

Catalytic Properties of Cobalt(II) Porphyrins Supported on Styrene–Divinylbenzene Copolymer

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SYNOPSIS

Polymeric pyridinium chloride was synthesized by treating pyridine with 2% divinylbenzene (DVB)-crosslinked chloromethyl polystyrene. Sodium 5,10,15,20-tetrakis(4-sulfo-phenyl)porphyrin was synthesized and appended on the above polymer through an ionic linkage. Cobalt(II) complex of the polymeric porphyrin was synthesized and characterized chemically and spectroscopically. This complex was employed as catalyst for the oxidation of dithiocarbamates to thiuram disulfide. Electronic and ESR spectra of the complex were analyzed before and after catalysis. pH dependence of catalytic reactions was also studied. These studies provide evidence for the catalytic ability of the polymeric cobalt(II) porphyrin system. A mechanism for the catalytic reaction is suggested on the basis of the above results. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Some metalloporphyrins exhibit remarkable catalytic properties in various chemical, electrochemical, and photochemical reactions.^{1–4} The high catalytic activity of metalloporphyrins is due to the aromatic character of the conjugated pi-system of the macro-ring, the conjugation of the coordinated metal atom to the pi-system of the ligand, and the ease with which the oxidation state of the central metal atom changes. It is also important that the extensive pi-electron system of porphyrins has a distinct electron buffer character.⁵ Mn(III) and Fe(III) derivatives of porphyrins have been reported to be quite efficient in several catalytic processes which include oxidation and oxygen transfer reactions involving various organic species.^{6–8} Judging from the redox potential of the Co(II)/Co(III) couple in their porphyrin complexes and the possibility of very smooth electronic modulation in closely lying Mn, Fe, Co triad in that order, including the accessibility of both +2 and +3 oxidation states, cobalt(II) porphyrins are also found to be potential catalysts. The present pa-

per describes the synthesis of polymer bound porphyrins with ionic polymer–porphyrin linkage, synthesis of their cobalt complexes, and testing of their catalytic efficiency in specific reactions.

EXPERIMENTAL

General

Two percent divinylbenzene (DVB)-crosslinked porous polystyrene was prepared by the suspension copolymerization of styrene and DVB in the required ratio. Chloromethyl polystyrene [A] was synthesized following the literature procedure.^{9,10} The chlorine capacity of the polymer was estimated by the modified Volhards method and found to be 4.1 meq/g of the polymer. IR spectra were recorded on a Shimadzu IR-470 spectrophotometer operating in the range 4000–400 cm⁻¹ using KBr disks. Solid state electronic spectra were recorded on a Carry-2390 UV-vis-near IR spectrophotometer and ESR spectra were recorded on a Varian E-12 spectrometer.

2% DVB-Crosslinked Polymeric Pyridinium Chloride [B]

Two percent DVB-crosslinked chloromethyl polystyrene (2 g) was suspended in dimethyl formamide

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(50 mL). Pyridine (1 mL) was added to it. The reaction mixture was refluxed for 2 h. This was cooled, filtered, and washed well with hot water and methanol. The resin was dried under vacuum. Ionic chlorine was estimated by treating the polymer with standard silver nitrate solution and back-titrating the excess silver nitrate with ammonium thiocyanate solution. The strength of ionic chlorine was found to be 2.4 meq/g of the polymer. This gives the capacity of pyridinium function in the polymer system.

Sodium 5,10,15,20-Tetrakis(4-sulfophenyl)porphyrin, H_2TPPS_4 [I]

H_2TPP (1 g) and conc. H_2SO_4 (15 mL) were ground together with mortar and pestle. The mixture was taken in an RB flask and heated carefully on a water bath for 4 h. The flask was stoppered and then set aside for 3 days. It was then transferred to a beaker, cooled in an ice bath, and neutralized carefully with sodium hydroxide (5%) solution. The neutral solution was concentrated by evaporation when sodium sulfate began to crystallize out. Methanol was added to cause further precipitation of the salt. It was filtered off and the filtrate was evaporated to dryness. The process was repeated by adding methanol until it was almost free from sodium sulfate.

The product obtained was freely soluble in water and further purified by column chromatography using silica gel as the adsorbent and a mixture of methanol (70%) and chloroform (30%) as the eluant. The sulfonation of all the four phenyl rings of H_2TPP was confirmed by TLC, which gave only one spot.^{11,12}

Polymer-Bound Porphyrin [BI]

Polymeric pyridinium chloride [B] (1 g) was added to a solution of H_2TPPS_4 (100 mg) in water and the reaction mixture was heated on a water bath for 4 h. The resulting polymer was repeatedly washed with water and methanol and dried in a vacuum oven at 60°C. This was kept under vacuum. The unreacted chlorine was estimated by treating the polymer with silver nitrate solution and found to be equivalent to 0.78 meq/g. The rest of the chlorine was replaced by the porphyrin groups.

