Studies of Electrochemical Catalytic Reduction Reactions of Tetraphenylporphinatocobalt/1,2-Dibromoethane and 1,2-Dichloroethane Systems in Nonaqueous Media*

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Received November 11, 1992; revised July 6, 1993.

Abstract Electrochemical catalytic reactions of tetraphenylporphinatocobalt were studied in DMF and $EtCl_2$ solutions in the presence of 1,2 dibromoethane and 1,2-dichloroethane utilizing cyclic voltammetry, thin-layer electrochemistry, *in situ* UV-visible spectroelectrochemistry and computer digital simulation methods. Homogeneous rate constants for reactions of electrogenerated Co(I)TPP species with 1,2-dibromoethane and 1,2-dichloroethane were determined as 1.2×10^3 and 5 $mol^{-1}\cdot dm^3\cdot s^{-1}$, respectively. Neither alkylation nor degradation of CoTPP was observed.

Keywords: **cobalt porphyrin, catalytic reduction, dichloride ethane, electrochemistry, spectroelectrochemistry.**

1 Introduction

1,2-Dibromoethane (DBE) is widely used as a fumigant in agriculture and also as a scavenger added to leaded-gasoline; however, it is also a plausible compound of carcinogen. On the basis of electrochemical catalytic reduction of DBE/Vitamin B_{12} system, a detection limit of 11 ppm DBE in gasoline has been reached utilizing square wave voltammetry conducted in a water-oil microemusion[1]. It is worth studying the possibility of electrochemical catalytic reduction of DBE in nonaqueous media by using synthesized Co(II)TPP.

Previously, electrode reactions of tetraphenylporphinatocobalt (Co(II)TPP) in methylene chloride solution were reported[2]. It has been found that the electrochemical reduction of Co(II)TPP is followed by the generation of alkyl-cobalt complexes[2]. However, no detailed study has been made on Co(II)TPP/DBE, DCE systems.

* Project supported by the National Natural Science Foundation of China.

This paper reports cyclic voltammetry, *in situ* UV-visible spectroelectrochemistry and digital simulation studies of Co(II)TPP in the presence of DBE in DMF. The homogeneous rate constant of catalytic reaction of Co(I)TPP and DBE has been determined to be $1.2\times10^3\ mol^{-1}\cdot dm^3\cdot s^{-1}$. This value shows a possibility for DBE determination in organic solvents. Electrochemical catalytic reduction of 1,2-dichloroethane is also studied for comparison.

2 Experimental

N,N-dimethylformamide (DMF) was distilled from CaH_2 before use. Tetrabutylammonium perchlorate (TBAP) was prepared by neutralization of tetrabutylammonium hydroxide with perchlorate acid, and twice recrystallized from ethanol. 1, 2-dichloroethane (DCE) was freshly distilled from P_2O_5. 1,2-dibromoethane (analytical) is received for use. Co(II)TPP was synthesized according to literature procedures[2,3].

The electrochemical system was a home-made cyclic voltammetric analyzer coupled with a YEW 3655 analytical recorder (Yocogawa Electronic Company, Japan). Three-electrode system was used. A platinum-button working electrode (0.5 mm in diameter) was used for conventional voltammetry together with a platinum wire auxiliary electrode and an SCE (saturated calomel electrode) reference electrode which was separated from the bulk solution by a glass frit. High-purity Ar was used for the removal of oxygen.

A long-path-length spectroelectrochemical cell with a plug-in platinum plate electrode was used for thin-layer electrolysis. The volume of the thin-layer chamber was 27 μl[4].

A light-transparent thin-layer spectroelectrochemical cell[5] with 90 mesh platinum gauze working electrode and 0.2 mm path-length was adapted to a TN6500 Tracor Northern multichannel analyzer for *in situ* spectroelectrochemical experiments.

3 Results and Discussion

3.1 *Electrochemistry in DMF*

In DMF solution, the cyclic voltammogram of Co(II)TPP is shown in Fig. 1(a). Two reversible one-electron reduction steps were observed at half wave potentials, ($E_{1/2}=(E_{pc}+E_{pc})/2$), of -0.8 V and -1.9 V (vs. SCE). These two steps have been assigned to the Co(II)/Co(I) and Co(I)TPP/Co(I)TPP$^-$ processes respectively[2,6].

