JOURNAL OF APPLIED ELECTROCHEMISTRY **27** (1997) 793–798

Electrocatalysis for the reduction of O_2 and H_2O_2 based on complex of copper(II) with the tris(3-aminopropyl)amine and imidazole ligands

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Received 16 April 1996; revised 7 September 1996

The Cu(II) complex of [tris(3-aminopropyl)][imidazole]Cu(II)perchlorate was synthesized. This complex can adsorb on a pyrolytic graphite electrode surface where it functions as an electrocatalyst for the reduction of O_2 and H_2O_2. The electrocatalytic kinetics of both substrate reductions were studied by cyclic voltammetric and rotating disc electrode methods. The catalyst accomplishes the four-electron reduction of O_2 to H_2O at a significantly greater rate than it catalyses the two-electron reduction of H_2O_2, so that the latter cannot be an intermediate in the reduction of O_2.

1. Introduction

Electrocatalytic reduction of oxygen using transition metal complexes is an active area in electrochemistry [1]. Copper complexes have been examined as potential catalysts for the reduction of O_2 and have received much attention [2–9]. However, the ligands are limited to a few aromatic compounds, mostly phenanthroline or substituted phenanthroline. There are few reports of using the Cu(II) complexes with other ligands to catalyse the reduction of O_2 or H_2O_2. The reduction of Cu(II) complexes may produce unstable Cu(I) complexes or, directly, Cu(0) complexes [7, 10]. These features of the reduction process are connected with the difference in the coordination geometry preferred by the Cu(II) and Cu(I) ions. Thus, a large change in the inner-coordination sphere rearrangements are required during the redox process to produce a stable Cu(I) form of the complexes. The phenanthroline may be strongly and irreversibly adsorbed on the graphite electrode surface, thereby binding the Cu^{2+} cation to the electrode surface. The interaction between the electrode and the complexes stabilizes the Cu(I) form complexes, which acts as the catalyst for the reduction of O_2 and H_2O_2.

Recently, we have synthesized a series of copper–zinc centre complexes bridged by imidazole, because these compounds provide adequate model systems for some enzymes and their study is helpful in the understanding of the relationship between an enzyme structure and function [11–13]. In studying the electrochemical properties of these Cu(II) complexes, we have found that the Cu(II) complexes containing a ligand of imidazole can be adsorbed on the pyrolytic graphite electrode surface, and exhibit electrocatalytic activity toward reduction of O_2 and H_2O_2. In this paper, we report the electrochemical behaviour of [tris(3-aminopropyl)][imidazole]Cu(II)perchlorate complex (abbreviated as $[Cu(trpn)(ImH)](ClO_4)_2$) on pyrolytic graphite and the electrocatalytic activity of $[Cu(trpn)(ImH)]^{2+}$ modified electrode toward O_2 and H_2O_2 reduction.

2. Experimental details

2.1. *Materials*

The ligand tris(3-aminopropyl)amine (abbreviated as trpn) and $[Cu(trpn)](ClO_4)_2$ were prepared by a conventional method [14, 15]. All other chemicals were of analytical grade. Stock solutions of H_2O_2 were prepared by diluting 30% H_2O_2. Their concentration was determined by titration with a standard solution of $KMnO_4$. The O_2 concentration was controlled by bubbling a mixture of nitrogen and air, of desired ratio adjusted by two gas flow meters, through the test solution to obtain the concentration range from 0.1 mmol dm^{-3} to 0.28 mmol dm^{-3} of O_2. The concentration of O_2 in an air saturated aqueous solution was 0.28 mmol dm^{-3}. 0.05 mol dm^{-3} Britton–Robinson buffer solutions containing 0.1 mol dm^{-3} $NaClO_4$ as supporting electrolyte were employed to control the pH of the test solutions. All solutions were prepared with deionized water. Highly pure nitrogen was used to remove dissolved oxygen in cyclic voltammetry experiments.

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2.2. *Instrumentation*

Infrared spectra were recorded on a Nicolet 5DX FTIR spectrophotometer (KBr disc). Electrical conductivity was measured using a BSD-A numerical conductometer (Jiangsu China) with a complex concentration of 1 mmol dm^{-3}. Electrochemical experiments were performed with a PAR M270 electrochemical system (EG&G). Rotating disc electrode measurements were carried out with a PAR M636 ring–disc electrode system (EG&G) using a pyrolytic graphite electrode(4.5 mm diam.).

