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Reversible binding of carbon monoxide with Ru(III) aminopolycarboxylic acid complexes

M M Taqui Khan*, N H Khan & R I Kureshy
Discipline of Coordination Chemistry & Homogeneous Catalysis, Central Salt & Marine Chemicals Research Institute
Bhavnagar 364 002

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The reversible binding of carbon monoxide to the complexes $[Ru^{III}(EDTA\text{-}H)(H_2O)]$ **1** and $[Ru^{III}(PDTA\text{-}H)(H_2O)]$ **2** have been studied in aqueous solution at $pH = 5$ by spectrophotometric and electrochemical studies. The equilibrium constant for carbonylation, K_{CO} was evaluated at 10°, 25° and 40°C. The thermodynamic parameters, $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the carbonylation of the complexes **1** and **2** have been evaluated. The complex $[Ru(PDTA\text{-}H)(CO)]$ **4** is more stable than the complex $[Ru(EDTA\text{-}H)(CO)]$ **3** in solution.

Understanding the role, the protein plays in regulating the binding of small ligands to hemoproteins continues to be a topic of active interest[1-4]. Recently attention has been focussed on the discrimination of the heme cavity between small ligand such as CO and O_2, thereby affecting their relative binding affinities[5-9]. In order to understand the role of the steric effect on the discrimination reaction in hemoproteins a series of model porphyrins were designed and synthesized[6-10].

Carbonyl complexes of ruthenium, osmium, rhodium and iridium in lower oxidation states are partly stabilized by CO to give rise to cluster formation[11,12]. Some pH-dependent kinetic and equilibrium studies of these metal carbonyl complexes were also reported in nonaqueous[13] and aqueous media[14,15]. Reaction of $RuCl_3.xH_2O$ with CO in acidic medium was studied in solution by IR technique[14]. Taqui Khan *et al.*[16] studied the rate of formation of the carbonyl species [Ru(EDTA-H)(CO)] by stopped flow method. No systematic attempt has, however, been made to evaluate the equilibrium constant for carbonylation in aqueous solution. In this paper we report the reversible binding of CO to $[Ru(EDTA\text{-}H)(H_2O)]$ **1** and $[Ru(PDTA\text{-}H)(H_2O)]$ **2** in aqueous medium at pH 5. The factors influencing the CO affinity were also evaluated in terms of thermodynamic parameters $\Delta H°$, $\Delta G°$ and $\Delta S°$ for the formation of these complexes in solution.

Experimental

$RuCl_3xH_2O$ was obtained from Johnson Matthey, ethylenedinitrilotetraacetic acid (EDTA-H) and propylenedinitrilotetraacetic acid (PDTA-H) were purchased from Aldrich. Doubly distilled deionized water was used for solution formation of the complexes. Carbon monoxide was prepared by the reaction of sodium formate with concentrated H_2SO_4 and purified by passing through a tower of KOH pellets. The complexes $[Ru(EDTA\text{-}H)(H_2O)]$[17] and $[Ru(PDTA\text{-}H)(H_2O)]$[18] were prepared by reported procedure and characterized by elemental analysis.

Physical measurements

The spectrophotometric measurements were carried out on Shimadzu UV/visible 160 spectrophotometer equipped with a temperature controller TCC-240A. Matched 10 or 2 mm cells were used to record the spectra. Cyclic voltammogram, D.C. and differential pulse polarogram were recorded on a PAR electrochemical system 174, equipped with a precision x-y recorder and model 173 galvanostat as described earlier[19]. Ag/AgCl was used as reference electrode with 0.1 M $NaClO_4$ as supporting electrolyte.

