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Investigation of the electrocatalytic behavior of halogenated acids at a C_{60}-*p-tert*-butylcalix[8]arene chemically modified electrode

Abstract The C_{60}-*p-tert*-butylcalix[8]arene (represented as C_{60}-L) chemically modified electrode has two redox wave couples in mixed solvents of MeCN and water (3:2, v/v), corresponding to C_{60}-L in the solution originating from partial film dissolution and from film reaction, respectively. Both the C_{60}-L in the solution state and in the film state exhibit catalytic activity towards the reduction of halogenated acids.

Keywords C_{60}-*p-tert*-butylcalix[8]arene ·
Chemically modified electrode · Electrocatalysis ·
Cyclic voltammetry

Introduction

The electrochemical behavior of fullerenes in solution [1, 2, 3] and in the film state [4, 5, 6] has been widely investigated. In solution, up to six one-electron reversible reduction steps in nonaqueous solvent solutions have been reported for C_{60} [1, 2]. The electrochemically generated C_{60}^{n-} anions have been shown to act as catalysts for the reduction of some halides [7, 8, 9, 10, 11]. The voltammetry of the C_{60} film-coated electrode is irreversible owing to structural rearrangements that accompany the $C_{60}^{n-/(n+1)-}$ electrode processes [4]. The reduction of 1,2-diiodoethane is catalyzed by both the first and second electroreductions of $C_{60}^{n-/(n+1)-}$ at the C_{60} film electrode [9]. An Au electrode modified with a monolayer of a C_{60} carboxylic derivative was reported to provide an active interface for mediating the bio-electrocatalyzed oxidation of glucose [12].

Since 1994, the host-guest complexes of fullerene with calixarenes have become one of the most interesting research areas in fullerene chemistry. C_{60} and *p-tert*-butylcalix[8]arene (L) form a 1:1 inclusion complex in toluene [13, 14] or carbon disulfide [15]. The unstable electrochemical behavior of C_{60}-*p-tert*-butylcalix[8]arene (C_{60}-L) film was reported by us [16] and by Cliffel and Bard [17]. In mixed MeCN and water, the electrochemical behavior of the C_{60}-L film becomes more stable [18]. In our previous work, the electrocatalysis of some biomolecules and organic compounds at electrodes modified with C_{60}/cyclodextrin or C_{60}/calixarene complexes was investigated [19, 20, 21, 22, 23, 24, 25, 26]. This enables us to explore the electrocatalytic activity of a C_{60}-L film chemically modified electrode.

Experimental

Instruments and chemicals

Cyclic voltammetric (CV) measurements were performed on an EG&G PAR 273 potentiostat/galvanostat with model 270 electrochemical software. All the experiments were performed with a three-electrode configuration at room temperature. A GC working electrode (4 mm in diameter), a platinum counter electrode, and a saturated calomel reference electrode (SCE) were employed in all measurements. Tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) was purchased from Sigma. Acetonitrile and toluene were distilled from P_2O_5 prior to use. All other reagents were of analytical grade. Water was triply distilled from an all-quartz still. High-purity nitrogen was used for deaeration.

The scanning electron microscope (SEM) images were obtained using a Amray 1910FE microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed using a VG Scientific ESCALab220i-XL photoelectron spectrometer.

Preparation of C_{60}-L film

The synthesis of C_{60}-L was the same as described previously [16]. A certain amount of C_{60}-L was dissolved in carbon disulfide to give a 5×10^{-4} M solution. The GC electrode surface was carefully polished with chamois leather containing Al_2O_3 slurry, and ultrasonically cleaned in distilled water and ethanol. The C_{60}-L film chemically modified electrode was prepared by dropping a solution of C_{60}-L (5 μL, 5×10^{-4} M) on the GC electrode surface and evaporating the solvent under an infrared heat lamp.

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Results and discussion

Electrochemical behavior of the C$_{60}$-L film modified electrode

Figure 1 shows the continuous cyclic voltammogram of C$_{60}$-L film in a 3:2 mixed solvent of MeCN and water containing 0.04 M Bu$_4$NClO$_4$ as the supporting electrolyte in the potential scan range from 0 to –1.4 V (vs. SCE). Two pairs of reduction/reoxidation waves, Pc$_1$/Pa$_1$ and Pc$_2$/Pa$_2$, were obtained. A potential shift between the first and subsequent cycles was observed, implying that there was a structural arrangement accompanying the release of the solvent which was entrapped during the evaporation process and injection of Bu$_4$N$^+$ and a small amount of anions into the film [27, 28, 29]. The cathodic currents changed little after the second cycle, although the current of Pa$_2$ decreased cycle by cycle. At a scan rate of 0.1 V s^{-1}, the peak potentials of Pc$_2$ and Pa$_2$ were –0.95 V and –0.64 V, respectively.

