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> PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Complexation of Sterically Hindered Cobalt Porphyrin with 1-Methylimidazole along the Axial Coordinate and the Reaction of Reversible Binding of Oxygen

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Abstract—The complexation of a sterically hindered cobalt porphyrin with 1-methyl imidazole and its reaction of reversible binding of oxygen was studied. Spectrophotometry and potentiometry were used to determine the equilibrium constant of the oxygenation process.

In the last decade, methods for synthesis and study of properties of model compounds of natural porphyrins reversibly binding oxygen have been developed successfully. Synthetic oxygen transporting agents of this kind find use as blood substitutes, gas sorbents, and materials for recovery of oxygen from liquid media [1-4].

Monitoring the partial pressure of oxygen in gases, liquids, and semi-liquid media is an important task in most of biochemical investigations and technological processes. It is of indubitable interest, in this context, to develop a potentiometric sensor for measuring the partial pressure on the basis of a redox system that contains cobalt porphyrin and reversibly binds oxygen [5]. A necessary stage in this case is a study of the properties of the cobalt porphyrin.

The goal of this study was to examine the complexation of sterically hindered cobalt(II) mesotetra($\alpha, \alpha, \alpha, \alpha$ -*ortho*-pivalamidophenyl)porphyrin [Co(II)TPivPP] with 1-methylimidazole along the axial coordinate and the reaction of reversible binding of oxygen.

EXPERIMENTAL

The meso-tetra($\alpha, \alpha, \alpha, \alpha$ -*ortho*-pivalamidophenyl)porphyrin was synthesized by the procedure suggested by Collman [6]. The compound [Co(II)TPivPP] was obtained by heating free porphyrin with CoCl₂ in a flow of argon under constant stirring in a solution of tetrahydrofuran [7]. The purity of the products synthesized was verified chromatographically and using spectra. The complexation with 1-methylimidazole was studied spectrophotometrically. In the experiments, the dependence of the optical density of [Co(II)TPivPP] solutions in propyl cyanide on the concentration of 1-methylimidazole was determined at a fixed wavelength and analyzed. Propyl cyanide was chosen as the solvent because it has a sufficiently high dielectric constant ($\varepsilon = 20.3$) and does not react with metal porphyrins. As supporting electrolyte served tetrabutylammonium perchlorate (TBAP), c(TBAP) = 0.1 M. All the measurements were performed in quartz cuvettes of thickness 0.1 and 1.0 cm on an SF-18 spectrophotometer. The titration with a solution of 1-methylimidazole was performed directly in the cuvette. The titrant was added dropwise to a solution of [Co(II)TPivPP] in the atmosphere of argon and a spectrum of the solution was recorded upon each addition. All the measurements were carried out at a temperature of $20 \pm 0.5^{\circ}$ C. Figure 1 shows the experimental data in the form of a dependence of the optical density $A(\lambda_{532})$ of the [Co(II)TPivPP] solution on the concen-



Fig. 1. Optical density A ($\lambda = 532$ nm) of the [Co(II)TPivPP] solution vs. the pc_{L} of 1-methylimidazole.

Fig. 2. Spectra of [Co(II)TPivPP] solutions in propyl cyanide in the presence of 1 M of 1-methylimidazole and 0.1 M of TBAP at different partial pressures of oxygen. (*A*) Optical density and (λ) wavelength. *P*_{O2} (mm Hg): (1) 0, (2) 38, (3) 84, (4) 114, (5) 190, (6) 380, and (7) 760.

tration of 1-methylimidazole (pc_L) . The first stage of the reaction of axial complexation of [Co(II)TPivPP] with 1-methylimidazole can be represented as

$$[Co(II)TPivPP] + L = [Co(II)TPivPPL], \quad (1)$$

where L is 1-methylimidazole.