CO uptake measurements

In order to evaluate the equilibrium constant for carbonylation K_{CO} by UV/visible spectrophotometry, the solutions of aquo species $[Ru(EDTA\text{-}H)(H_2O)]$ **1** and $[Ru(PDTA\text{-}H)(H_2O)]$ **2** were prepared in the concentration of $5 \times 10^{-4} M$ at $pH = 5$ in doubly distilled water. The chloro complexes immediately underwent aquation in solution to form the aquo species $[Ru(EDTA\text{-}H)(H_2O)]$ **1** and $[Ru(PDTA\text{-}H)(H_2O)]$ **2**. Solutions of complexes **1** and **2** were saturated with CO by varying the concentration of CO in the range 1:1, 1:2 and 1:3 with respect to the degassed doubly distilled water. The wavelength of maximum absorbance (λ_{max}) at 386-390 nm for carbonyl complexes was found by passing CO through the solution of the complexes **1** and **2** and recording the spectra. For each concentration, the spectrum was recorded immediately at 10°, 25° and 40° and a constant value of absorbance was noted. The solubility of CO was also measured separately in water at different temperatures. The reaction of the complexes with CO may be written as:

$$Ru^{III}L(H_2O) + CO \rightleftharpoons Ru^{III}(L)(CO) + H_2O$$

$$K_{CO} = \frac{[Ru^{III}L(CO)]}{[Ru^{III}(L)(H_2O)][CO]}$$

L = EDTA-H; PDTA-H

Table 1—Thermodynamic parameters and equilibrium constant for CO binding in Ru(III) aminopolycarboxylic acid complexes in aqueous medium

Complexes	Temp. °C	log K_{CO}	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$(25°) (kJ mol^{-1})	$\Delta S°$(25°) (J deg^{-1} mol^{-1})
1 [Ru(EDTA-H)(H_2O)	10	2.80 ± 0.2			
	25	2.65 ± 0.3	−28 ± 1	−15.1 ± 0.5	−43 ± 4
	40	2.31 ± 0.1			
2 [Ru(PDTA-H)(H_2O)]	10	3.01 ± 0.1			
	25	2.73 ± 0.02	−30 ± 1	−15.5 ± 0.5	47 ± 4
	40	2.45 ± 0.1			

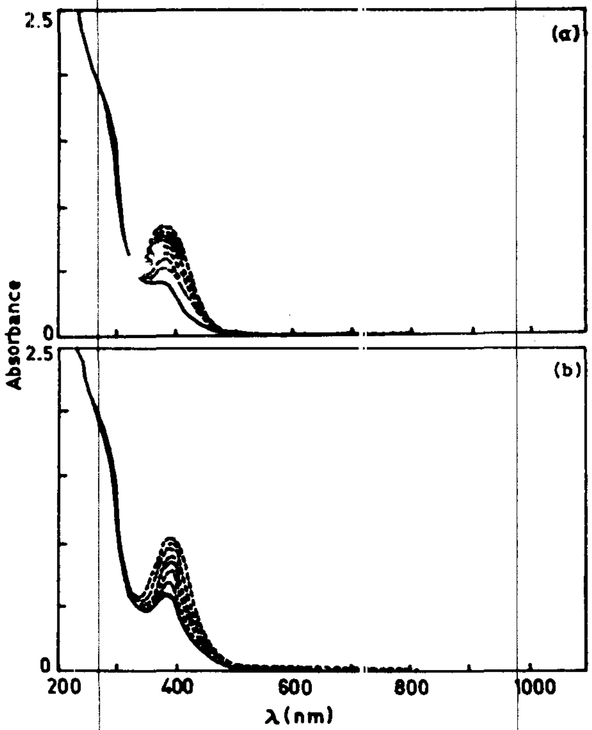

Fig. 1—(a) The UV-vis. absorption spectral change during carbonylation of [Ru(EDTA-H)(H_2O)] in water at $pH = 5$ (1×10^{-3} M) with time (——) soon after preparation (----) after 4 h; in 15 min intervals at 303°K and path length 1 = 1 cm.

Fig. 1—(b) The UV-vis. absorption spectral change during carbonylation of [Ru(PDTA-H)(H_2O)] in water at $pH = 5$ (1×10^{-3} M) with time (——) soon after preparation, (----) after 4h; in 15 min intervals at 303°K and path length 1 = 1 cm.