2.3. *Procedures*

The [Cu(trpn)(ImH)](ClO$_4$)$_2$ was prepared by adding 0.075 g (1.1 mmol) of imidazole(ImH) to the solution of 0.4509 g (1.0 mmol) of [Cu(trpn)](ClO$_4$)$_2$ in 10 ml water. After stirring for 20 min, the solution was filtered and the filtrate was concentrated at room temperature in vacuum. A blue product was collected and washed with water and ethanol. The yield was 60%.

Elemental analysis confirmed the formula $C_{12}H_{28}N_6Cl_2O_8Cu$, $M_r = 518.9$. Calculated: C, 27.75%; H, 5.40%; N, 16.19%; Cu, 12.33%. Experimental: C, 27.43%; H, 5.26%; N, 15.83%; Cu, 11.90%. Infrared spectra showed the presence of $\nu_{N\text{–}H}$ of ImH at 3463 and 3397 cm^{-1}, $\nu_{N\text{–}H}$ of trpn at 3330 and 3288 cm^{-1} and the ClO_4^- at 1102 cm^{-1}. The infrared data indicated that the imidazole is coordinated with Cu^{2+} using the N atom of the 3 position not the N of the 1 position. Molar conductivity values (Λ_M(H$_2$O, 293 K) = 201 s^{-1} cm^2 mol^{-1}) showed that the complex behaves as a 1:2 electrolyte [16], indicating that the cation of the complex has a +2 charge. All these factors showed that the complex has the formula [Cu(trpn)(ImH)](ClO$_4$)$_2$.

A conventional three-electrode system with a platinum wire as the counter electrode, a saturated calomel electrode (SCE) as reference and a pyrolytic graphite electrode (0.25 mm^2) as the working electrode was employed. The pyrolytic graphite electrode was prepared by sealing the pyrolytic graphite rod to a copper shaft with polyolefin heat shrinkable tubing. The electrode was polished with sandpaper and 0.05 μm alumina slurry and then cleaned ultrasonically in doubly distilled water. Adsorption of the Cu(II) complex on the pyrolytic graphite electrode was obtained by exposing the freshly polished electrode to a solution of the complex for some time. To study the electrochemical properties, the electrode was removed from the solution, rinsed carefully with water and transferred to the buffer solution containing 1×10^{-4} mol dm^{-3} imidazole. All electrochemical experiments were carried out at ambient temperature.

3. Results and discussion

3.1. *Electrochemical behaviour of [Cu(trpn)(ImH)]$^{2+}$ on a pyrolytic graphite electrode*

Figure 1 shows the structure of the [Cu(trpn)(ImH)](ClO$_4$)$_2$ complex. When adsorbing on the pyrolytic graphite electrode surface, the complex yields well defined redox peaks in pure supporting electrolyte. The cyclic voltammogrammes at various scan rates are shown in Fig. 2. The anodic and cathodic peak current increase linearly with scan rate up to about 200 mV s^{-1}, as predicted for a surface controlled reaction. A pyrolytic graphite electrode, without adsorbing the complex or just adsorbing the ligands, does not give rise to the redox peaks as shown in Fig. 2. Therefore, the redox peaks in Fig. 2 are attributed to a surface reaction of [Cu(trpn)(ImH)]$^{2+}$ complex adsorbed on the pyrolytic graphite electrode surface.

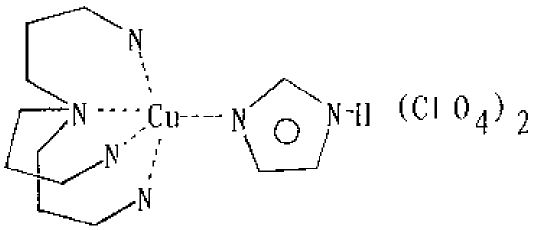

Fig. 1. Structure of [Cu(trpn)(ImH)](ClO$_4$)$_2$ complex.