Introduction of 1-methylimidazole into a porphyrin solution leads to a decrease in the optical density at $\lambda = 532$ nm. It can be shown, with account of this circumstance, that the dependence of the optical density of the solution on the ligand concentration $c_{\rm L}$ can be expressed as

$$A = \frac{A_0 + A_1 K_1 c_{\rm L}}{1 + K_1 c_{\rm L}},\tag{2}$$

where A is the optical density measured in the experiment; A_0 , optical density of a solution without ligand; A_1 , optical density of a solution in which the complexation is complete; and K_1 , complexation constant found from the equation

$$K_1 = \frac{[\text{Co(II)TPivPPL}]}{[\text{Co(II)TPivPP}][L]}.$$

The experimental dependence is described by a smooth single-step curve, which is due to the occurrence of the reaction of 1-methylimidazole addition by Eq. (1). The logarithm of the stability constant for [Co(II)TPivPP] with 1-methylimidazole, calculated by Eq. (2), is 3.3 ± 0.2 . The data obtained suggest that, at a 1-methylimidazole concentration of 0.1 M, the complexation in the system constituted by porphyrin and 1-methylimidazole is complete. This result is of primary importance for a study of the reaction in which oxygen is reversibly bound in the presence of 1-methylimidazole.

The reversible binding of O_2 was studied by means of spectrophotometry in a hermetically sealed quartz cuvette. The partial pressure of O_2 was set by mixing argon and oxygen in various volume ratios at 1 atm in calibrated gas meters. Each mixture of gases, preliminarily dried over KOH, was bubbled through the cuvette for 20 min, and the spectrum of the solution was recorded after that. All the measurements were performed at a temperature of $20 \pm 0.5^{\circ}C$.

It is known that, in the presence of an axial ligand, 1-methylimidazole, and O_2 in a [Co(II)TPivPP] solution, there exist the equilibrium

$$[Co(II)TPivPPL] + O_2 \rightleftharpoons [Co(II)TPivPPLO_2], (K_{O_2}). (3)$$

The fact that logarithm of the stability constant of [Co(II)TPivPP] with 1-methylimidazole has a value of 3.3 ± 0.2 shows that the complex [Co(II)TPivPPL] is formed to an extent exceeding 99% at a 1-methylimidazole concentration of 1 M. To determine K_{O_2} , spectra of a [Co(II)TPivPP] solution in propyl cyanide were recorded in the presence of 0.1 M of 1-methylimidazole and 0.1 M of TBAP at different partial pressures of O₂. Typical changes in the spectrum of a [Co(II)TPivPPL] solution in propyl cyanide in the presence of O₂ are shown in Fig. 2. It can be seen that, as the concentration of O₂ increases, the peak at 534 nm, associated with the deoxygenated form, is shifted to longer wavelengths, and a new peak associated with the oxygenated form appears at 552 nm.

Two clearly pronounced isobestic points are observed at 540 and 470 nm, which points to the presence of two interconvertible species in the solutions. In deoxygenation of the solution by bubbling of argon, the spectrum changes in the opposite direction and virtually coincides with the initial spectrum, i.e., the starting cobalt porphyrin is oxidized only slightly. It should be noted that the oxygenated form Co(II)TPivPPLO₂ and the oxidized species Co(II)TPivPPL⁺ have the same spectrum. K_{O_2} was calculated using the Drago equation [6]



$$P_{1/2} = K_{O_2}^{-1} = P_{O_2} \left(\frac{[\text{CoP}]_{\text{tot}} l\Delta\varepsilon}{\Delta A} - 1 \right), \tag{4}$$

where $[CoP]_{tot}$ is the total concentration [Co(II)TPivPP]in solution; *l*, cuvette thickness; $\Delta \varepsilon$, difference of the absorption coefficients of the oxygenated and deoxygenated species; and ΔA , difference of the optical densities at a certain P_{O_2} and in the absence of oxygen.

This equation is convenient in that it does not require any knowledge of the optical density of the oxygenated form, because the oxygenation is not complete even at $P_{O_2} = 1$ atm and 0°C. Transformation of Eq. (4) yields

$$P_{O_2} = [CoP]_{tot} l \Delta \varepsilon \left(P_{O_2} / \Delta A \right) - P_{1/2}.$$
 (5)

The plot of P_{O_2} against $(P_{O_2}/\Delta A)$ is a straight line with a slope equal to $[CoP]_{tot}/\Delta \epsilon$. This plot (Fig. 3) was used to determine K_{O_2} .

At a temperature of $20 \pm 0.5^{\circ}$ C in propyl cyanide in the presence of 0.1 M of TBAP, $P_{1.2} = 140 \pm 7$ mm Hg $(K_{O_2} = 7.2 \times 10^{-3})$.