The first oxidation step of Co(II) is at $E_{1/2}$ of 0.25 V, corresponding to the metal-centered oxidation to Co(III). However, the cyclic voltammetric peak-to-peak separation of this electron transferred step is about 250 mV at 200 mV/s scan rate. This phenomenon is similar to that of cobalt porphyrins in the presence of pyridine or chloride

anions[3,7]. Becuase Co(II) center prefers five-coordinate configuration while Co(III) prefers six-coordinate state, in strong binding solvent (DMF, DN=26.6) Co(III)/Co(III) redox processes can be expected to associate with kinetic processes of configuration changes.

The second one-electron oxidation step was observed at $E_{1/2}$ of 1.05 V which is close to the limiting potential of this solution system. This step corresponds to the porphyrin-ring oxidation generating π-cation radicals[5].

To investigate the catalytic characteristics of this system, cyclic voltammograms were recorded at different DBE concentrations. The peak current maximum of the first reduction peak at -0.8 V increased with increasing DBE concentration while the peak potential remained the same. At the same time, the reoxidation peak gradually decreased and finally disappeared; an S-shaped voltammetric curve was formed as shown in Fig. 1(b). At further increased DBE concentrations, the catalytic reduction current became diffusion-controlled and independent of potential scan rate.

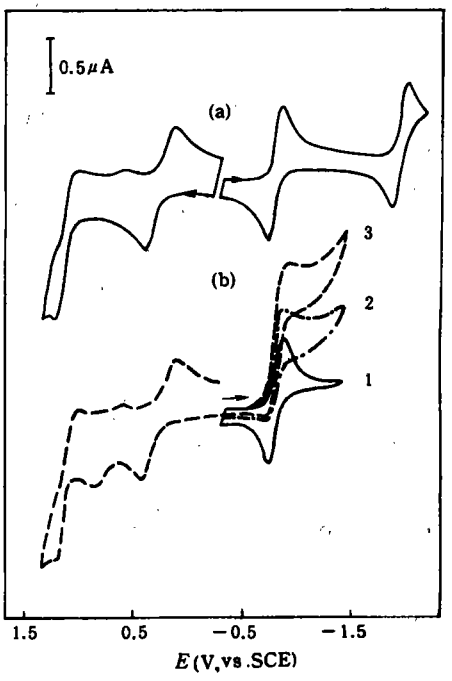

Fig. 1. Cyclic voltammograms of Co(II)TPP (1.87 mmol · dm^{-3}) in DMF/0.1 mol · dm^{-3} TBAP in the absence (a), and presence of DBE (b). DBE concentration: 1, 0.0; 2, 1.74; 3, 4.06 × 10^{-3}. Potential scan rate: 0.2 V/s.

When DBE concentration is much larger than that of Co(II)TPP, the catalytic process can be treated as a pseudo-first-order reaction. Based on the equation of $I = nFSD^{1/2}C_s(K_1^{1/2}C_p)$[3], a homogeneous rate constant of $K_1 = 1.2\times10^3$ mol^{-1} · dm^3 · s^{-1} was calculated. This value is comparative with $K_1 = 10^4$ mol^{-1} · dm^3 · s^{-1} for catalytic reduction of DBE/Vitamin B_{12} system in a water-oil microemulsion[1].

Previous studies indicated that Co(I)TPP can react with some halide alkanes to generate alkyl cobalt porphyrins, and these Co—C bond complexes can further be reduced at potentials from -1.3 V to -1.37 V[3]. However, this is not the case of the Co(II)TPP/DBE system. No reduction peak was found in the potential region of -0.1 V to -1.5 V even if in the presence of excessive amount of DBE. An irreversible cathodic peak appeared at -1.6 V which was assigned to direct reduction processes of DBE[9].

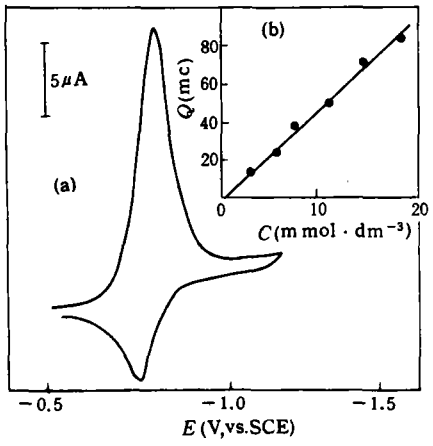

Fig. 2. (a) Thin-layer voltammogram of Co (II) TPP(1.14×10^{-3}mol · dm^{-3}) in the presence of DBE, with the scan rate of 5 mV/s; (b) plot of coulombs vs. DBE concentration.