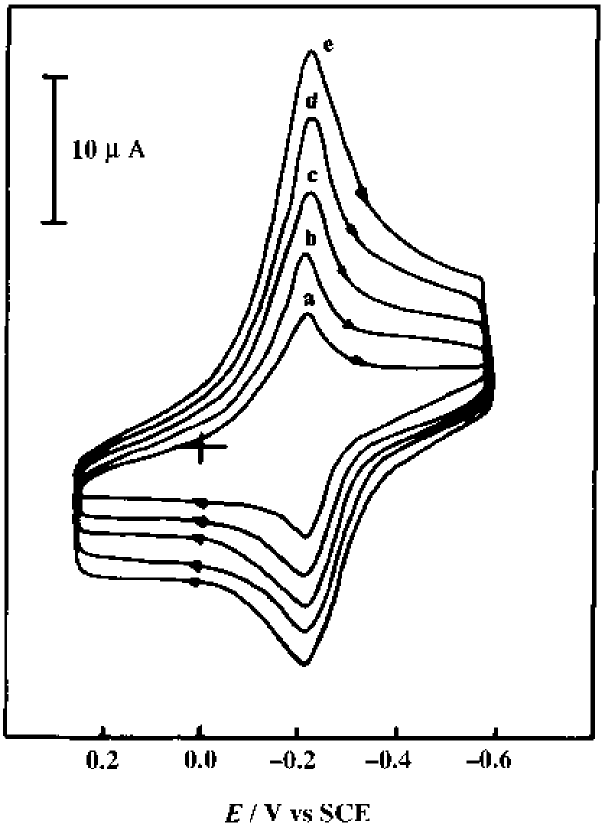

Fig. 2. Cyclic voltammogrammes of [Cu(trpn)(ImH)]$^{2+}$ complex adsorbed on pyrolytic graphite electrode ($\Gamma = 5.7 \times 10^{-10}$ mol cm^{-2}) at scan rate of (a) 20, (b) 40, (c) 60, (d) 80 and (e) 100 mV s^{-1}. 0.05 mol dm^{-3} Britton–Robinson buffer solution containing 0.1 mol dm^{-3} NaClO$_4$ as supporting electrolyte adjusted to pH 6.4.

The formal potential, which was obtained by averaging the anodic and cathodic potential, is about −0.23 V. The cyclic voltammogrammes are symmetrical about the formal potential. The half-peak width is about 96 ± 5 mV, which coincides with the theoretical value of a one-electron process. Based on results for the Cu(II) complex using other ligands by Zhang and Anson [3–5], the redox peak in Fig. 2 can be assigned to the one-electron transfer Cu^{II}/Cu^{I} process of $[Cu(trpn)(ImH)]^{2+}$ adsorbed on the pyrolytic graphite electrode surface.

The peaks of the cyclic voltammogrammes shown in Fig. 2 decreased with increasing scan number, and finally disappeared when imidazole was not contained in the buffer solution. This is probably due to the fact that the Cu(II) complex prefers the five coordinate and the Cu(I) complex prefers the four coordinate. The reduction of the five-coordinate Cu(II) complex produces a four-coordinate Cu(I) complex in which the imidazole may no longer be coordinated. When the imidazole was again added to the solution, the peak increased with continuous subsequent scans. This demonstrates that the imidazole is essential for the redox reaction of $[Cu(trpn)(ImH)]^{2+}$ complex.

3.2. *Electrocatalysis of the reduction O_2 and H_2O_2*

The adsorbed $[Cu(trpn)(ImH)]^{2+}$ complex was tested as a catalyst for the reduction of the O_2 and H_2O_2. The cyclic voltammogrammes shown in Fig. 3 demonstrate the ability of the adsorbed complex to catalyse the reduction of H_2O_2. There is a large increase in the cathodic current when the buffer solution contains H_2O_2. The catalytic reduction of H_2O_2 commences near the formal potential of the complex. Neither the bare electrode nor the ligands show catalytic activity for reduction of H_2O_2, confirming that the reduction of H_2O_2 is catalysed by the copper centre. Cyclic voltammetric experiments indicate that the complex can also catalyse the reduction of O_2; the cyclic voltammogramme is similar to that shown in Fig. 3, but the cathodic current is almost twice that for reduction of H_2O_2 at the same concentration.

