Oxygen-Binding to Simple Cobaltporphyrins Combined with Polyvinylmidazole

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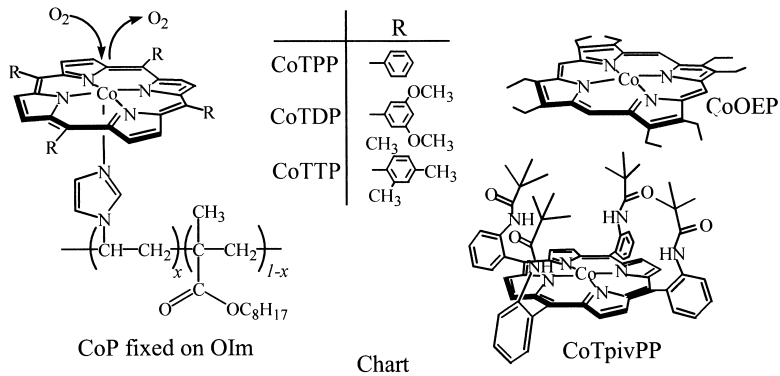
Summary: Reversible oxygen-binding was observed at low temperature for the poly(vinylimidazole-*co*-octyl methacrylate) complexes of the simple or planar cobaltporphyrins (CoP) such as cobalt-tetraphenylporphyrin and cobalt-octaethylporphyrin. The oxygen-binding affinity and rate constants were compared with those for the cobalt-picketfence porphyrin, a typical oxygen-carrier. The low oxygen-binding affinity for the CoP complexes was attributed to the enormously large oxygen-releasing rate constant.

Introduction

Much research has been devoted to mimicing oxygen carriers like hemoglobin by synthesizing modified metalloporphyrins from the middle of the 70's.[1-3] A typical example is the iron- or cobalt-picketfence porphyrin or -*meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrinatocobalt (CoTpivPP, Chart)[4] which has four pivalamido groups on one side of the porphyrin plane to provide a cavity for oxygen-binding and the other side is available for complexing with a nitrogenous ligand such as imidazole to improve the oxygen-binding affinity. On the other hand, while a simple or planar cobaltporphyrin without any cavity structure (CoP) forms the 5-coordinated complex with imidazole in a solution at room temperature, the CoP complex cannot bind oxygen and is gradually oxidized from cobalt(II) to (III) upon exposure to air.



Chart

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Ibers et al.[5-7] reported in the early 70's that even simple CoPs with a nitrogeneous ligand reversibly form their oxygen adducts at low temperature (-5–-40°C) in an organic solvent and have described the formation constant of the oxygen adducts, their temperature dependency, and effects of the ligands. The present authors have also reported the oxygen-binding by the cobalt-protoporphyrin IX dimethyl ester complex of poly(4-vinylpyridine-*co*-styrene) in a cooled toluene solution and studied the polymer complex as one of the hemoglobin models at that time.[8,9] This paper describes the reversible oxygen-binding to cobalt-tetraphenylporphyrin (CoTPP) and its derivatives and cobalt-octaethylporphyrin (CoOEP) combined with the copolymer of vinylimidazole and octyl methacrylate (OIm) in a cooled dichloromethane solution.

Reversible Oxygen-Binding in Cooled Solution

Poly(1-vinylimidazole-*co*-octyl methacrylate)(OIm) was prepared by radical polymerization and used as a polymer-ligand (content of the vinylimidazolyl residue = 25 mol%; [η] = 0.64 g/dl, toluene, 30°C; T_g = -1°C). The chart shows the CoPs used in this study: cobalt-*meso*-tetraphenylporphyrin (CoTPP), cobalt-*meso*-tetrakis(3,5-dimethoxyphenyl)porphyrin (CoTDP), cobalt-*meso*-tetrakis(2,4,6-trimethylphenyl)porphyrin (CoTTP), and cobalt-2,3,7,8,12,13,17,18-octaethylporphyrin (CoOEP). The CoP and OIm complexes were soluble in organic solvents such as toluene, chloroform, and THF. Complexation of CoP with the imidazolyl residue of OIm or the 5-coordinated structure as presented in the chart was confirmed by an ESR signal ($g_{//}$=2.03 and $g_{\perp}$=2.00) with an eight-line hyperfine splitting spectrum attributed

