

Electrocatalytic Reduction of α,ω -Diiodoalkanes $\text{I}(\text{CH}_2)_m\text{I}$ ($m = 1-8$) by C_{60}^{n-} ($n = 1-3$) Anions in Solution and at the C_{60} Film-Modified Electrodes

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Electroreduction of a homologous series of α,ω -diiodoalkanes $\text{I}(\text{CH}_2)_m\text{I}$ ($m = 1-8$) is shown to be catalyzed by C_{60}^{n-} anions ($n = 2, 3$) both in solution and at a C_{60} film-coated electrode. Solution electrocatalysis occurred for the anions of $n = 2$ and 3 in 0.1 M (TBA)PF₆ in benzonitrile at a platinum working electrode. Electrocatalysis at the film-coated electrode occurred for anions of $n = 1$ and 2 in 0.1 M (TBA)PF₆ in acetonitrile. For solution electrocatalysis, the second-order catalytic rate constants were determined by voltammetry at a rotating disk electrode under pseudo-first-order conditions with respect to the α,ω -diiodoalkanes. The determined k values increase in the order $\text{C}_5 < \text{C}_8 < \text{C}_4 < \text{C}_3 < \text{C}_6 \ll \text{C}_2$ for the number of carbon atoms of the alkyl chain of the α,ω -diiodoalkanes. The GC-MS and HPLC product analyses of the constant potential bulk electrolyses revealed that alkanes, alkenes, and monoiodoalkyl derivatives are formed primarily, except for the reaction of C_{60}^{3-} with either 1,3-diiodopropane or 1,5-diiodopentane where formation of the C_{60} adducts is favored.

Introduction

Electroreductive voltammetry of C_{60} is very rich.¹ That is, it displays six one-electron reversible $\text{C}_{60}^{n-(n+1)-}$ redox couples in nonaqueous solvent solutions, in agreement with theoretical predictions.²⁻⁵ Formal redox potentials of these couples are almost equally and largely separated, that is, by as much as about 0.4 V, depending on experimental conditions.⁶ Therefore, it is facile to generate selectively C_{60}^{n-} anions either chemically, by using suitable reductants,⁷⁻⁹ or electrochemically, by electrolysis at constant potential.^{10,11} The C_{60}^{n-} anions play important role for (i) formation of highly uniform films of genuine C_{60} ,^{10,11} (ii) preparation of C_{60} salts,¹² (iii) selective formation of different alkyl¹³⁻¹⁶ and aryl¹⁵ adducts of C_{60} by reacting the anions with suitable organic halides, and (iv) selective homogeneous catalytic reduction of a range of halogenated organic compounds.^{17,18}

In contrast to the C_{60} solution voltammetry, voltammetry of the solid C_{60} compound immobilized at the electrode is irreversible owing to structural rearrangements that accompany the $\text{C}_{60}^{n-(n+1)-}$ electrode processes¹⁹ and possible C_{60} dimerization.²⁰ Either the C_{60} film-coated electrodes^{10,11,19-31} or the C_{60} -graphite-PTFE composite ones³² are used for studies of solid C_{60} electrochemistry. Under voltammetric conditions, electrode reactions of several redox organic compounds are mediated by the solid C_{60} film coats.²⁴

Direct electroreduction of α,ω -diiodoalkanes is irreversible and yields linear and cyclic alkanes.³³ Similarly, indirect, i.e., catalyzed, reduction of halogenated hydrocarbons also produces hydrocarbons.³⁴⁻³⁶ Anion radicals of aromatic hydrocarbons, such as naphthalene, anthracene, or pyrene, can be used as catalysts for indirect reduction of halogenated hydrocarbons,

and a theoretical treatment for determination of the respective second-order rate constants has been developed.³⁷

Like anion radicals of aromatic hydrocarbons, the C_{60}^{n-} ($n = 1-3$) anion radicals have also been shown to act as redox catalysts for indirect reduction of halogenated hydrocarbons, and the second-order rate constants for electron transfer from C_{60}^{n-} anions to electron-deficient bromohydrocarbons were determined.¹⁷ Also, preparative-scale electrolysis followed by product analysis of *vic*-dihalides and perfluoroalkyl halides using a C_{60}^{n-} catalyst was reported.¹⁸ Recently, we reported on electrocatalytic reduction of 1,2-dihaloethanes by C_{60}^{n-} resulting in formation of ethane and monohalogenated ethyl radicals.³⁸ It appeared that dehalogenation of 1,2-dihaloethanes, catalyzed by C_{60}^{n-} ($n = 2$ and 3) rather than by alkyl addition to C_{60}^{n-} , prevailed on the voltammetry time scale.