When the potential was reversed at a more positive value, –0.8 V, a small pair of reduction/reoxidation waves was more clearly seen (Fig. 2). Upon continuous scanning, the currents of both the reduction peak and the reoxidation peak did not change much. In our previous work [18], we attributed this small pair of waves to the electrochemical reaction of C$_{60}$-L in the solution originating from the partial film dissolution, for similar small cathodic and anodic prewaves were also seen on the steady-state voltammograms of the C$_{60}$ film by other researchers [29, 30].

XPS characterization of the C$_{60}$-L film

XPS experiments were performed to confirm the important role of the large cation, Bu$_4$N$^+$, during the reduction and reoxidation. The XPS spectra of two C$_{60}$-L film electrodes, one after a linear sweep voltammetric scan, the other after a cyclic voltammetric scan between 0 and –1.5 V, were measured. The N 1s spectrum of the former electrode is shown in Fig. 3A. Two N 1s peaks, located at binding energies of 400.0 and 402.5 eV, respectively, were observed. For the latter electrode, only one N 1s peak at 400.0 eV was apparent (Fig. 3B). The N 1s XPS centering at –402.5 eV resulted from the positively charged nitrogen, indicating the existence of Bu$_4$N$^+$ in the film. The N 1s signal at 400.0 V originated from the GC electrode itself (not shown), which is in accordance with the literature [31].

The result mentioned above suggests that, upon reduction, the Bu$_4$N$^+$ ion diffuses into the C$_{60}$-L film to balance the negative charges; after reoxidation, most Bu$_4$N$^+$ leaves the film.

SEM characterization of the C$_{60}$-L film

C$_{60}$-L film morphology was studied by SEM techniques. The SEM image of a newly prepared C$_{60}$-L film on a GC disk (4 mm in diameter) showed irregular column-structured crystallites of different size (Fig. 4, top). After several cycles of potential scan, the structure of the C$_{60}$-L film changed from crystallite to reticular (Fig. 4, bottom). The result confirmed that a structural arrangement of the C$_{60}$-L film happened after the potential scan.

In our previous report [18], a two-electron reduction/reoxidation process of the C$_{60}$-L film was suggested as follows, on the basis of comparison with the CV for the C$_{60}$ film. The reduction process:
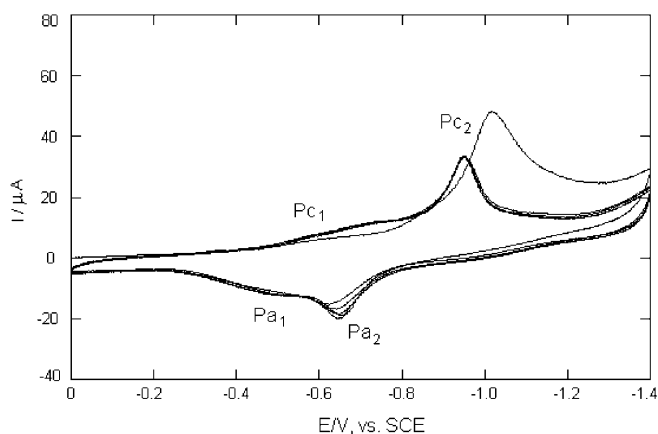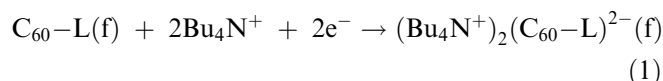
$$C_{60}-L(f) \ + \ 2Bu_4N^+ \ + \ 2e^- \rightarrow (Bu_4N^+)_2(C_{60}-L)^{2-}(f) \tag{1}$$