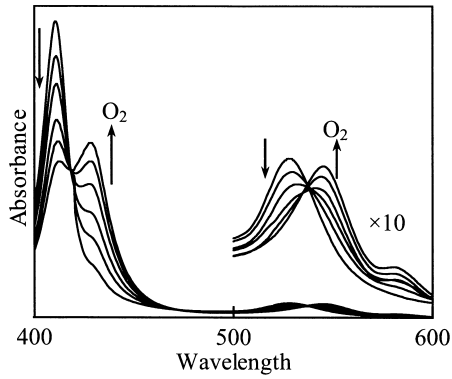

Figure 1. Visible absorption spectra of the CoTPP-OIm complex in CH_2Cl_2 at –15°C. O_2 concn= 0, 20, 40, 60, 80, 100%.

Table 1. Oxygen-binding Affinity, Thermodynamic and Kinetic Parameters for the CoP-OIm Complexes in CH_2Cl_2 at -15°C

CoP	p_{50} [cmHg]	ΔH [kcal/mol]	ΔS [e.u.]	$10^{-8}k_{on}$ [$M^{-1}s^{-1}$]	$10^{-5}k_{off}$ [s^{-1}]
CoTPP[a)]	19	-14	-43	6.3	6.5
CoTPP	22	-12	-40	2.0	2.2
CoTDP	28	-13	-48	1.8	3.7
CoTTP	33	-13	-50	1.5	3.9
CoOEP[a)]	21	-9.4	-35	0.7	0.8
CoOEP	17	-11	-43	0.2	0.5

[a)] The CoP complex with *N*-benzylimidazole

to the nitrogen on the CoP's 5th site.

The dichloromethane solution of the CoP-OIm complex was cooled (e.g., at -15°C). The UV/visible absorption of CoTPP (and CoTDP, CoTTP)-OIm changed from the spectrum (λ_{max}= 412 and 530 nm) attributed to deoxy CoP under a nitrogen atmosphere to the spectrum (λ_{max}= 429 and 547 nm) attributed to oxy CoP (Co/O_2= 1/1 adduct) immediately after exposure to oxygen (Figure 1). The deoxy-oxy spectral change was reversible in response to the oxygen partial pressure with isosbestic points at 420 and 535 nm. For the CoOEP-OIm complex, deoxy: λ_{max}= 392 and 550nm, oxy: λ_{max}= 413, 528 and 561nm, isosbestic points = 400, 519, 537 and 558 nm. The oxy (oxygen-binding) equilibrium curves obeyed Langmuir isotherms to give the oxygen-binding affinity p_{50} (oxygen partial pressure at which half of the CoP binds with oxygen).

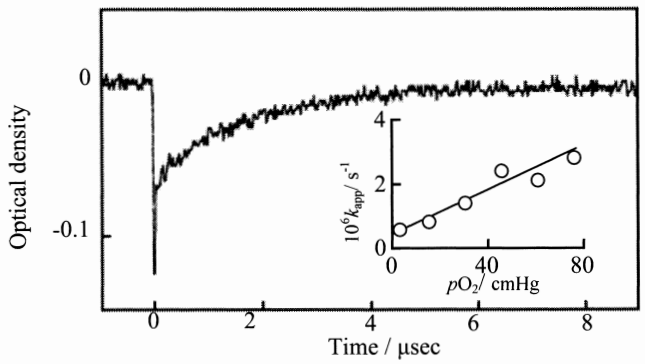

Figure 2. Absorbance change at 430nm after the laser irradiation for the CoTPP-OIm complex in CH_2Cl_2 at –15°C. Inset: Apparent oxygen-binding rate constant k_{app} vs partial oxygen pressure.