In the present paper, we describe our systematic study involving reduction of the α,ω -diiodoalkane homologous series $\text{I}(\text{CH}_2)_m\text{I}$ ($m = 1-8$) catalyzed by the C_{60}^{n-} anions under cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry conditions. The C_{60}^{n-} ($n = 2$ and 3) anions are electrochemically generated at a platinum electrode in a benzonitrile solution and also C_{60}^{n-} ($n = 1$ and 2) at a C_{60} film-coated electrode in acetonitrile solution. In our study (i) the preference of α,ω -diiodoalkanes toward either C_{60} adduct formation or electrocatalytic reduction of α,ω -diiodoalkane is sorted out, (ii) the effect of the alkyl chain length on the second-order reaction rate constant is elucidated, (iii) mechanistic details are obtained by virtue of bulk electrolysis of C_{60} in the presence of α,ω -diiodoalkane, at different applied potentials, followed by product analysis by GC-MS and HPLC, and (iv) homogeneous catalysis in solution is compared to the heterogeneous one involving a C_{60} film-modified electrode.

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} , (+99.95%) was from BuckyUSA (Bellaire, TX). All α,ω -diiodoalkanes, i.e., 1,2-

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diiodoethane, 1,3-diiodopropane, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, and 1,8-diiodooctane, as well as tetrabutylammonium hexafluorophosphate, (TBA)PF₆, (98%), and anhydrous benzonitrile (99+%, water <0.005%) were from Aldrich Chemicals (Milwaukee, WI). All chemicals were used as received.

Instrumentation. Both cyclic and differential pulse voltammetry (DPV) experiments were performed by using a Model 263A potentiostat/galvanostat of EG&G Princeton Applied Research (Princeton, NJ) and a typical three-electrode electrochemical cell. A 1.6 mm diameter disk platinum electrode of Bioanalytical Systems (West Lafayette, IN) was used as the working electrode, while a platinum wire and sodium chloride-saturated Ag/AgCl electrode served as the auxiliary and reference ones, respectively. A C₆₀ film-coated Pt electrode was prepared according to the procedure described earlier.²⁴ Voltammetry at the rotating disk electrode was carried out by using a Model AFCB1 bipotentiostat, a MSRX speed control unit, and a AFMSRX modulated speed rotator of Pine Instrument Co. (Grove City, PA). The diameter of the rotating platinum electrode was 4.6 mm. Bulk electrolyses of ca. 0.2 mM C₆₀ and 0.1 M (TBA)PF₆ in benzonitrile solutions in the presence of α,ω -diiodoalkanes were carried out by using an EG&G Model 377A coulometry cell. All potentials cited are against the Ag/AgCl reference electrode. All electrochemical experiments were performed at ambient temperature, 20 \pm 1 $^{\circ}$ C, in dark in order to avoid decomposition of α,ω -diiodoalkanes. Solutions were deaerated prior to experiments by N₂ purge.

The GC analysis of the bulk electrolyses products was performed by using a Model 5890A gas chromatograph equipped with a Model 7673A automatic injector and an FID detector of Hewlett-Packard on a SPB-5 nonpolar phase fused silica capillary column (30 m \times 0.53 mm) of Supelco (Bellefonte, PA). The GC-MS analysis was carried out by using a Model Q-Mass 910 of Perkin-Elmer Co. (Norwalk, CT) on a DB-1 nonpolar phase fused silica capillary column (30 m \times 0.253 mm) operating in an electron ionization mode.

The HPLC analysis of the bulk electrolyses products was performed by using an isocratic chromatograph of Perkin-Elmer consisting of a Model 250 binary pump and a LC-290 UV-vis spectrophotometric detector set at 340 nm. Analytical Cosmosil Buckyprep column (250 mm \times 4.6 mm) of Nacalai Tesque (Kyoto, Japan) was used with toluene as a mobile phase of the 1 mL min⁻¹ flow rate.