Fig. 1 Effect of continuous cycling of a C$_{60}$-L film modified electrode in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$ as supporting electrolyte at a scan rate of 0.1 V s^{-1}
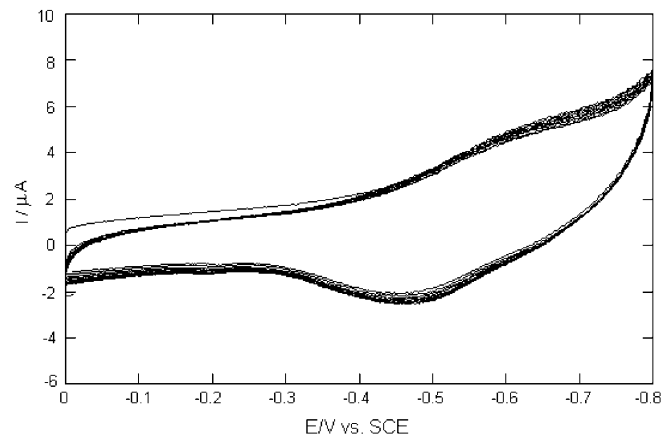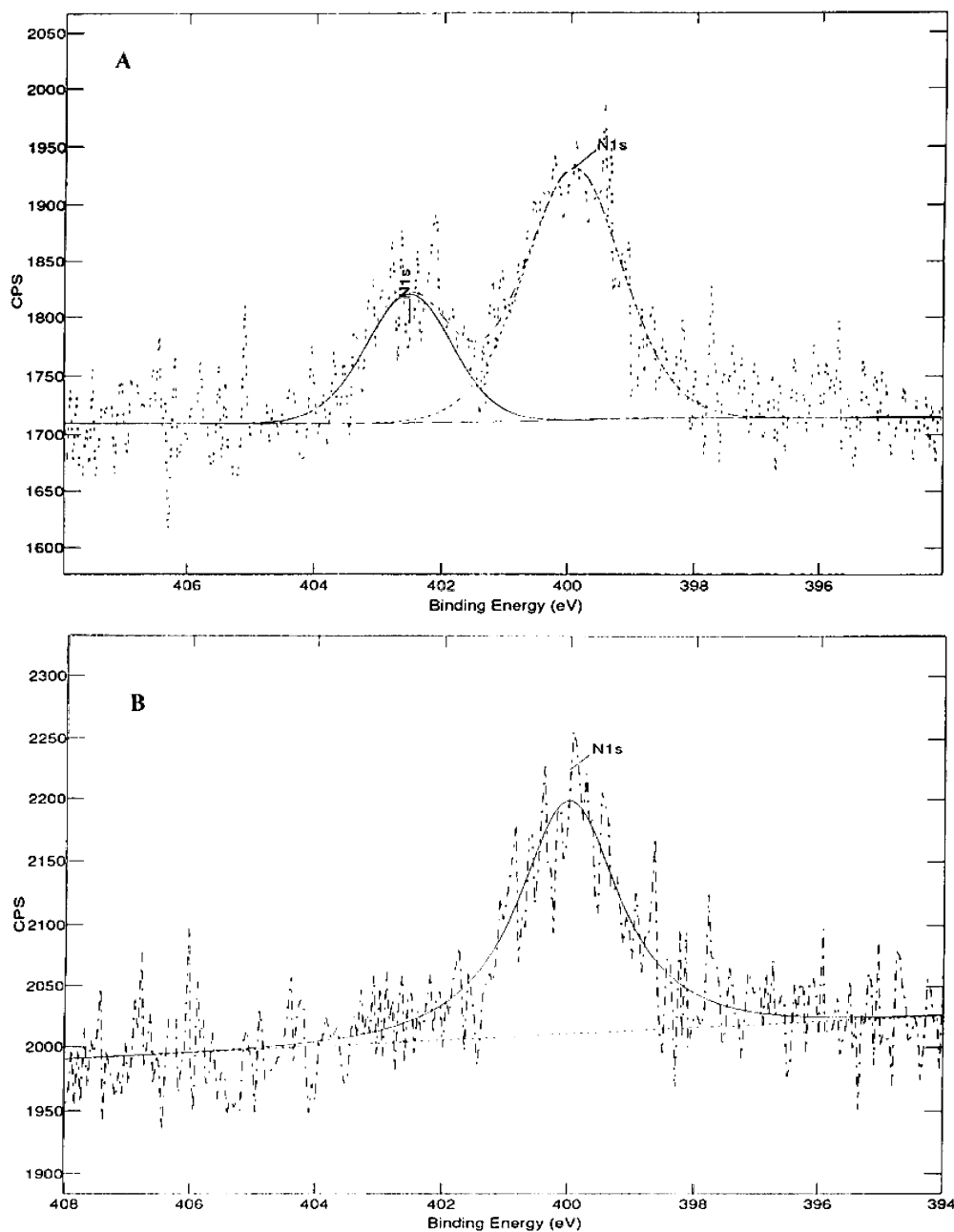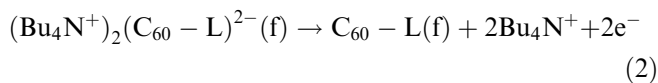