Affinity and Kinetic Parameters

The oxygen-binding affinity p_{50} is listed in Table 1. The enthalpy and entropy changes (ΔH and ΔS) for the oxygen-binding were determined from the temperature dependence of the p_{50} and are also given in Table 1. ΔH or the enthalpy gain through the oxygen-binding for the polymeric CoP-OIm complexes was smaller than that for the corresponding monomeric CoP complex, which caused a slight decrease in the oxygen-binding affinity. The affinity for the CoTDP and CoTTP complexes were lower than that for CoTPP. These results suggest a steric hindrance effect by the OIm polymer-ligand.

$$\text{CoP-O}_2 \xrightarrow{h\nu} \text{CoP} + \text{O}_2 \xrightarrow{k_{app}} \text{CoP-O}_2 \qquad (1)$$

$$\text{CoP} + \text{O}_2 \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} \text{CoP-O}_2 \qquad K(=1/p_{50}) = k_{on} / k_{off} \qquad (2)$$

Photodissociation and recombination of the bound oxygen from and to the CoP complex (Eq. 1) in the cooled solution were monitored by laser flash photolysis. An example of the oxygen recombination time curve is shown in Figure 2. The reaction was completed within a few microseconds, and it was very rapid despite a reaction at low temperature. The oxygen-binding and -releasing rate constants (k_{on} and k_{off} in Eq. 2) were estimated by pseudo-first-order kinetics, as shown in the inset of Figure 2, and are also given in Table 1. The oxygen-releasing k_{off} values were on the order of 10^5 s^{-1} for the CoP complexes, and this significantly large k_{off} is the origin of the very low oxygen-binding affinity of the CoP complexes (or the reason why an oxygen adduct could be observed only at low temperature).

Extrapolation to Room Temperature

In Figure 3 are shown the linear logarithmic p_{50} and k_{on} vs $1/T$ plots (van't Hoff and Arrhenius plots) and their extrapolations to 25°C. The extrapolated p_{50}, k_{on}, and k_{off} values at 25°C for the CoTPP-OIm complex are given in Table 2, with those for the typical oxygen carrier, CoTpivPP. The p_{50} value of 790 cmHg indicates a very weak oxygen-binding affinity of the CoP complex at 25°C (ca. 1/30 of the CoTpivPP's affinity), but suggests that an oxygen adduct could be observed for CoP under a high oxygen pressure, for example, 10 atm. The extrapolated k_{off} value was on the order of 10^8 s^{-1} for the CoP complex and more than 200 times larger than that of CoTpivPP, and

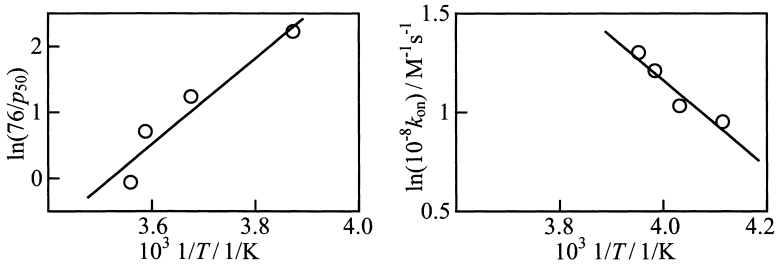

Figure 3. van't Hoff and Arrhenius plots of the oxygen-binding affinity p_{50} and rate constant k_{on}, respectively, for the CoTPP-OIm complex in CH_2Cl_2.

Table 2. Oxygen-binding Affinity and Binding and Releasing Rate Constants for the CoTPP-OIm and the CoTpivPP-OIm Complex at 25°C

Porphyrin	p_{50} [cmHg]	$10^{-8}k_{on}$ [$M^{-1}s^{-1}$]	$10^{-5}k_{off}$ [s^{-1}]
CoTPP[a)]	790	13	1700
CoTpivPP	25	8.4	7.3

[a)] Extrapolated from the dependency at low temperature range

it is concluded that this extremely large oxygen-releasing rate constant causes the very low oxygen-binding affinity.

These results suggest that the polymer-combined simple cobaltporphyrins would reversibly bind oxygen under a high oxygen pressure and are potentially applicable as an oxygen-permselective membrane.

Acknowledgment

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 13031072) from MEXT, Japan.

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