Results and Discussion

Electrocatalytic reduction of α,ω -diiodoalkanes was investigated by using the C₆₀ⁿ⁻ anions generated electrochemically in solution and also in a C₆₀ solid film-coated electrode, and these homogeneous and heterogeneous electrocatalyses are separately presented and then compared in the sections below.

Electrocatalytic Reduction of α,ω -Diiodoalkanes in Solution. The studied systems were characterized qualitatively by CV and quantitatively by the RDE voltammetry. This technique selection was made because RDE voltammetry, a steady-state technique, is more accurate than transient CV in discriminating background currents of irreversible electroreduction of α,ω -diiodoalkanes observed in the absence of C₆₀.

In the presence of the α,ω -diiodoalkane in the benzonitrile solution of C₆₀, the second, the third, or both the second and the third CV electroreduction peaks of the C₆₀ⁿ⁻⁽ⁿ⁺¹⁾⁻ redox couples are increased, compared to the peaks observed in the absence of the α,ω -diiodoalkane, and moreover, the correspond-

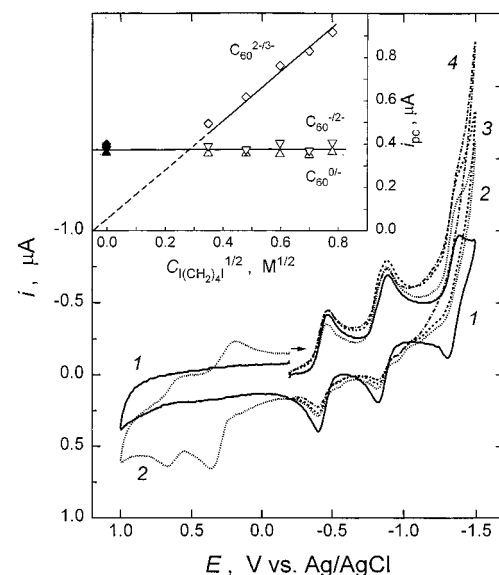


Figure 1. Cyclic voltammograms for 0.15 mM C₆₀ and (1) 0, (2) 0.24, (3) 0.36, and (4) 0.60 M 1,4-diiodobutane in 0.1 M (TBA)PF₆ in benzonitrile. The potential scan rate is 0.1 V s⁻¹. Inset is the peak potential dependence on the square root of the 1,4-diiodobutane concentration for the first three C₆₀ⁿ⁻⁽ⁿ⁺¹⁾⁻ electroreductions.

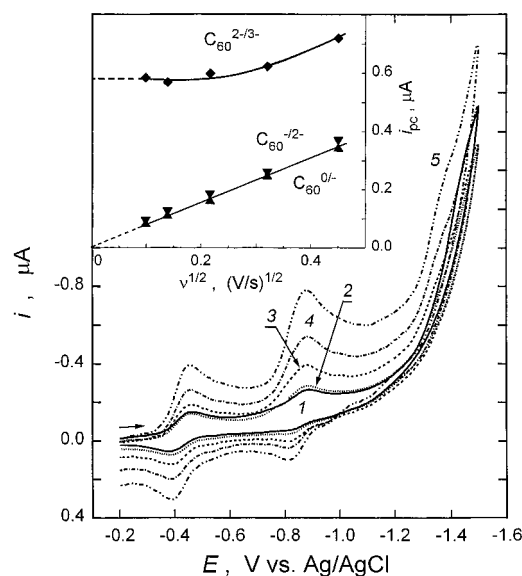


Figure 2. Cyclic voltammograms for 0.15 mM C₆₀ and 0.6 M 1,4-diiodobutane in 0.1 M (TBA)PF₆ in benzonitrile at (1) 0.01, (2) 0.02, (3) 0.05, (4) 0.1, and (5) 0.2 mV s⁻¹. Inset is the peak potential dependence on the square root of the potential scan rate for the first three C₆₀ⁿ⁻⁽ⁿ⁺¹⁾⁻ electroreductions.