Preparation of Polymer-Bound Cobalt(II) Porphyrins: General Procedure

The metal complex was prepared by the reaction of the polymer-bound porphyrin (1 g) with an aqueous solution of the cobalt(II) chloride (20 mg/20 mL) in a mixture of methanol and chloroform in 1 : 1

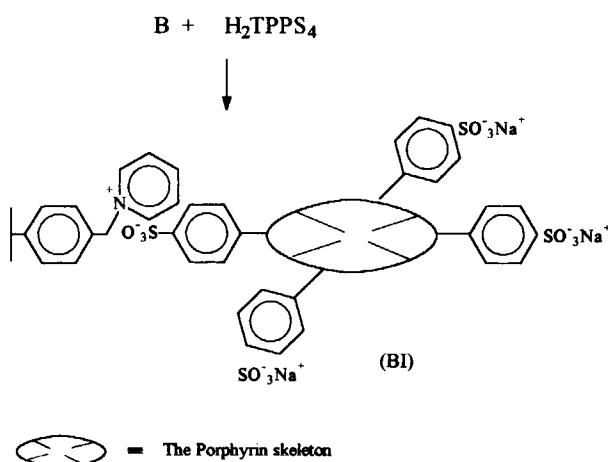
ratio. Acetic acid (0.1 mL) and sodium acetate (50 mg) were added. The mixture was refluxed for 2 h. This was then cooled, filtered, and washed well with water and methanol and kept under vacuum.

RESULTS AND DISCUSSION

In recent years, several types of polymeric cobalt porphyrin complexes have been synthesized. But the method involved in them was essentially the copolymerization of styrene and vinyl derivatives of porphyrins followed by metallation.⁴ Such polymer systems have the disadvantages that the porphyrin units would be distributed entirely in the bulk of the solid polymer and hence majority of them would not be available for either metallation or for catalytic functions. Further, since many of the reactions are facilitated in a polar medium, a polymer support bearing ionic porphyrins would be more compatible in such reactions.

Insoluble polymer support bearing pyridinium functions were prepared from pyridine and 2% DVB-crosslinked chloromethyl polystyrene. Anionic tetrasulfonated porphyrin was anchored onto the polymer by anion-exchange method (Scheme 1).

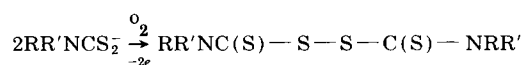
The immobilization of H_2TPPS_4 was confirmed by IR and electronic spectroscopy. The polymer shows typical absorptions at 1370 and 1160 cm^{-1} corresponding to S—O asymmetric and S—O symmetric stretching vibrations, respectively. The electronic spectra of the polymer was recorded in solid state at room temperature. The spectrum consists of two sets of bands, an intense soret band (at 422.5 nm) and four Q-bands (at 520, 556, 592, and 649 nm).



Scheme 1 Preparation of polymer-bound porphyrin.

Cobalt complex of the polymer was synthesized and characterized. Electronic spectra gave a *soret* band at 425 nm and *Q*-bands at 540 and 586 nm. The spectral values are not characteristic of a dioxxygen bound cobalt porphyrin complex. The ESR spectral data are in agreement with these observations. The complex gave spectra only at liquid nitrogen temperature. The complex has *g*-anisotropy at $g_{\parallel} = 2.0645$ and $g_{\perp} = 1.9777$ and ^{59}Co hyperfine couplings $A_{\parallel} = 17.85$ G and $A_{\perp} = 19.2$ G. While these *g* values generally agree with an oxygen free low spin cobalt(II) system, the *A* values are less than what are reported for such systems. However, both A_{\parallel} and A_{\perp} are noticeably higher than that of the oxygenated species.

The reaction that has been considered for testing the catalytic efficiency of BI(Co) complex is the oxidation reaction of different dithiocarbamates to their corresponding disulfides using O_2 , as typified in the equation,



where $\text{R} = \text{R}' = \text{C}_2\text{H}_5-$ or

$\text{R} = \text{C}_6\text{H}_5-$, $\text{R}' = \text{H}$ or

$\text{R} = \text{C}_6\text{H}_5\text{CH}_2-$, $\text{R}' = \text{H}$

The air oxidation of dithiocarbamates does not effectively proceed in the absence of the catalyst while stoichiometric reactions are reported on using appropriate oxidizing agents.