To obtain more quantitative kinetic data, the catalysed reduction of O_2 was examined at a rotating disc electrode on which the $[Cu(trpn)(ImH)]^{2+}$ was adsorbed. For calculation of the diffusion-convection limited current at the rotating disc electrode, the following parameters were employed:

Table 1. Diffusion coefficient (D) for O_2 and H_2O_2 and the kinematic viscosity (ν) of aqueous solution (data from [12])

D_{O_2} / $cm^2\ s^{-1}$	$D_{H_2O_2}$ / $cm^2\ s^{-1}$	ν / $cm^2\ s^{-1}$
1.7×10^{-5}	1.6×10^{-5}	0.01

A set of current–potential curves for the reduction of O_2 is shown in Fig. 4A. The cathodic current increases with increasing rotational speed, but the square root plot is non-linear (Fig. 4B). This nonlinear behaviour shows that a chemical reaction is involved in the rate limiting step. The Koutecky–Levich theory has been widely employed to elucidate electrocatalytic processes, and relevant plots are shown in Fig. 4C. The broken line in Fig. 4C was theoretically calculated using the following equation with $n = 4$:

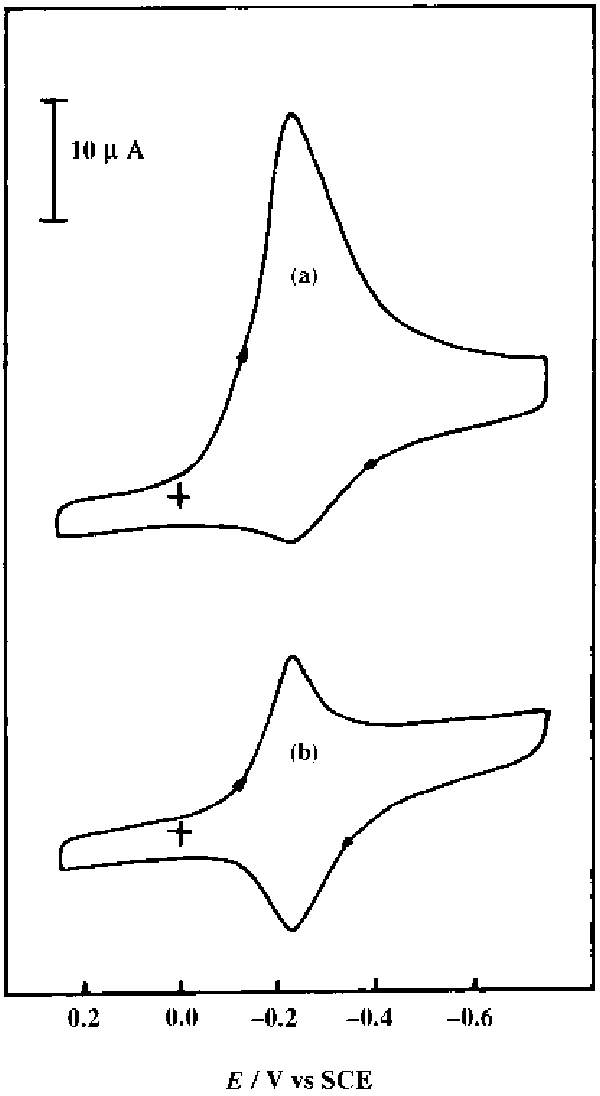

Fig. 3. Cyclic voltammogrammes of $[Cu(trpn)(ImH)]^{2+}$ adsorbed on pyrolytic graphite electrode ($\Gamma = 4.5 \times 10^{-10}$ mol cm^{-2}) in presence (a) and absence (b) of 0.3 mmol dm^{-3} H_2O_2 in 0.05 mol dm^{-3} Britton–Robinson buffer solution containing 0.1 mol dm^{-3} $NaClO_4$ as supporting electrolyte (pH 6.4), scan rate 50 mV s^{-1}.

$$1/i = 1/0.62nFAD^{2/3}\nu^{-1/6}C_{\mathrm{sub}}\omega^{1/2} + 1/nFAk\Gamma_{\mathrm{cat}}C_{\mathrm{sub}} \qquad (1)$$

where C_{sub} is the bulk concentration of substrate, ω is the rotational speed, Γ_{cat} is the surface coverage of the complex on the electrode, k is a rate constant and all other parameters have their usual meaning. The value of Γ_{cat} can be evaluated from the charge (q) by using the equation:

$$\Gamma_{\mathrm{cat}} = q/nFA \qquad (2)$$

The value of q can be obtained by integrating the cathodic peak in Fig. 2 under background correction.