ing electro-oxidation peaks are gone. By way of example, Figure 1 illustrates such a behavior, for $n = 1$ to 3, for different concentrations of 1,4-diiodobutane in 0.1 mM C₆₀ and 0.1 M (TBA)PF₆ in benzonitrile. For the third, C₆₀^{2-/3-} couple, the limiting current step is developed instead of a peak. This step increases linearly with the square root of the 1,4-diiodobutane concentration (inset in Figure 1). Also, it is proportional to the C₆₀ concentration at constant 1,4-diiodobutane concentration (not shown). In an excess of 1,4-diiodobutane, i.e., under pseudo-first-order conditions with respect to 1,4-diiodobutane, this current step is potential scan rate independent from 0.01 to 0.2 V s⁻¹ (Figure 2). This behavior indicates that reduction of 1,4-diiodobutane is catalyzed by the C₆₀^{2-/3-} couple. Noticeably, the peak currents of the first two C₆₀ⁿ⁻⁽ⁿ⁺¹⁾⁻ electroreductions linearly increase with the square root of both the

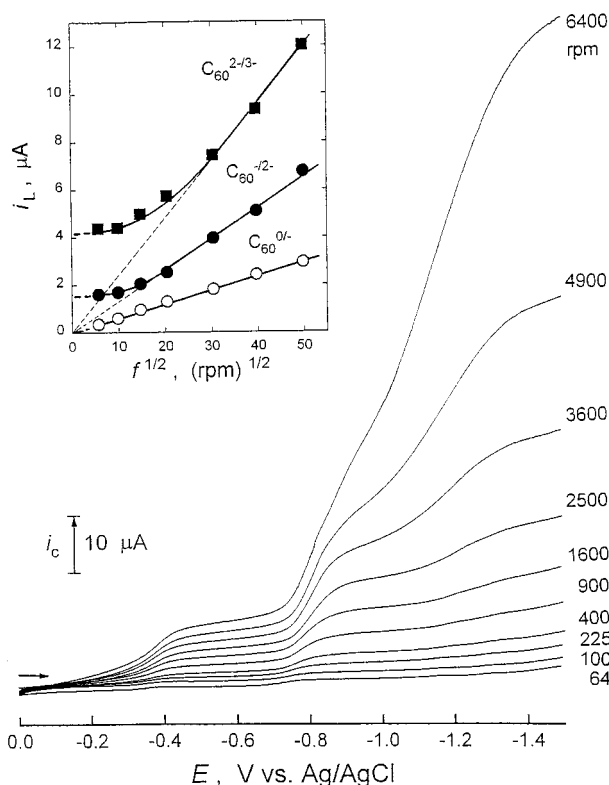


Figure 3. Rotating disk electrode voltammetry curves for 0.1 mM C_{60} and 0.8 mM 1,6-diiodohexane in 0.1 M (TBA)PF₆ in benzonitrile for different rotation rates indicated at each curve. Inset is the dependence of the limiting current i_L on the square root of the rotation rate for the first three $C_{60}^{n-/(n+1)-}$ electroreductions.

1,4-diiodobutane concentration and the potential scan rate (insets in Figures 1 and 2). This indicates that they remain under diffusion control under these solution conditions. Furthermore, when 1,4-diiodobutane is added to the C_{60} solution, two new pairs of electro-oxidation and electroreduction peaks appear (curve 2 in Figure 1) during subsequent cycling over the positive potential range that followed the initial electroreduction cycling. Formal redox potentials of these peak pairs are located at about 0.19 and 0.64 V. Apparently, iodide is released during the initial electroreduction cycle, and hence, the former peak pair corresponds to the irreversible I^-/I_3^- couple and the latter to the quasi reversible I_3^-/I_2 couple.³⁹

The values of the second-order rate constant, k , of the electrocatalytic reduction of α,ω -diiodoalkanes catalyzed by the C_{60}^{n-} ($n = 2$ and 3) anions were determined by using the RDE voltammetry. Figure 3 shows respective RDE voltammograms for the first three $C_{60}^{n-/(n+1)-}$ electroreductions in the presence of 1,4-diiodobutane for different rotation rates. The limiting current plateaus are well defined for all three electroreductions. For the excess of 1,4-diiodobutane with respect to C_{60} , i.e., under pseudo-first-order conditions with respect to 1,4-diiodobutane, k is given by⁴⁰

$$k = \frac{i_{\text{cat}}^2}{(nFAC_R)^2 D_R C_S} \quad (1)$$

where i_{cat} is the catalytic limiting current, D_R and C_R are the diffusion coefficient and concentration of C_{60} , respectively, C_S is the concentration of the substrate, i.e., α,ω -diiodoalkane, F is the Faraday constant, n is the number of electrons transferred, and A is the electrode surface area. The values of i_{cat} were determined by extrapolating the curves of limiting currents i_L