For the case of switching potential at −1.5 V, an irreversible oxidation peak appeared at 0.73 V, which corresponds to the oxidation of electrogenerated Br^- anions as shown in Fig. 1 (b). Similar oxidation waves of halide anions were also observed for Rh(I)TPP/bromobenzene system[10] and Co(I)-TPP/alkyl mono-halides system[3]. Although halide anions may axially bind to the cobalt center, it seemed not to happen in the strong binding DMF solution since the redox potential of Co(III)/Co(II) step did not shift.

Thin-layer cyclic voltammetric experiments were carried out for Co(II)TPP reduction in the presence of DBE. As shown in Fig. 2(a), a well developed catalytic reduction peak was obtained at −0.80 V; reoxidation peak of Co(I) was also observed at −0.73 V. From the difference of these two peak areas, coulombs of the DBE reduction in the thin-layer chamber can be calculated as a function of the DBE concentration. The result was plotted as shown in Fig. 2(b), and a straight line through the origin was obtained. The slope of the line can be expressed as slope$=nFV$ (n is the number of electrons of the DBE reduction; V is the volume of the thin-layer chamber; F is the Faraday constant), and gives $n=1.74$, indicating that the catalytic reduction process involves predominantly two electrons per DBE molecule. The reactions can be expressed by Eqs. (1)—(4):

$$Co(II)TPP+e \rightleftharpoons Co(I)TPP, \qquad K^0 \qquad (1)$$

$$Co(I)+CH_2BrCH_2Br \rightarrow Co(II)+[CH_2BrCH_2]^{\cdot}+Br^-, \qquad k_1 \qquad (2)$$

$$Co(I)+[CH_2BrCH_2]^{\cdot} \rightarrow Co(II)+CH_2CH_2CHBr^-, \qquad k_2 \qquad (3)$$

$$CH_2CH_2Br^- \rightarrow CH_2CH_2+Br^-. \qquad (4)$$

According to this mechanism, Co(II)TPP is regenerated by reactions of DBE and its derivatives and totally two halide anions are released and one ethylene molecule is generated for each DBE molecule. Similar reaction machanisms were also proposed[9].

Digital simulations of this process were carried out utilizing an exponentially expanded space grid[11]. Assuming that reactions (3) and (4) are all fast and reaction (2) is the control step of the catalytic process ($k_2 \gg k_1$), catalytic voltammograms were simulated for various k_1 values (see Fig. 3(a)). A working curve was plotted in Fig. 3(b), from which a k_1 value of 1.2×10^3 mol^{-1} · dm^3 · s^{-1} was also obtained.

3.2 *In situ Thin-Layer Spectroelectrochemistry in DMF*

Electrogenerated species can be characterized utilizing *in situ* thin-layer spectroelectrochemical techniques for identification of electrode reactions. UV-visible spectral changes for the reduction of Co(II)TPP in the presence of DBE are shown in Fig. 4(a). The initial Co(II)-TPP spectrum shows absorption peaks at 406 nm (S-band) and 524 nm (Q-band). After the electrode potential was stepped from 0.0 V to −1.0 V, the absorption peak at 406 nm split into double peaks at 355—408 nm, while the Q-band shifted into a broad absorption platform between 450 and 550 nm. The final spectrum is characteristic of Co(I)TPP and well distinguished from that of alkyl-cobalt porphyrins[2,3,6]. Four isosbestic points at 308, 381, 420 and 545 nm were observed, which indicates that only Co(I)TPP is the final state of the porphyrin.

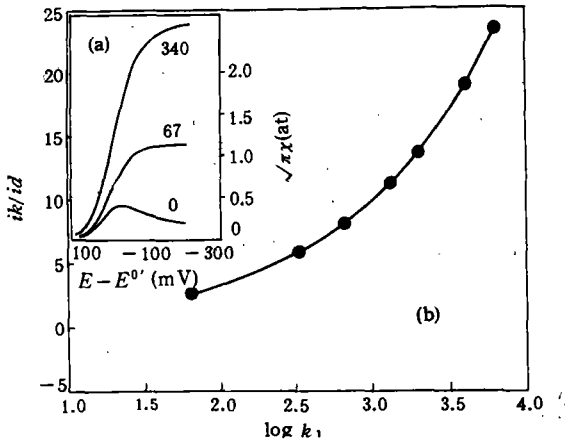

Fig. 3. Digital simulation for catalytic reduction of Co(II)TPP/DBE system. (a) Simulated voltammograms, (b) working curve of I_p/I_d vs. k_1. Simulation parameters: K_o for Co(II)TPP/Co(I)TPP: 1.2×10^{-2}cm · s^{-1}[6]; $C_{DBE}/C_{CoTPP}=40$; diffusion coefficient $D_{DBE}=1.3\times10^{-5}cm^2 \cdot s^{-1}$[1], $D_{CoTPP}=2.0\times10^{-6}cm^2 \cdot s^{-1}$. Potential scan rate is 0.1 V/s.