Fig. 2 Effect of continuous cycling of C$_{60}$-L film modified electrode in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$; scan rate 0.1 V s^{-1}

and the reoxidation process:

$$(Bu_4N^+)_2(C_{60} - L)^{2-}(f) \rightarrow C_{60} - L(f) + 2Bu_4N^+ + 2e^-$$

$$(2)$$

where "f" represents the film on the GC electrode.

Electrocatalytic reduction of halogenated acid at the C_{60}-L modified electrode

Monochloroacetic acid (MA) showed an irreversible reduction peak at –1.27 V on the bare GC electrode in 0.04 M Bu_4NClO_4 in 3:2 mixed acetonitrile/water (Fig. 5a), while the C_{60}-L modified electrode showed a stable cyclic voltammetric response in the potential range from 0 to –1.5 V (Fig. 5b). As shown in Fig. 5c, when 1.0×10^{-3} M MA was added to the solution, the reduction of MA at –1.27 V disappeared, and a considerable electrocatalytic reduction peak at –1.00 V was observed at the C_{60}-L modified electrode while the reoxidation peak of C_{60}-L at –0.64 V decreased significantly. This result suggests that the electroactive C_{60}-L in the modified electrode acts as an electron transfer mediator to the reduction of MA.

When the potential scan range was restricted to 0 to –0.8 V, the C_{60}-L film electrode showed a stable cyclic voltammogram (Fig. 6a), corresponding to the redox process of dissolved C_{60}-L in the solution, as discussed

above. When 1.0×10^{-3} M MA was added to the solution, the cathodic peak current increased greatly, accompanying a little positive potential shift (Fig. 6b), indicating that the C_{60}-L in the solution also can electrocatalyze the
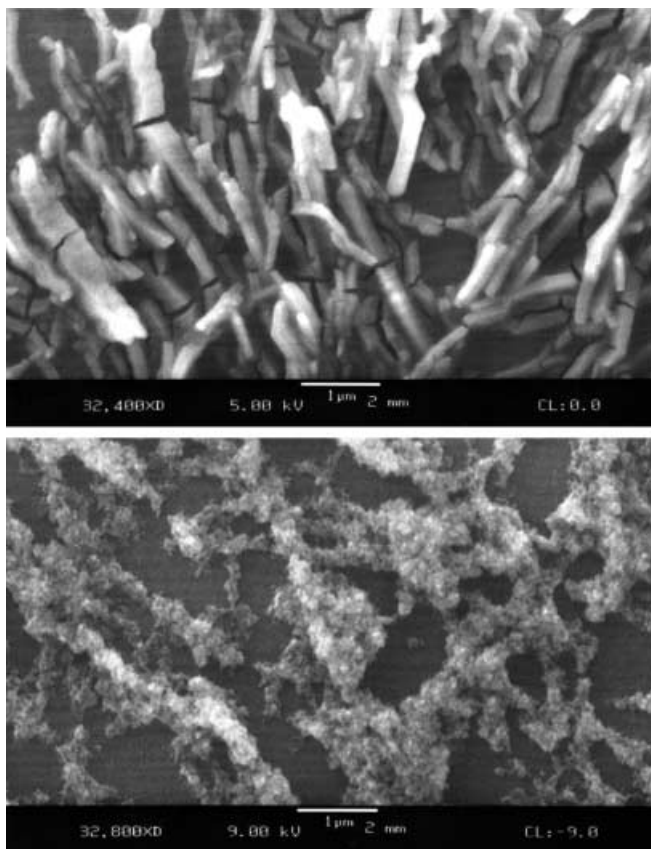
reduction of MA. Moreover, D'Souza et al. [9, 10, 11] have reported that the electrochemically generated C_{60}^{n-} anions act as catalysts for the reduction of some halides. According to our present work, the C_{60}-L anion can also electrocatalyze the reduction of halogenated acids just like the performance of C_{60} anions.