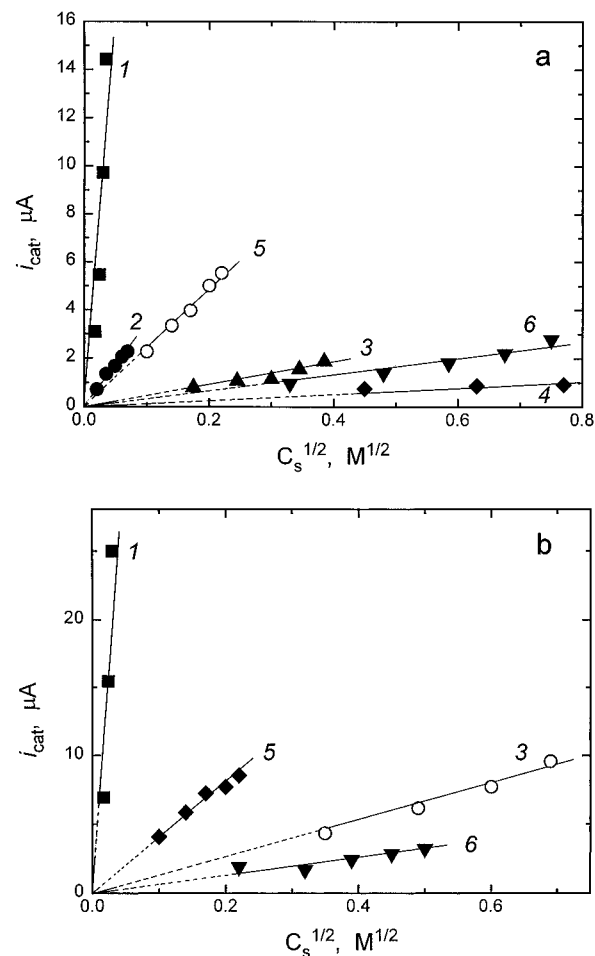


Figure 4. Dependence of the rotation rate independent RDE voltammetry catalytic currents i_{cat} on the square root of the concentration of (1) 1,2-diiodoethane, (2) 1,3-diiodopropane, (3) 1,4-diiodobutane, (4) 1,5-diiodopentane, (5) 1,6-diiodohexane, and (6) 1,8-diiodooctane for (a) $C_{60}^{-/2-}$ and (b) $C_{60}^{2-/3-}$ electroreduction in 0.1 mM C_{60} and 0.1 M (TBA)PF₆ in benzonitrile.

vs the square root of the rotation rate to the zero abscissa (inset in Figure 3). For small rotation rates, these curves deviate positively from the linear Levich plots of i_L vs the square root of the rotation rate revealed in the absence of 1,4-diiodobutane (dash lines in the inset in Figure 3). The Levich behavior is also observed for large rotation rates (inset in Figure 3). That is, the dependencies of i_L vs the square root of the rotation rate are linear for large rotation rates and the slopes increase as 1:2:3 for the three consecutive $C_{60}^{n-/(n+1)-}$ electroreductions, as expected. Note that catalytic RDE currents both for the $C_{60}^{-/2-}$ and $C_{60}^{2-/3-}$ couple were obtained for larger concentrations of 1,4-diiodobutane than that used for CV experiments.

Parts a and b of Figure 4 show the dependence of i_{cat} on the square root of C_S for the second and the third $C_{60}^{n-/(n+1)-}$ electroreduction, respectively, for different α,ω -diiodoalkanes. Straight lines with zero plot intercepts are obtained, indicating that the pseudo-first-order conditions are met. The k values calculated from the slopes of the lines by using eq 1 are presented in Table 1. Generally, the electrocatalysis rates for the $C_{60}^{2-/3-}$ mediating couple are larger by 1 order of magnitude than those for the $C_{60}^{-/2-}$ couple. In any case, we did not observe electrocatalysis for the first, $C_{60}^{0/-}$, electroreduction. The determined k values increase in the order $C_5 < C_8 < C_4 < C_3 < C_6 < C_2$ for the number of carbon atoms of the alkyl chain of the α,ω -diiodoalkanes. The k values for reduction of 1,3-diiodopropane and 1,5-diiodopentane catalyzed by the