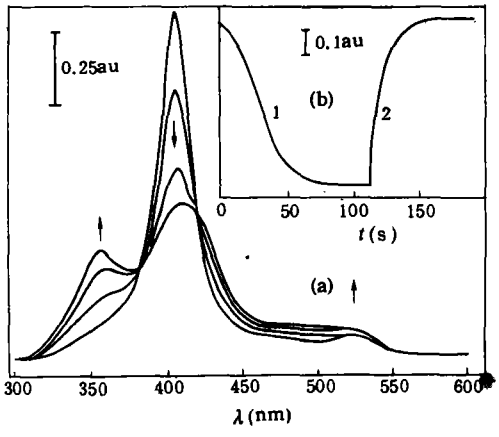

Fig. 4. (a) *In situ* spectral changes of Co(II)TPP in the presence of 4.2×10^{-3} mol · dm^{-3}DBE with electrode potential stepped from 0.0 V to −1.0 V; (b) chronoabscrption curve at 410 nm; 1, from 0.0 V to −1.0 V; 2, from −1.0 V to 0.0 V (vs. SCE).

A time-resolved absorption curve (monitored at 410 nm) was obtained from a double-potential step experiment, which is shown in Fig. 4(b). From this figure, it can be seen that in the presence of 0.4 mmol · dm^{-3} DBE, about 50% Co(II) species were reduced in 30 s after the cathodic potential jump, while 90% Co(I) species were reoxidized in 30 s after the anodic potential jump. More time needed to complete the thin-layer electrolysis of Co(II) is obviously due to the catalytic regeneration process of Co(II)TPP which should exist until all the DBE molecules in the thin-layer chamber are exhausted.

3.3 *Electrochemistry in DCE*

In DMF solution, no significant catalytic effect could be observed even when DCE concentration is several times larger than the Co(II)TPP concentration.

Cyclic voltammograms of Co(II)TPP in neat DCE solution are shown in Fig. 5(a), three reversible one-electron oxidation steps appeared at $E_{1/2}$ of 0.78, 0.98 and 1.15 V. The first step associates to the metal-centered oxidation to generate Co(III) state, the second and the third can be associated with formations of porphyrin-ring cation radicals and dications, respectively.

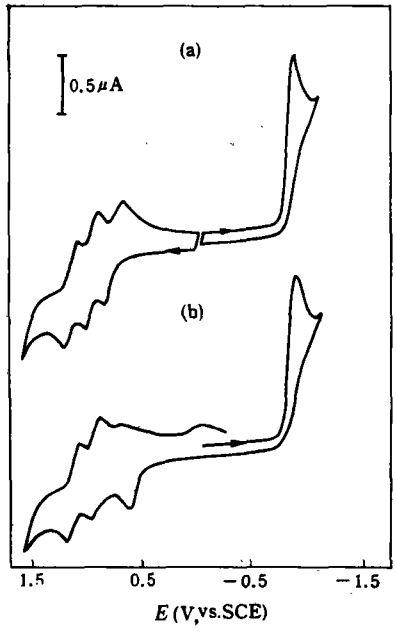

Fig. 5. Cyclic voltammogram of Co(II)-TPP (1.0×10^{-3} mol · dm^{-3} in DCE/0.1 mol · dm^{-3}) TBAP. Scan rate: 0.2 V/s.

Because DCE is a non-binding solvent, the cathodic-to-anodic peak separation of Co(III)/Co(II) redox step was normal. However, the first reduction of Co(II)TPP gave an S-shaped cathodic peak at −0.8 V. The peak was about 4.5 times as high as that of Co(II) oxidation step. This indicates that a catalytic reduction of DCE is proceeded by the Co(II)TPP/Co(I)TPP redox reaction. Because of the existence of a large amount of DCE (solvent), the rate of the electrode reaction should be controlled by the diffusion process of Co(II)TPP. When the kinetic parameter λ is above 1.5 ($\lambda=(kC/v)(RT/nF)$, where C is the concentration of DCE, v is the potential scan rate, and others have their usual meanings)[8], the relationship between the catalytic current (I_p) and the diffusion current (I_d) can be described as $I_p/I_c=\lambda^{1/2}\pi^{1/2}$[8].