The reductions of dichloroacetic acid, α-bromoacetic acid, α-bromopropionic acid, and α-bromobutyric acid were found to be electrocatalyzed at the C_{60}-L modified electrode. Figure 7 shows the catalytic reduction of dichloroacetic acid at the C_{60}-L modified electrode, which was similar to that of MA. Figure 8 shows the reductions of α-bromoacetic acid, α-bromopropionic acid, and α-bromobutyric acid at the C_{60}-L modified electrode in the potential range from 0 to–0.8 V, corresponding to the electrocatalytic reduction process by C_{60}-L in solution. Under the conditions of the same

Fig. 4 SEM images of newly prepared C_{60}-L film on a GC disk (*top*) and after three cycles of potential scans in the range from 0 to –1.5 V in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$ (*bottom*)
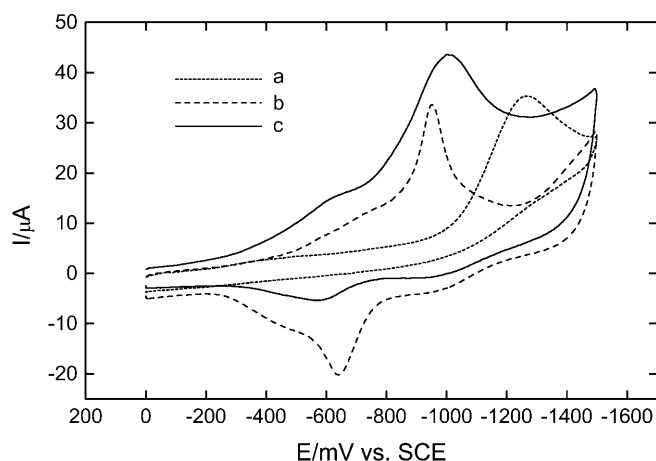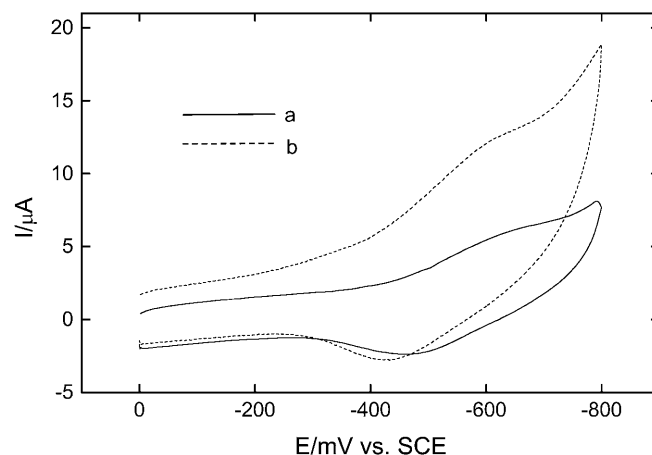

Fig. 6 Cyclic voltammograms for a C_{60}-L modified GC electrode in the absence of monochloroacetic acid (*a*) and in the presence of 1 mM MA (*b*) in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$. Scan rate 0.1 V s^{-1}; potential range 0 to –1.5 V

Fig. 5 Cyclic voltammograms for a bare (*a*) and C_{60}-L modified GC electrode in the absence of MA (*b*) and in the presence of 1 mM MA (*a* and *c*) in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$. Scan rate 0.1 V s^{-1}; potential range 0 to –1.5 V
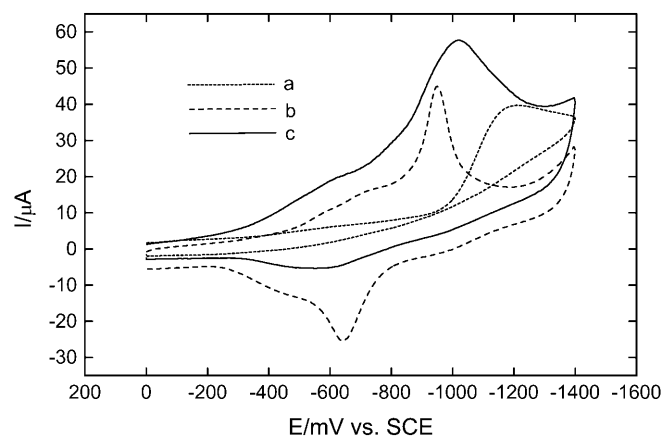