The reversible binding of O_2 was also studied by means of potentiometry and, in particular, by the method of the oxidation potential [8]. The equation for the oxidation potential φ of the system $Co(II)TPivPPL-Co(III)TPivPPL^+$ can be written as

$$\varphi = \varphi^{0} + \vartheta \log \frac{[Co(III)TPivPPL^{+}]}{[Co(II)TPivPPL]}, \quad (6)$$

where $\vartheta = 2.3RT/F$ and the concentrations of the oxidized and reduced forms of the redox system are given in the square brackets.

It was shown preliminarily that the oxidation potential of this system at a 1-methylimidazole concentration $c \ge 0.1$ M is independent of pc_L , which indicates the formation of complexes of the same composition for the oxidized and reduced forms. If reaction (1) is regarded as complexation of Co(II)TPivPPL with O₂, then the material balance equations can be written as

$$c^{O} = [Co(III)TPivPPL^{+}],$$

$$c^{R} = [Co(II)TPivPPL] + [Co(II)TPivPPLO_{2}]$$

$$= [Co(II)TPivPPL] (1 + K_{O_{2}}P_{O_{2}}), \quad (7)$$

where

$$K_{O_2} = \frac{[Co(II)TPivPPLO_2]}{[Co(II)TPivPPL]P_{O_2}},$$



Fig. 3. $P_{O_2}/\Delta A$ vs. the partial pressure of oxygen, P_{O_2} . $\lambda = 530$ nm, c(TBAP) = 0.1 M, $T = 25^{\circ}\text{C}$.

and c^{O} and c^{R} are the total concentrations of the oxidized and reduced forms of cobalt porphyrin.

With account of (7), the equation for the oxidation potential is transformed into

$$\varphi = \varphi^0 + \vartheta \log \left(c^{O}/c^{R} \right) + \vartheta \log \left(1 + K_{O_2} P_{O_2} \right),$$

and then, at constant concentrations c^{O} and c^{R} ,

$$\varphi = \varphi_0 + \vartheta \log \left(1 + K_{O_2} P_{O_2} \right),$$
 (8)

where $\varphi_0 = \varphi^0 + \log(c^O/c^R)$.

It follows from Eq. (8) that at high P_{O_2} , when $K_{O_2}P_{O_2} >> 1$, the dependence φ -log P_{O_2} must be linear with a slope equal to ϑ .

The experimental study consisted in finding the dependence φ -log P_{O_2} . The oxidation potential was determined by measuring the electromotive force of the galvanic cell Hg |Hg₂Cl₂, LiCl(sat.) || solution under study |Pt.

All the measurements were performed at 25° C. The concentration of 1-methylimidazole was 0.1 M. The ionic strength was maintained with 0.1 M of TBAP. The cobalt porphyrins Co(II)TpivPP and Co(III)TPivPP⁺ were taken in a 1 : 1 molar ratio.

The experimental dependence $E - \log P_{O_2}$ is shown in Fig. 4. The oxidation potential φ is given relative to a saturated calomel electrode. It can be seen that this dependence is represented by a straight line at high P_{O_2} , in agreement with Eq. (8). At $P_{O_2} = 0$, $\varphi = \varphi_0$. The graphically found φ_0 made it possible to calculate, using Eq. (8), $K_{O_2}(K_{O_2} = 1/P_{1/2})$ and, accordingly, $P_{1/2}$. The calculation was performed using the values of P_{O_2} falling within the range in which the dependence φ -log P_{O_2} is linear. The averaged value of

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Fig. 4. Oxidation potential *E* of a solution of the redox system Co(II)TPivPPL-Co(III)TPivPPL⁺ in propyl cyanide in the presence of 1-methylimidazole (1-MeIm) vs. $\log P_{O_2}$. c(1-MeIm) = 0.1 M, c(TBAP) = 0.1 M, $T = 25^{\circ}C$.

 $P_{1/2}$ is 160 mm Hg, i.e., the results of spectrophotometric and potentiometric studies are in agreement within the experimental error.

CONCLUSION

The functional dependence of the oxidation potential of the redox system Co(II)TPivPPL-Co(III)TPivPPL⁺

on the partial pressure of oxygen was determined on the basis of experimental data.

These results can be used to design a potentiometric sensor for molecular oxygen in aqueous solution and to assess the region and limits of its applicability.

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