TABLE 1: Second-Order Rate Constant k for Electrocatalytic Reduction of α,ω -Dihaloalkanes by C_{60}^{n-} ($n = 2$ and 3) Anions Determined by Voltammetry at the Rotating Disk Electrode; 0.1 M (TBA)PF₆ in Benzonitrile

α,ω -dihaloalkane	$k, M^{-1} s^{-1}$			ref
	C_{60}^{2-}	C_{60}^{2-}	C_{60}^{3-}	
1,2-diiodoethane	$(2.8 \pm 0.1) \times 10^5$	$(9.4 \pm 0.2) \times 10^5$	38	
1,3-diiodopropane	$(2.2 \pm 0.1) \times 10^2$	<i>a</i>	this work	
1,4-diiodobutane	$(1.5 \pm 0.1) \times 10$	$(1.5 \pm 0.1) \times 10^2$	this work	
1,5-diiodopentane	1.7 ± 0.1	<i>a</i>	this work	
1,6-diiodohexane	$(3.2 \pm 0.2) \times 10^2$	$(4.9 \pm 0.1) \times 10^2$	this work	
1,8-diiodooctane	9.4 ± 0.1	6.1 ± 0.1	this work	
1,2-dichloroethane	35.1 ± 0.2	$(5.5 \pm 0.2) \times 10$	38	
1,2-dibromoethane	$(1.6 \pm 0.1) \times 10^2$	$(3.2 \pm 0.2) \times 10^2$	38	

^a Alkane addition to C_{60}^{3-} competes.

$C_{60}^{2-/-3-}$ couple (Table 1) could not be measured owing to extensive formation of C_{60} adducts (vide infra).

Electrocatalytic Reduction of α,ω -Diiodoalkanes at a C_{60} Film-Modified Electrode. Electrocatalysis at electrodes modified with a catalyst is an area of active research.⁴¹ However, no electrocatalysis at a C_{60} -modified electrode has been reported to date, although the electrochemical behavior of the fullerene film-modified electrodes has been extensively characterized in nonaqueous solvent systems.¹ In acetonitrile solution, the C_{60} film is insoluble under CV conditions for the potential range corresponding to the first two $C_{60}^{n-/(n+1)-}$ electroreductions. For charge compensation, a counteranion must enter the film in order that the C_{60} solid be electroreduced. Many different counteranions were examined, and TBA⁺ was found to perform almost reversibly with respect to its ingress and egress to the C_{60} film during repeatable CV electroreduction and electro-oxidation. Herein, we have attempted electrocatalytic study at a C_{60} film-modified electrode in relation to the presently investigated solution electrocatalytic systems.

The C_{60} film-modified electrodes were prepared by consecutive evaporation of several 10 μ L drops of dichloromethane solution of C_{60} repeatedly dispensed on a platinum electrode surface. Fast evaporation of dichloromethane with the use of a hot air gun resulted in microcrystalline C_{60} films. CV behavior of thick films, used in the present study, was much more reproducible than that of the thin films, as reported earlier.²⁴

Figure 5 shows cyclic voltammograms for a C_{60} film-modified electrode in the absence and presence of 1,2-diiodoethane in 0.1 M (TBA)PF₆ in acetonitrile. In contrast to the solution CV behavior, only the first two $C_{60}^{n-/(n+1)-}$ electroreductions could be examined. This is because the film dissolves if the negative potential reversal is extended beyond the third, $C_{60}^{2-/3-}$, electroreduction. For the first, $C_{60}^{0/-}$, electroreduction, potential splitting of the electroreduction and electro-oxidation peak is large, the currents for the electroreduction and electro-oxidation processes are nearly equal, and a steady-state electrochemical behavior is exhibited, even after ca. 15 potential cycles (curve 2 in Figure 5).