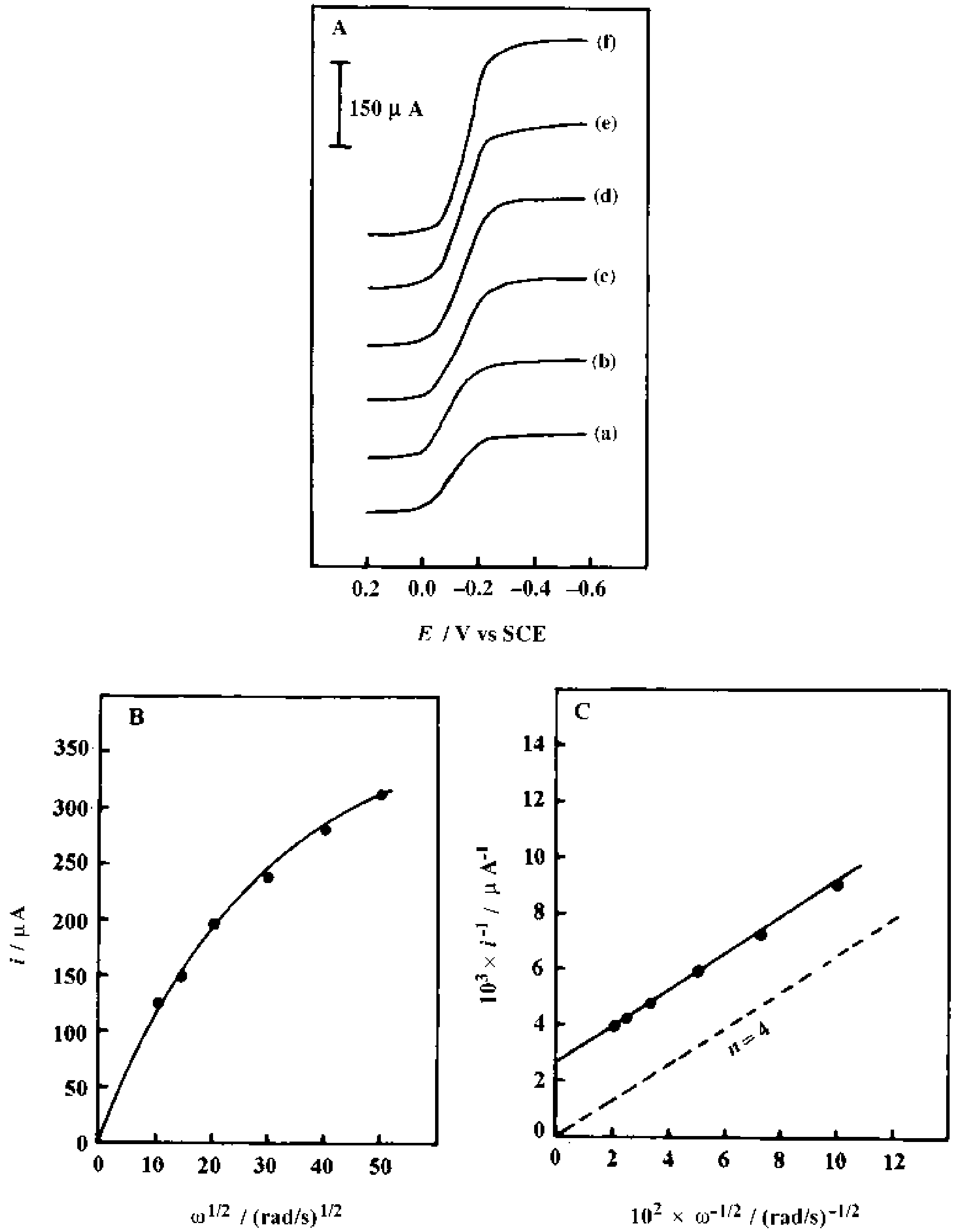

Fig. 4. (A) Current–potential curves for the reduction of 0.28 mmol dm^{-3} O_2 at a rotating disc pyrolytic graphite electrode on which 5.7×10^{-10} mol cm^{-2} $[Cu(trpn)(ImH)]^{2+}$ was adsorbed (scan rate: 10 mV s^{-1}). Rotational speed (rpm) is (a) 100, (b) 200, (c) 400, (d) 900, (e) 1600 and (f) 2500, supporting electrolyte as in Fig. 2. (B) Levich plot of the limiting currents against $\omega^{1/2}$. (C) Koutecky-Levich plot of the data from (B), the broken line is calculated theoretically for the four-electron reduction of O_2.

The slope of the Koutecky–Levich plot (solid line in Fig. 4C) matches, approximately, that calculated for the four-electron reduction of O_2 to H_2O.

The catalysed reduction of H_2O_2 was also examined at the rotating disc electrode. A typical set of current–potential curves and the corresponding Levich and Koutecky–Levich plot are shown in Fig. 5. The slope of the Koutecky–Levich plot is nearly parallel to that calculated for the two-electron reduction of H_2O_2 to H_2O.

The intercept of the Koutecky–Levich plot is much larger than that for the reduction of O_2, indicating that the reduction of H_2O_2 proceeds much more slowly than the reduction of O_2. This shows that the electrocatalytic pathway reduction of O_2 at the electrode may not involve H_2O_2 as an intermediate.

The reciprocal intercept of the Koutecky–Levich plots in Fig. 4 and Fig. 5 gives a kinetic current, i_K, which is defined as

