	Im	FePc(DMSO)(Im)	9.8×10^3	10
FePc(DMSO)(Im) (DMSO)	Im	$FePc(Im)_2$	5.4	10
RuPc(DMF)(CO) (DMF)	CN	$RuPc(CN)_2$	5.2×10^{-2}	this work
$RuPc(DMSO)_2$ (DMF)	CN	$RuPc(CN)_2$	7.2×10^{-2}	this work

[a] Solvent shown in brackets. P = porphyrin, TPPS = tetrakis(4-sulfonatophenyl) porphyrin. [b] X is the nucleophile. [c] Rate constants in units of $M^{-1}\ s^{-1}$ unless otherwise stated. [d] Units of s^{-1}.

The coordination of cyanide to the ruthenium(II) porphyrin (P) complex, (CO)Ru(II)P, occurs in two steps with the formation of (CN)(CO)RuP followed by $(CN)_2RuP$ and as already mentioned, the substitution reactions in phthalocyanine complexes are also known to occur in a stepwise manner. The exchange of the first ligand in $(L)_2FePc$ complexes is known to occur very fast and to cause only minor spectral changes [10]. These changes are often difficult to detect by conventional absorption spectral techniques. The absence of any detectable absorption effect of the exchange of the first ligand may often give an impression that both ligands are exchanged at the same time.

The fact that the reaction of the RuPc complexes with cyanide is first order in both cyanide and phthalocyanine, confirms a stepwise substitution mechanism for these complexes. The mechanisms are represented as follows for $(DMSO)_2RuPc$ (reactions (3) and (4)) and (CO)(DMF)RuPc (reactions (5) and (6)).

$$(DMSO)_2RuPc + CN^- \xrightleftharpoons{k_1} (DMSO)(CN)RuPc + DMSO \quad (3)$$

$$(DMSO)(CN)RuPc + CN^- \xrightleftharpoons{k_2} (CN)_2RuPc + DMSO \quad (4)$$

$$(CO)(DMF)RuPc + CN^- \xrightleftharpoons{k_1} (CO)(CN)RuPc + DMF \quad (5)$$

$$(CO)(CN)RuPc + CN^- \xrightleftharpoons{k_2} (CN)_2RuPc + CO \quad (6)$$

A small increase in absorbance of the Q band was observed immediately after the addition of cyanide to $(DMSO)_2RuPc$, prior to the decrease in absorbance shown in Fig. 1(b). An initial increase in the absorbance of $(DMSO)_2FePc$ after additions of small amounts of pyridine to this complex was attributed to the formation of (DMSO)(py)FePc, where only the first ligand has been substituted [11]. In comparison with the FePc complexes, we assign the initial decrease in the intensity of the Q band during cyanide addition to the $(DMSO)_2RuPc$ complex to the formation of the (DMSO)(CN)RuPc species, with a rate constant k_1. This mono-cyano substituted complex forms very fast, hence it was not possible to determine the kinetic data associated with its formation under our experimental conditions. There was no detectable increase in the Q band absorbance on addition of cyanide to the RuPc(CO)(DMF) complex.

Thus, reactions (3) and (5) are very fast, consistent with the observations for the FePc complexes. The specific rate constants reported in this work correspond to k_2, the rate constants for the coordination of the second cyanide ligand to $(DMSO)_2RuPc$ and (CO)(DMF)RuPc. This is in agreement with the observation that the reaction is first order in both cyanide and phthalocyanine and that the product observed after addition of cyanide is the dicyano RuPc complex. k_2 values are expected to be much lower than k_1 values.

It is widely accepted [10] that axial ligand substitution reactions in phthalocyanine complexes are dissociative with the formation of a reactive five-coordinate intermediate. Hence reactions (3) and (5) are most likely preceeded by steps (7) and (8), respectively

$$(DMSO)_2RuPc \longleftrightarrow (DMSO)RuPc \quad (7)$$

$$(CO)(DMF)RuPc \longleftrightarrow (CO)RuPc \quad (8)$$

DMF is known to be a more labile ligand than CO in RuPc complexes [15]. Also, the replacement of the CO ligand in (CO)RuP is known to be a slow process [2]. It is thus expected that the DMF ligand will be replaced before the CO ligand in (CO)(DMF)RuPc, to give an intermediate (CO)RuPc species.

Table 1 shows the kinetic data for ligand exchange in some metalloporhyrin and metallophthalocyanine complexes. Coordination of the second cyanide ligand to CoTPPS complexes occurs more rapidly than the coordination of the first ligand. The reverse is true for the ruthenium porphyrin complex. The rate behaviour described in this work for RuPc complexes suggests a fast intake of the first ligand and a much slower intake of the second ligand as observed for the (CO)RuP complex [2]. Studies on the (CO)RuP complex have, however, shown that the second cyanide coordination is independent of the cyanide concentration.

Even though the $(CN)_2RuPc$ complex is soluble in water [8], the (DMF)(CO)RuPc and $(DMSO)_2RuPc$ complexes are insoluble in water, making the comparison of the rates of cyanide coordination between the water soluble porphyrins and the RuPc complexes unreliable. It has been observed that axial ligand exchange is much faster in porphyrins than in phthalocyanine complexes [14]. Table 1, however, shows that the rate of the second cyanide coordination to the ruthenium porphyrin complex is slower than for the RuPc complexes. It is also clear from Table 1 that the rate of axial ligand exchange in FePc complexes is much higher than the corresponding rate in RuPc complexes.

Acknowledgments

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