On passing air at room temperature through a solution of dithiocarbamate in methanol containing a suspension of BI(Co) gave colorless crystals that are characterized to be the corresponding thiuram disulfides. The characterization of the disulfides was done by melting point measurements and by IR spectroscopy. The IR spectra showed two characteristic peaks at 430 and 480 cm^{-1} corresponding to $-\text{S}-\text{S}-$ stretching vibrations. The peak at 670 cm^{-1} is due to the $-\text{C}-\text{S}$ stretching vibrations and the peak at 1150 cm^{-1} corresponds to $\text{C}=\text{S}$ stretching vibrations. The authenticity of the compound was verified by preparing the corresponding thiuram disulfides from the dithiocarbamates by stoichiometric I_2 oxidation and comparing the melting point and the IR spectra.

The efficiency of the catalyst BI(Co) for the above reactions is quite high as about 0.154 mmol/100 mg of the polymer could convert more than 1 g of the dithiocarbamate to the corresponding disulfide in a single step. Further, it was found that the catalyst did not get poisoned and could be recycled.

The polymer beads, after using as the catalyst, after filtration and washing with water, was found to be as active as before with a fresh batch of dithiocarbamates.

The next attempt was to probe the nature of intermediates and also the reaction pathway. Various spectral techniques were employed for studying the reaction. IR spectra of the catalyst before and after the catalytic reaction were recorded and compared. The O—O stretching frequency of the coordinated dioxygen was found near 1200 cm^{-1} for the catalyst after carrying out the catalytic reaction. This peak was absent in the case of BI(Co) before using as a catalyst. The infrared O—O stretching gave evidence that the bound dioxygen in the used catalyst was analogous to superoxide.

Electronic absorption spectra of the used sample and that of the fresh sample suggest that the catalyst gets converted entirely to an oxygen-bound species after the reaction. The spectral data indicated a red shift for absorption bands for the used catalyst. The fresh catalyst showed an intense *soret* band at 425 nm and two *Q*-bands at 544 and 587 nm. The *soret* band for the used catalyst was shifted to 438.5 nm and the *Q*-bands to 550.5 and 600 nm. This observation suggests the formation of a dioxygen bound species after using BI(Co) as a catalyst.¹³

ESR spectra also gave evidence for the reaction pathway of the catalysis. On recording the ESR spectra of the used catalyst and comparing it with that of the fresh sample, some striking changes were observed. While the fresh catalyst gave spectra only at low temperature (LNT), the used catalyst gave good signals even at room temperature (RT); further, the spectral features were markedly different (Fig. 1).

The observed *g*-anisotropy ($g_{\parallel} = 2.0546$, $g_{\perp} = 1.9716$) along with ^{59}Co hyperfine couplings ($A_{\parallel} = 16.5$ G, $A_{\perp} = 17.8$ G) of the used catalyst is very typical of the dioxygen bound cobalt(II) center with or without an axially coordinating base. The ability to exhibit ESR spectra at room temperature along with smaller line widths (due to longer electron spin relaxation time) confirms that the catalyst gets converted entirely to an O_2 -bound species. But no ESR signal was observed for the catalyst before use, at room temperature. This suggests the presence of an oxygen-free state of the polymer metal complex. When the used catalyst, which on the basis of various spectral studies was found to be essentially BI(Co)(O_2), is filtered, washed, and reused to oxidize a fresh stock of dithiocarbamates as above, it was found to be very effective catalytically. These observations clearly indicate that, in fact, the BI(Co)(O_2) is the catalytic intermediate.