The equilibrium constant K_{CO} was calculated by reported method[20].

Results and discussion

The UV-visible spectra recorded in doubly distilled water at pH 5 saturated with CO show an increase in absorbance at (λ_{max} = 390-386 nm) with time. Representative absorption spectra of [Ru(EDTA-H)(H_2O)] and [Ru(PDTA-H)(H_2O)] in aqueous solution saturated with CO are depicted in Fig. 1a and 1b, respectively. The maximum increase in absorbance was observed at 390 and 386 nm and assigned to MLCT M → CO band. The reversible binding of CO is confirmed by flushing nitrogen through the solution which displaces CO and the original spectrum of the complexes was obtained. This reflects on the low stability of Ru(III) carbonyl complexes over those of Ru(II) carbonyl species which are more stable because of greater softness and lower value of electronegativity of Ru(II) as compared to Ru(III).

Carbonylation of the complexes does not cause a reduction of Ru(III) to Ru(II). This was confirmed by the measurement of $E_{1/2}$ of Ru(III)/Ru(II) couple in D.C. and differential pulse polarograms of the solutions. Under N_2, the $E_{1/2}$ values lie at −0.18 volts (RuPDTA) and −0.15 volts (RuEDTA) while under CO the Ru(III)/Ru(II) couple shift towards more negative side and lie at −0.25 volts in RuPDTA and −0.20 volts in RuEDTA. This behaviour was also seen in CO binding to Ru(III) Schiff base complexes[21-23].

On dissolution of the complexes **1** and **2** in aqueous media Cl^- is immediately displaced by water to form aquo complex and later by displacement of H_2O by CO to form carbonyl complexes. The lability of chloro group is very important for catalysis of the complexes in carbonylation reaction[24].

The discrimination in binding of CO depends on the polarity of the solvents as well as the electron-donating substituent attached. A good σ donor increases[25] the electron density on ruthenium(III) and assists in the labilization of H_2O molecule in a nucleophilic displacement reaction.

From the data in Table 1 the equilibrium constant for carbonylation K_{CO} was comparatively more for [Ru(PDTA-H)(H_2O)] **2** compared to [Ru(EDTA-H)(H_2O)] **1**. It may be due to the inductive effect of the methyl group attached to ethylenediamine collar in PDTA complex. The stability of carbonyl complexes with respect to the ligands (EDTA and PDTA) decreases in the order RuPDTA> RuEDTA. The same trend was also reported elsewhere[26]. The stability K_{CO} of the [Ru(EDTA-H)(CO)] complex at 25° agrees very well with that obtained indirectly[16] by kinetic method.

The thermodynamic parameters associated with reversible binding of CO to complexes **1** and **2** are given in Table 1. Since the overall reaction involves a displacement of H_2O molecule by CO the enthalpy should depend on the labilization of H_2O molecule in the complexes and depends[25] on the extent of σ donation and π-backbonding of the ligands present in the coordination sphere of the metal ion. The stability of the carbonyl complex of Ru(III)EDTA-H and Ru(III) PDTA-H complexes are about an order to magnitude lower than that of Ru(III) schiff base complexes[20-22]. The complexes exhibit discrimination towards CO binding as compared to oxygen[21,23]. The lower stability of Ru(III) carbonyls seems to be predominantly due to decrease in the $d\pi$-$p\pi$ back-bonding of CO in these complexes. From the thermodynamic data the enthalpy values which are a measure of metal ligand bond strength are more endothermic in [Ru(EDTA-H)(CO)] **3** as compared to [Ru(PDTA-H)(CO)] **4** complex which reflects on a weaker M-CO bond strength in **3** as compared to **4**. The entropy is more positive in **3** compared to **4** indicating a loss of vibrational and rotational degrees of freedom of CO on coordination to the metal ion.

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