

# Electrocatalytic reduction of 1,2-diiodoethane by anions of supramolecular complex of $(\beta\text{-CD})_2/\text{C}_{60}$ in DMF solution

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Received 27 November 2006; received in revised form 23 April 2007; accepted 23 April 2007

Available online 29 April 2007

## Abstract

The homogeneous electrocatalytic reduction of 1,2-diiodoethane by anions of the supramolecular complex of  $(\beta\text{-CD})_2/\text{C}_{60}$  in DMF solution is reported. The results show that the trianion of  $(\beta\text{-CD})_2/\text{C}_{60}$  exhibits electrocatalytic behavior towards the reduction of 1,2-diiodoethane, whereas the dianion is unable to reduce the diiodoethane. The second-order catalytic rate constant in DMF solution was determined to be  $3.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  by analysis of voltammetric responses under pseudo-first-order conditions with respect to  $(\beta\text{-CD})_2/\text{C}_{60}$ . The results suggest that the host  $\beta$ -cyclodextrin molecules have little effect on the electrocatalytic ability of the encapsulated  $\text{C}_{60}$  toward organic halides.

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**Keywords:** Cyclodextrins; Electrocatalysis; Fullerenes; Organic halides; Supramolecular inclusion complex

## 1. Introduction

Electrocatalytic reduction of organic halides (RX) has received great attention for the last few decades [1–6], and is one of the most important topics in organic electrochemistry [7–9] because of the important roles it plays in synthetic [10,11] and environmental [12,13] applications, especially in considering that halogenated organic compounds belong to a class of compounds known as persistent organic pollutants, which are slow to biodegrade in nature.

$\text{C}_{60}$  has displayed a rich electrochemistry due to its unique dimensional and electronic structures [14–16]. It has been shown that  $\text{C}_{60}$  possesses a strong electron-accepting ability [14], and the anions of  $\text{C}_{60}$  are readily generated and stable due to the large spacing of the formal potentials of each individual redox process [14]. Previous studies on  $\text{C}_{60}$  anions have shown that they are electron-rich species, and in addition to their reactivity towards electrophiles [17–20], they are also good electron-transfer mediators. Both the dianion and trianion of  $\text{C}_{60}$  in solution, as well as the monoanion and dianion at  $\text{C}_{60}$  film-modified electrodes, have

displayed electrocatalytic reductive ability towards halogenated organic compounds [21–24].

The study of the supramolecular inclusion complex of cyclodextrin (CD) and  $\text{C}_{60}$  has drawn a lot of attention recently [25–34], not only because the formation of the complex can increase the solubility of  $\text{C}_{60}$  in aqueous solution for possible applications in biology and medicinal chemistry [35,36], but also because the complex has displayed some interesting properties such as dinitrogen fixation [37] and reduction of  $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$  and  $\text{N}-\text{N}^+$  bonds under mild conditions [38]. However, previous studies on the supramolecular inclusion complexes of cyclodextrin and  $\text{C}_{60}$  have been focused on the use of  $\gamma$ -cyclodextrin as the host molecule [25–32], whereas only few papers appeared involving the use of  $\beta$ - and  $\alpha$ -cyclodextrin to date [33,34], probably due to the size compatibility between the cyclodextrin ( $\gamma$ -CD, 0.84 nm;  $\beta$ -CD, 0.66 nm and  $\alpha$ -CD, 0.52 nm) [39] and  $\text{C}_{60}$  (1 nm) [40]. The investigation of water-soluble supramolecular inclusion complexes of  $\text{C}_{60}$  with other cyclodextrins such as  $\beta$ -cyclodextrin is of importance since it helps to gain a better understanding on the cyclodextrin effect on the encapsulated  $\text{C}_{60}$ . Due to the difficulty of obtaining inclusion complexes of  $\text{C}_{60}$  with parent  $\beta$ -cyclodextrin, studies on such complexes have been involving the use of  $\beta$ -cyclodextrin derivatives [41–46], which are, however, still different from the

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complex of  $C_{60}$  with parent  $\beta$ -cyclodextrin. Stimulated by previous report on the stabilization of  $C_{60}$  monoanion in aqueous solution by means of inclusion with  $\gamma$ -cyclodextrin [28], we have recently developed a method of preparing inclusion complexes as well as self-assembled monolayers (SAMs) of cyclodextrin and  $C_{60}$  using anionic  $C_{60}$  [34,47], where complexes of  $\beta$ - and even  $\alpha$ -cyclodextrin with  $C_{60}$  have been obtained.

Herein, we report the first homogeneous electrocatalytic reduction of 1,2-diiodoethane by supramolecular inclusion complex of  $\beta$ -cyclodextrin and  $C_{60}$ . The results show that the trianion of the inclusion complex exhibits electrocatalytic reductive ability towards 1,2-diiodoethane similar to  $C_{60}$  anions, indicating that the effect of host  $\beta$ -cyclodextrin molecule on the electrocatalytic reductive ability of the encapsulated  $C_{60}$  is limited.

## 2. Experimental

### 2.1. Chemicals

99.5%  $C_{60}$  was purchased from SES, Houston, USA, and used as received.  $\beta$ -Cyclodextrin was purchased from Tokyo Chemical Industry Co. Ltd., Japan. 1,2-Diiodoethane was obtained from Sigma–Aldrich, USA. Tetra-*n*-butylammonium perchlorate (TBAP), purchased from Fluka, was recrystallized from absolute ethanol and dried in vacuum at 40 °C prior to use. All other reagents were of analytical reagent grade, purchased from the Beijing Chemical Works, China, and used without purification. Deionized water was triply distilled from an all-quartz still. High-purity nitrogen was purchased from Juyang Gas Co., Changchun, China. DMF was distilled over  $MgSO_4$  under vacuum at 25 °C. Experiments were carried out at  $25 \pm 1$  °C in the dark in order to avoid decomposition of 1,2-diiodoethane.