$$i_K = nFAkC_{sub}\Gamma_{cat} \qquad (3)$$

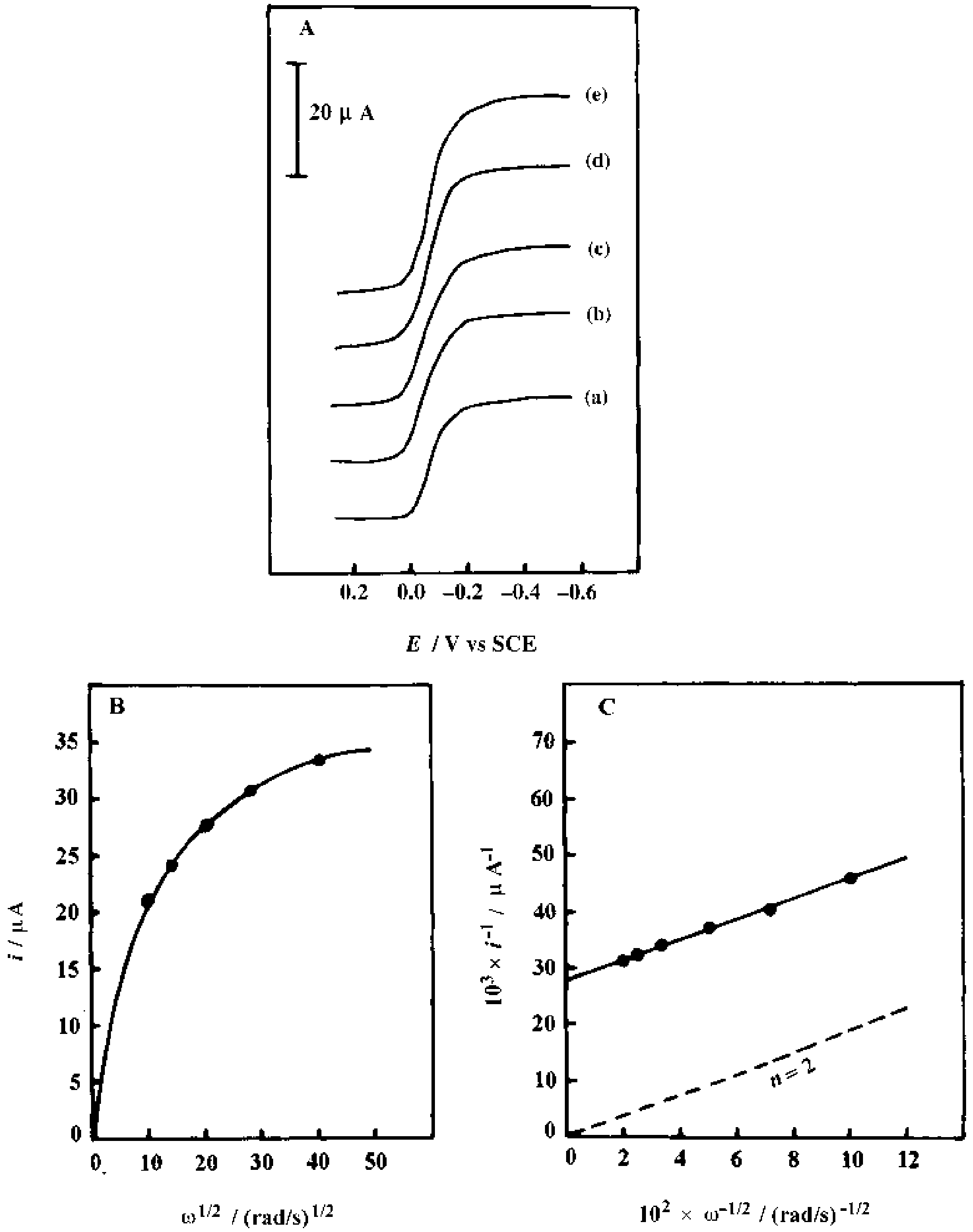

Fig. 5. Catalysed reduction of 0.21 mmol dm^{-3} H_2O_2 at a rotating disc pyrolytic graphite electrode on which 3.8×10^{-10} mol cm^{-2} $[Cu(trpn)(ImH)]^{2+}$ was adsorbed. Conditions for the curves and plots correspond to those in Fig. 4. The broken line is calculated theoretically for the two-electron reduction of H_2O_2.

The rate constant k can be calculated from the values of i_K. The k values for reduction of O_2 and H_2O_2 at various concentration of substrate and Γ_{cat} are given in Tables 2 and 3, respectively. The values indicate that the complex-catalysed reduction of H_2O_2 is much slower than the reduction of O_2, clearly demonstrating that the reduction of O_2 proceeds without the formation of H_2O_2 as an intermediate.

A rotating graphite disc–platinum ring electrode was employed to determine the H_2O_2, which may be the intermediate of the O_2 reduction at a graphite disc electrode on which the complex was adsorbed. The platinum ring electrode was