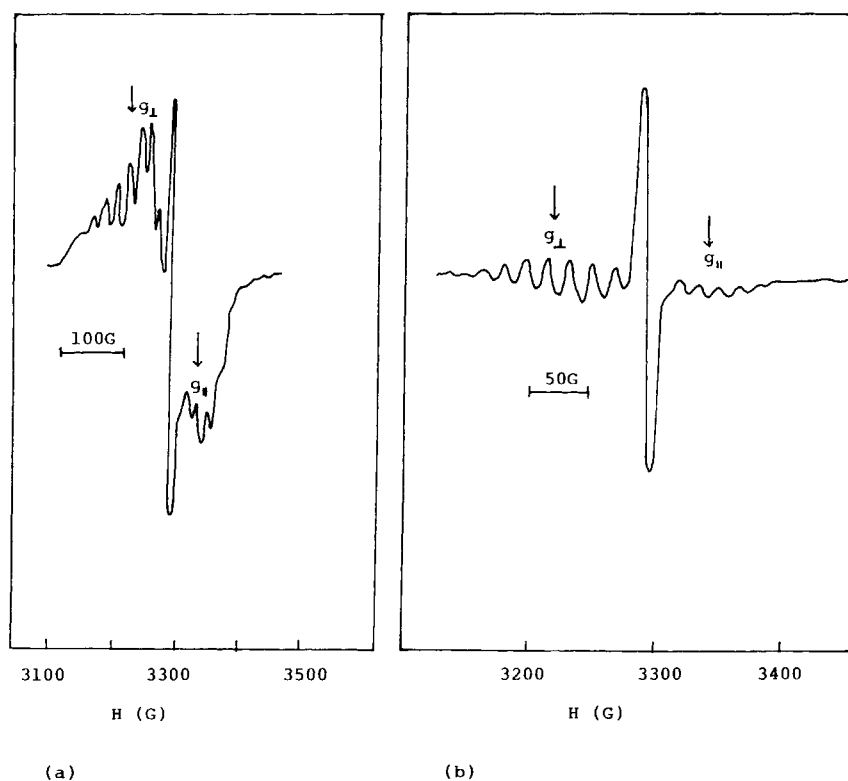


Figure 1 ESR spectra of BI(Co) complex at LNT: (a) before catalysis; (b) after catalysis.

The reaction pathway is further evidenced by the pH studies conducted at regular intervals during the course of the reaction. It was found that the pH of the solution increases as the catalytic reaction progresses. The pH values also monitored in the absence of the catalyst and the catalytic efficiency were compared (Fig. 2).

From the pH studies it was revealed that the pH of the solution increased, as the oxygen that is stoichiometrically involved in the reaction was reduced to OH^- ions.

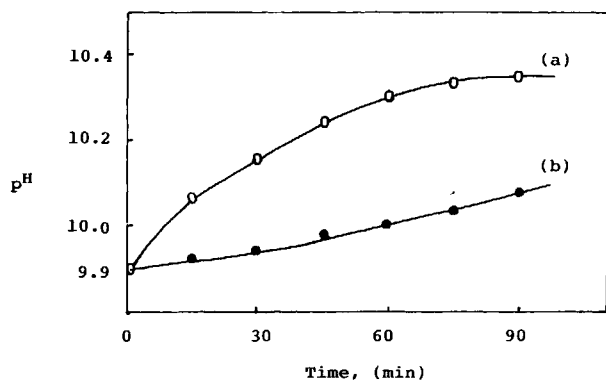
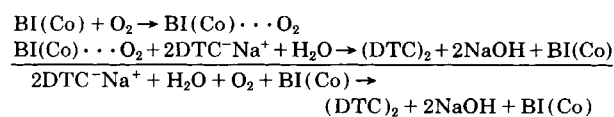


Figure 2 pH dependence of oxidation of dithiocarbamate: (a) in the presence of catalyst; (b) in the absence of catalyst.

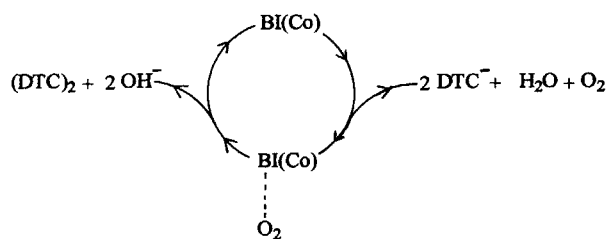
Based on the above facts a catalytic cycle as shown in Scheme 2 can be thought to be operative.

From the catalytic cycle, the mechanism of the catalytic oxidation reaction is evidenced as follows:



CONCLUSION

On electronic grounds, cobalt (II) porphyrins can be used as potential catalysts in many oxidation type



Scheme 2 Catalytic cycle.

reactions. The catalytic efficiency of the polymer-supported cobalt complexes was studied. The polymer-bound porphyrin complexes with ionic systems were used for the present study because of the ideal compatibility of these systems with polar medium when employed for catalytic reaction. It was found that the cobalt complexes are quite efficient catalysts for the oxidation of dithiocarbamates into their thiuram disulfides. We intended to study two key aspects: (1) try out an air oxidation using a solid phase polymer-supported cobalt (II) porphyrin catalyst disposed in an environment highly conducive for catalytic reaction and evaluate the nature of the product and the catalytic efficiency and (2) probe the nature of intermediates and the possible reaction pathways. The catalyst supported firmly on the surface of a solid polymer matrix provides several additional advantages.

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