### 2.2. Instrumentation

All electrochemical measurements were performed with a CHI 620B electrochemical workstation (CH Instruments Inc., USA). A conventional three-electrode cell consisted of a glassy carbon working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). UV–vis spectra were recorded with a Varian Cary 500 Scan UV–vis–NIR spectrophotometer using a 1 cm path length quartz cuvette.

### 2.3. Preparation of supramolecular inclusion complex of $\beta$ -cyclodextrin and $C_{60}$

The supramolecular inclusion complex of  $\beta$ -cyclodextrin and  $C_{60}$  was prepared according to a previously reported method [34]. Briefly, 20 mg of  $C_{60}$  (0.028 mmol) was added to 1-methylnaphthalene radical anion (0.28 mmol), which was prepared by reduction of 1-methylnaphthalene with sodium after vigorous stirring under argon in distilled DMF for 3 h at ambient temperature.  $\beta$ -CD (0.14 mmol) was then added to this solution and stirred for 3 h. After that, iodine (0.14 mmol) was added to oxidize the anions back to neutral form. The solvent was then removed under vacuum and a yellow-brown crude product

was obtained. The crude product was washed with methanol to remove iodine and iodide, and then dissolved in water to remove the uncomplexed  $C_{60}$ . The filtrate was dried at room temperature, a yellow-brown solid product consisting of a mixture of  $(\beta\text{-CD})_2/C_{60}$  and unreacted  $\beta$ -CD was obtained, and was then directly used for electrochemical measurement. The concentration of  $(\beta\text{-CD})_2/C_{60}$  used in the electrochemical experiments was determined spectroscopically by using the absorption coefficient  $\varepsilon = 51,900$  at 330 nm for  $C_{60}$  [31].

## 3. Results and discussion

### 3.1. UV–vis spectroscopy and electrochemistry of $(\beta\text{-CD})_2/C_{60}$

Fig. 1 shows the UV–vis spectrum of the  $(\beta\text{-CD})_2/C_{60}$  supramolecular inclusion complex in aqueous solution, which displays absorption bands at 222, 268 and 334 nm. The absorption bands are in good agreement with those of  $C_{60}$  (see Fig. 1a), indicating that a water-soluble supramolecular inclusion complex of  $\beta$ -CD and  $C_{60}$  is obtained. Notably, the absorption bands at 268 and 334 nm for the  $(\beta\text{-CD})_2/C_{60}$  inclusion complex are broader than those of  $C_{60}$  and  $(\gamma\text{-CD})_2/C_{60}$  [31], indicating the formation of aggregates for the complex in aqueous solution as observed for the highly water-soluble (2:1)  $\beta$ -cyclodextrin–fullerene conjugates [44,45]. A singlet resonance at 142.1 ppm corresponding to the carbon atoms of  $C_{60}$  is observed for the  $^{13}C$  NMR of the complex in aqueous solution; the same resonance was also observed for  $\gamma$ -cyclodextrin-bicapped  $C_{60}$  [26,31,34], consistent with formation of a water-soluble inclusion complex of  $\beta$ -CD and  $C_{60}$ . For MALDI MS measurement, ions at  $m/z = 3013, 3029, 1878$  and  $1894$  are observed and assigned to  $[\beta\text{-CD}/C_{60} (2:1) + Na]^+$ ,  $[\beta\text{-CD}/C_{60} (2:1) + K]^+$ ,  $[\beta\text{-CD}/C_{60} (1:1) + Na]^+$  and  $[\beta\text{-CD}/C_{60} (1:1) + K]^+$ , respectively. The results thus confirm the formation of the water-soluble supramolecular inclusion complex of  $\beta$ -CD and  $C_{60}$ . Since it has been reported that the water-soluble supramolecular complex of  $\gamma$ -CD and  $C_{60}$  is formed mainly with

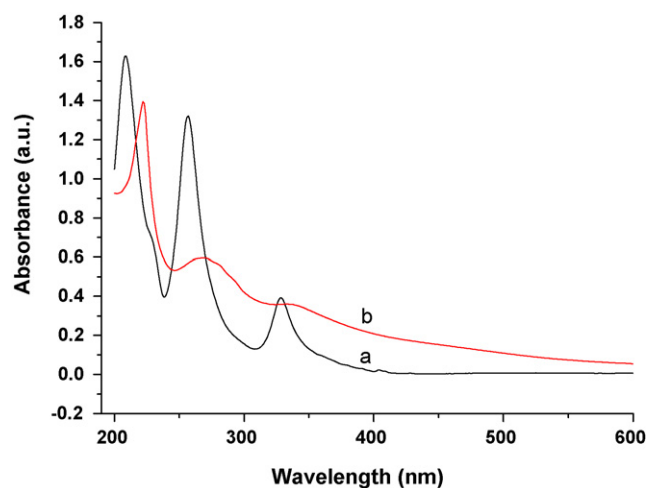


Fig. 1. UV–vis spectra of (a)  $C_{60}$  in hexane and (b)  $(\beta\text{-CD})_2/C_{60}$  supramolecular inclusion complex in aqueous solution.

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