Fig. 7 Cyclic voltammograms at a bare (*a*) and C_{60}-L modified GC electrode in the absence of dichloroacetic acid (*b*) and in the presence of 1 mM dichloroacetic acid (*a* and *c*) in acetonitrile/water (3:2 v/v) containing 0.04 M Bu$_4$NClO$_4$. Scan rate 0.1 V s^{-1}; potential range 0 to –1.5 V
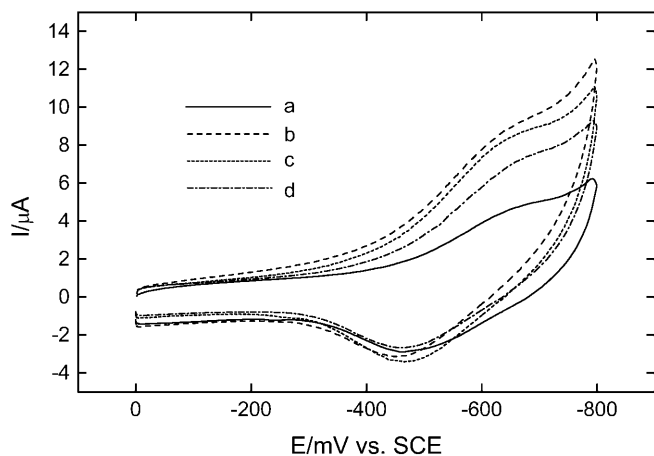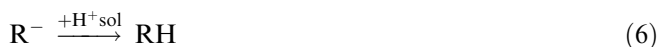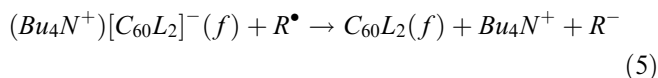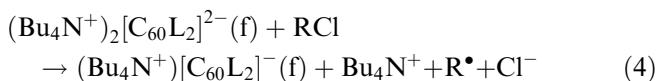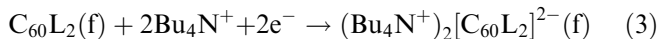
Fig. 8 Cyclic voltammograms at C_{60}-L modified GC electrode in the absence of halogenated acid (*a*) and in the presence of 1 mM α-bromoacetic acid (*b*), 1 mM α-bromopropionic acid (*c*), or 1 mM α-bromobutyric acid (*d*) in acetonitrile/water (3:2 v/v) containing 0.04 M Bu_4NClO_4. Scan rate 0.1 V s^{-1}; potential range 0 to –0.8 V

concentration of the three α-substituted bromo acids, the electrocatalytic reduction current decreased in the order: α-bromoacetic acid > α-bromopropionic acid > α-bromobutyric acid.

D'Souza et al. [10] reported the electrocatalytic reduction of α,ω-dihaloalkanes, $X(CH_2)_mX$ (X = Cl, Br, I; m = 2–8) by both the di- and trianions of C_{70}. The initial electron transfer to $X(CH_2)_mX$, to produce the radical $X(CH_2)_mX\bullet$, was assumed to be the rate-determining step governed by an outer-sphere electron transfer mechanism, and the subsequent reactions could follow the formation of this radical. On the basis of this previous report [10] and our experimental results, the mechanism of the catalytic reduction of these five halogenated acids might be expressed as follows:

$$C_{60}L_2(f) + 2Bu_4N^+ + 2e^- \rightarrow (Bu_4N^+)_2[C_{60}L_2]^{2-}(f) \quad (3)$$

$$(Bu_4N^+)_2[C_{60}L_2]^{2-}(f) + RCl$$
$$\rightarrow (Bu_4N^+)[C_{60}L_2]^-(f) + Bu_4N^+ + R^\bullet + Cl^- \quad (4)$$

$$(Bu_4N^+)[C_{60}L_2]^-(f) + R^\bullet \rightarrow C_{60}L_2(f) + Bu_4N^+ + R^- \quad (5)$$

$$R^- \xrightarrow{+H^+sol} RH \quad (6)$$

where RX represents the halogenated organic acid.

Conclusions

The C_{60}-L chemically modified electrode had two redox wave couples in mixed solvents of MeCN and water (3:2,

v/v), corresponding to the reactions of C_{60}-L in the solution state and film state, respectively. Both of the two states of C_{60}-L served as electron transfer mediators towards the reduction of halogenated acids.

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