When 1,2-diiodoethane is added to the supporting electrolyte solution, the peak currents of both the first and the second $C_{60}^{n-/(n+1)-}$ electroreduction increase while those of the $C_{60}^{0/-2-}$ and $C_{60}^{0/-}$ electro-oxidation peaks decrease and increase, respectively (curve 4 in Figure 5). After subsequent potential cycling over the positive potential range, a new electro-oxidation peak is seen (curve 4 in Figure 5) at about 0.5 V. Similarly as for the solution CV, this peak is ascribed to electro-oxidation of iodide released during the preceding electroreduction cycle. The peak is ill-defined most likely because of a significant ohmic potential loss across the film due to high resistance of the C_{60} film.^{10,11} Importantly, the 1,2-diiodoethane reduction is cata-

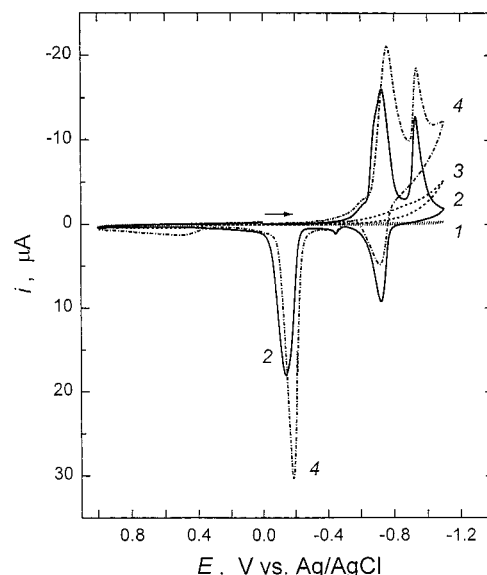


Figure 5. Cyclic voltammetry curves at a bare (curve 1) and C_{60} film-coated Pt electrode (curves 2–4) in the absence of 1,2-diiodoethane (curves 1 and 2) and 4 mM 1,2-diiodoethane (curves 3 and 4), in 0.1 M (TBA)PF₆ in acetonitrile. The potential scan rate is 0.1 V s⁻¹.

lyzed by both the first and second $C_{60}^{n-/(n+1)-}$ electroreduction at the film electrode. In this respect, the film CV differs from the solution CV where the second and the third $C_{60}^{n-/(n+1)-}$ electroreduction is involved in the electrocatalysis. Noticeably, the peak potentials of the first and second $C_{60}^{n-/(n+1)-}$ electroreduction for the C_{60} film electrode are negatively shifted by ca. 30–40 mV in the presence of 1,2-diiodoethane, compared to the peak potentials for the blank solution. Such a negative shift could originate from the formation of a C_{60} adduct at the electrode surface. To verify this hypothesis, a multicyclic voltammetry experiment at the C_{60} film electrode was performed in the presence of 1,2-diiodoethane. After 25 cycles, the electrode was removed from the solution, rinsed with acetonitrile, dried, and dissolved in a drop of toluene. The resulting solution was analyzed by HPLC. Surprisingly, no other peaks were observed in the chromatogram (not shown) except that corresponding to C_{60} , indicating thus the absence of C_{60} adducts. Hence, one may speculate that the negative shift of the electroreduction peaks is due to either reorganization of the film or some other phenomenon of unknown origin at this point. Therefore, no attempt was made to determine catalytic rate constants of the 1,2-diiodoethane reduction.

Electrocatalytic Reduction of α,ω -Diiodoalkanes versus Formation of C_{60} Adducts. The results of our investigations performed so far have shown that C_{60}^{n-} anions electrocatalytically reduce α,ω -diiodoalkanes both in solution and at a C_{60} film-modified electrode. Our earlier study involving 1,2-dihaloethanes has also demonstrated electrocatalytic dehalogenation.³⁸ This behavior is in contrast to that of chemically or electrochemically generated dianions and trianions of C_{60} in the presence of n -iodoalkanes that results in the C_{60} adduct formation.^{13,14} These results led us to conclude that electrocatalytic deiodation resulting in alkanes rather than C_{60} adduct formation is favored for α,ω -diiodoalkanes. For better understanding of the mechanistic details of these two different reaction routes, we analyzed the products of bulk electrolyses at constant potentials of α,ω -diiodoalkanes in the presence of C_{60} by both GC–MS and HPLC. In independent experiments, both the dianion and trianion of C_{60} were electrochemically generated in a benzonitrile solution of the α,ω -diiodoalkane. For the 1,2-