It has been calculated that a homogeneous rate constant of the catalytic reaction is 5 mol^{-1} · dm^3 · s^{-1}. This value is much less than the value determined for DBE in the previous section. Since the reduction potential of DBE is −1.6 V and that of DCE is more negative than −2.0 V, the catalytic reaction of Co(II)TPP/Co(I)TPP reduces their overpotentials for 800 mV and >1200 mV, respectively.

For the switching potential of −1.0 V, the first oxidation peak shifted from 0.78 to 0.57 V, as shown in Fig. 5(b), and the second oxidation peak also shifted in the negative direction. This is understandable because chloride anions generated from the catalytic reactions can coordinate to the cobalt center at axial positions. Previous work

indicated that at low Cl^- concentrations, 1 : 1 axial ligation takes place and causes negative shifts of redox peak potentials of Co(III)/Co(II) only. However, at high Cl^- concentration, 2 : 1 axial ligation forming six-coordinated species takes place and leads to significant negative shifts of redox potentials for both Co(III)/Co(II) and the porphyrin-ring cation radical formation steps[2].

3.4 *Thin-Layer Spectroelectrochemistry in DCE*

In situ thin-layer spectral changes are shown in Fig. 6(a) and (b). As seen in Fig. 6(a), the spectrum of Co(II)TPP (S- and Q-band at 402 and 521 nm, respectively) remained for the electrode potential scanned from 0.0 V to −1.0 V, while about 25% decrease at absorbance maxima was observed. It is obvious that only a small amount of Co(I)TPP could be reserved in the thin-layer chamber due to the regeneration reaction of Co(II)TPP by the catalytic reduction of DCE.

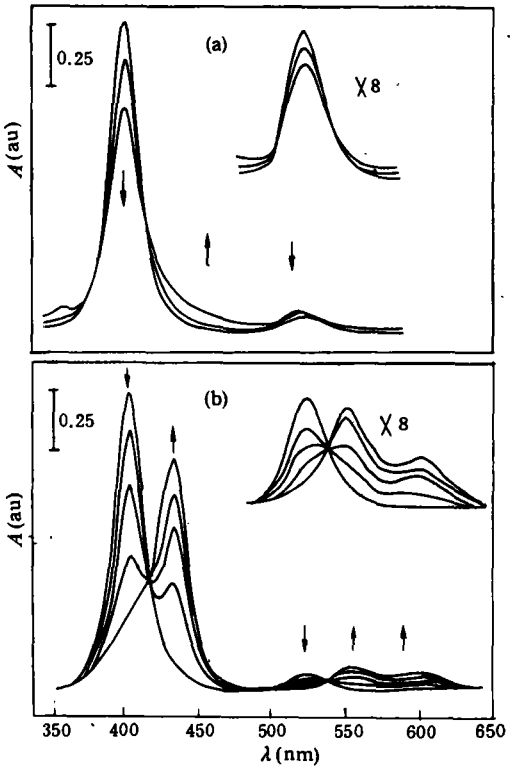

Fig. 6. *In situ* spectral changes of Co(II)TPP in DCE/0.1 mol · dm^{-3} TBAP, with eleckrode potential stepped (a) from 0.0V to −1.0 V and (b) from −1.0 V to 0.55 V (vs. SCE).

When the electrode potential turned back in the positive direction, the absorption peaks restored their original heights. This is also an indication that the catalytic regeneration reaction of Co(II)TPP from Co(I)TPP is chemically reversible. When the electrode potential was scanned to 0.55 V, new spectral changes were observed. This is seen in Fig. 6(b). The absorption peaks of Co(II)TPP gradually decreased and finally disappeared, a new set of absorption peaks appeared at 432, 540 and 596 nm. Four isosbestic points were observed at 379, 416, 475 and 535 nm. This newly generated spectrum is characteristic of (TPP)Co(III)Cl_2[2]. For the electrode potential shifted further to 0.65 V, the (TPP)Co(III)Cl_2 spectrum gradually disappeared and a new spectrum was formed, which is characteristic of porphyrin-ring cation radicals. This is also in agreement with the spectroelectrochemistry of (TPP)Co(III)Cl_2[2].

Co(II)TPP is an easily synthesized model-compound of P-450. Although Co(II)TPP is not always chemically stable and alkylation or degradation reactions may occur in some cases, as shown in this paper, it is not the case for the catalytic reduction

reactions of DBE and DCE. It is possible that in nonaqueous solvents, the reduction of 1,2-haloalkanes has a strong tendence to form double bond compounds and no cobalt-carbon bond compound could be generated.

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