held at +1.2 V. The experimental result indicated that no anodic currents for the ring electrode were detected when the disc electrode was scanned from +0.2 to −0.6 V. This result shows that the reduction of O_2 at the electrode does not involve H_2O_2 as an intermediate.

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Table 2. Rate constants for O_2 reduction catalysed by $[Cu(trpn)(ImH)]^{2+}$ on pyrolytic graphite

C_{O_2} /mmol dm^{-3}	$10^{10}\Gamma$ /mol cm^{-2}	i_K /μA	$10^{-4}k_{O_2}$ /mol^{-1} dm^{-3} s^{-1}
0.10	5.7	125.6	3.57
0.14	5.7	186.3	3.78
0.20	5.7	260.1	3.69
0.28	5.7	374.6	3.80
0.28	4.5	291.7	3.75
0.28	3.2	212.3	3.84
0.28	2.3	146.4	3.68

Table 3. Rate constants for H_2O_2 reduction catalysed by $[Cu(trpn)(ImH)]^{2+}$ on pyrolytic graphite

$C_{H_2O_2}$ /mmol dm^{-3}	$10^{10}\Gamma$ /mol cm^{-2}	i_K /μA	$10^{-3}k_{H_2O_2}$ /mol^{-1} dm^{-3} s^{-1}
0.12	3.8	10.2	7.24
0.21	3.8	18.0	7.30
0.30	3.8	23.2	6.65
0.43	3.8	35.7	7.08
0.43	4.5	45.1	7.55
0.43	5.7	54.0	7.13
0.43	6.3	57.6	6.90

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