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Electrocatalytic Oxidation of C-C Double Bond of Styrene Mediated with Copper Ion Immobilized in Polyaniline Matrix. Electrochemical Model Reaction of Quercetin-2,3-dioxygenase

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1 INTRODUCTION

The development of new biomimetic mediator systems is one of the attractive subjects in the field of bioelectrochemistry and organic electrochemistry. We have already reported on the electrochemical model reactions of a copper-containing monooxygenase such as tyrosinase¹⁾ and dopamine-β-hydroxylase²⁾. The hydroxylation reaction is mediated by Cu(I) / Cu(II) redox couple in the presence of molecular oxygen.

Quercetin-2,3-dioxygenase (Quercetinase) is a copper-containing dioxygenase and catalyzes oxidative cleavage of C-C double bond of quercetin (Scheme 1). In a previous communication³⁾, we have reported the oxidative C-C double bond cleavage reaction of styrene with molecular oxygen catalyzed by CuCl₂ to form benzaldehyde accompanied with accumulation of Cu(I). Since carbon monoxide was detected as the counterpart of benzaldehyde, this reaction is similar to that of quercetinase (Scheme 2). In this paper, we would like to report on the highly selective electrochemical model reaction of quercetinase mediated with copper ion immobilized in polyaniline / polyanion modified electrodes.

2 EXPERIMENTAL

Immobilization of copper ion on electrode surface was performed by loading of Cu²⁺ into polymeric anion doped polyaniline film coated onto electrode surface. Platinum plate (2 x 2 cm) was used as a base electrode. Polyaniline (PAn) modified electrode was prepared by electrochemical polymerization of aniline at 0.8

V (vs. SCE) in 1 M H₂SO₄ solution containing 1.2 (w/v) % sodium polystyrene sulfonate (PSSNa) and 0.5 M aniline. The amount of electricity passed during potentiostatic polymerization was 5.25 Ccm⁻². Loading of Cu²⁺ into PSS / PAn composite film was carried out with potentiostatic electrolysis at -0.5V in an acetonitrile solution containing 20 mM Cu²⁺.

Electrocatalytic oxidation of C-C double bond with modified electrodes was conducted in an H type cell divided with cation exchange membrane equipped with a reflux condenser at 82 °C under O₂ atmosphere. Silver wire was used as a quasi-reference electrode and styrene was used as a model substrate. Reaction products were determined with an HPLC.

Scheme 1

Scheme 2

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3 RESULTS and DISCUSSION

In this model reaction (Scheme 2), electrolytic regeneration of Cu(II) species from inactive Cu(I) would produce benzaldehyde continuously. Figure 1 shows the results of controlled potential electrolysis when CuCl₂ was existed in the solution phase. The total yield increased with increasing the electricity at the beginning of electrolysis, but reached to steady value when the electricity was beyond 30 C. This may be caused by composition change of active species from consumption of Cl⁻. As shown in Fig. 1, the yield increased by the addition of Et₄NCl. Because the presence of chloride anion was essential to maintain catalytic activity of copper species, the selectivity of benzaldehyde was 70 % due to the simultaneous formation of phenacyl chloride as a by-product.

Fig. 1 Effect of chloride ion on total yield of electrocatalytic oxidation of styrene. Reaction conditions: 100 mM styrene + 5 mM CuCl₂ + 100 mM NaClO₄ in CH₃CN solution, Pt working electrode, (■) Without Et₄NCl, (○) 5 mM Et₄NCl was added, (●) 15 mM Et₄NCl was added.

When copper immobilized electrode (Cu / PSS / PAN electrode) was used as the working electrode in CH₃CN solution containing 15 mM Et₄NCl, however, phenacyl chloride was not produced at all. In marked contrast to the homogeneous mediatory system, benzaldehyde was continuously obtained even in the absence of chloride ion (Fig. 2). Therefore, the product selectivity of the oxidative cleavage reaction of C-C double bond increased to 100 %. These results indicate catalytic activity of copper-PAN complex is comparable to that of copper-chloride

complex. It should be noted that oxidized product was not formed with using PSS / PAN electrode.

Fig. 2 Electrochemical oxidation of styrene with Cu/PSS/PAN electrode in the absence of Et₄NCl.

Almost same results were obtained when polyvinyl sulfate (PVS) was used as polyanion instead of PSS. To evaluate the turnover number of copper ion, the amount of copper ion in PAN matrix was determined with an atomic absorption spectroscopy. As listed in Table 1, the turnover number was in the order of 10² after electrolyzing for 150 min. In conclusion, highly selective electrochemical model system of quercetinase was achieved utilizing copper ion immobilized PAN modified electrodes.

Table 1 Turnover number of copper ion in PAN.

Polyanion	Copper / μmol	Turnover number
PSS	0.08	160
PVS	0.2	95

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