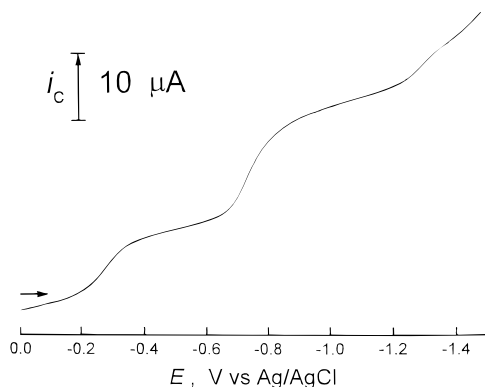


Figure 6. Rotating disk electrode voltammetry curve for 0.1 mM C_{60} in 0.2 M 1,5-diiodopentane and 0.1 M (TBA)PF₆ in benzonitrile. Rotation rate is 4900 rpm.

diiodoethane substrate, ethane and ethylene are the major electrolysis products. However, for the longer alkyl chain α,ω -diiodoalkane, initially, monoiodoalkanes are the main reaction products. Moreover, prolonged electrolysis of C_{60} in the presence of a large excess of α,ω -diiodoalkanes at potentials more negative than C_{60}^{-2-} or $C_{60}^{2-/3-}$ results in small amounts of C_{60} alkyl adducts. This is manifested by new one-electron reversible DPV peaks at potentials more negative by ca. 100 mV than those corresponding to the $C_{60}^{n-(n+1)-}$ electroreductions and new peaks of retention time smaller than that of the C_{60} peak in the HPLC chromatogram. Formation of monoiodoalkanes is indicative of stepwise elimination of iodides, resulting eventually in the corresponding alkanes.

Interestingly, the C_{60}^{n-} anions, depending on the alkyl chain length of the α,ω -diiodoalkane, show a certain selectivity toward electrocatalytic alkane formation or C_{60} adduct formation. Although C_{60}^{-} is not reactive in terms of either adduct formation or electrocatalysis in solution, both C_{60}^{2-} and C_{60}^{3-} exhibit some selectivity in this respect. That is, C_{60}^{2-} , electrocatalytically reduces both 1,3-diiodopropane and 1,5-diiodopentane. Accordingly, enhanced current plateaus are observed for the C_{60}^{2-} electroreductions, compared to those observed in the absence of the α,ω -diiodoalkane. However, the current plateaus corresponding to the $C_{60}^{2-/3-}$ electroreduction are diminished, being nearly 40% smaller than that for the $C_{60}^{0/-}$ electroreduction. These results, illustrated for 1,5-diiodopentane in Figure 6, indicate presumably that the addition route prevails over the electrocatalysis route. Bulk electrolysis of C_{60} in the presence of either 1,3-diiodopropane or 1,5-diiodopentane at -1.6 V, i.e., at the potential at which C_{60}^{3-} is generated in solution, revealed extensive C_{60} adduct formation. Similar electrolyses performed at -1.2 V, i.e., at the potential at which C_{60}^{2-} is produced, in the presence of each of these α,ω -diiodoalkanes resulted in much less extensive adduct formation. The reason for this unique electrochemical behavior of C_{60} in the presence of 1,3-diiodopropane or 1,5-diiodopentane is not clear. One can speculate that such a behavior, which bares further scrutiny, can be attributed to the stability of the intermediate monoiodoalkyl products or monoalkylated C_{60} adducts.

Conclusions

Reduction of a homologous series of α,ω -diiodoalkanes $I(CH_2)_mI$ ($m = 1-8$) at a platinum working electrode is catalyzed by the C_{60}^{n-} ($n = 2$ and 3) anions in 0.1 M (TBA)-PF₆ in benzonitrile, while this reduction is catalyzed by the C_{60}^{n-} ($n = 1$ and 2) anions at a C_{60} film-modified electrode in 0.1 M (TBA)PF₆ in acetonitrile. For solution electrocatalysis, the

second-order catalytic rate constants, determined by RDE voltammetry under pseudo-first-order conditions, follow the trend $C_5 < C_8 < C_4 < C_3 < C_6 \ll C_2$ for the number of carbon atoms of the alkyl chain of the α,ω -diiodoalkanes. The GC-MS and HPLC analyses of the reaction products, obtained by bulk electrolyses, revealed formation of alkanes, alkenes, and monoiodoalkanes for the investigated series of α,ω -diiodoalkanes except for the reaction of C_{60}^{3-} with either 1,3-diiodopropane or 1,5-diiodopentane where C_{60} adduct formation is favored.

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