

Catalytic Reduction of α,ω -Dihaloalkanes, $X(\text{CH}_2)_mX$ ($X = \text{Cl}, \text{Br}, \text{or I}$ and $m = 2-8$), by Electrochemically Generated C_{70}^{n-} ($n = 2$ or 3) in Benzonitrile Solutions

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The first report on the homogeneous electrocatalytic reduction of halogenated alkanes by C_{70} anions is presented. Cyclic voltammetry (CV) measurements indicate that C_{70}^{n-} ($n = 2$ or 3), electrochemically generated in 0.1 M (TBA)PF₆, benzonitrile, catalyzes the dehalogenation of α,ω -dihaloalkanes, $X(\text{CH}_2)_mX$ ($X = \text{Cl}, \text{Br}, \text{or I}$ and $m = 2-8$). Values of the second-order rate constant, k , for the electrocatalytic dehalogenation of the α,ω -dihaloalkanes by the C_{70}^{n-} anions were determined by using the rotating-disk electrode (RDE) voltammetry under pseudo-first-order conditions with respect to the α,ω -dihaloalkanes. In accordance with Savéant's theory of dissociative reduction, the k values increase in the order $\text{Cl} < \text{Br} < \text{I}$ for the investigated 1,2-dihaloethanes. The k values also decrease with the number of carbon atoms of the alkyl chain for the investigated series of α,ω -diiodoalkanes. The calculated k values for the C_{70}^{n-} ($n = 2$ or 3) catalysts are generally smaller than those for the C_{60}^{n-} ($n = 2$ or 3) catalysts. Unlike the C_{60}^{n-} electrocatalysis, reported earlier to be accompanied by a chemical reaction between C_{60}^{n-} and certain α,ω -diiodoalkanes yielding alkyl adducts of C_{60} , no reaction between C_{70}^{n-} ($n = 2$ or 3) and the α,ω -diiodoalkanes leading to alkylated C_{70} was observed on the voltammetry time scale.

Introduction

Since the first report on electrochemical behavior of C_{60} in 1990,¹ several laboratories have contributed to the research on fundamental and application aspects of the fullerene and fullerene derivative electrochemistry.² Now, it is well documented that both C_{60} and C_{70} are electroreduced by six one-electron reversible steps in nonaqueous solvent solutions,³⁻⁶ in agreement with quantum chemistry calculations.⁷⁻¹⁰ Owing to the high stability of the resulting C_{60} and C_{70} anions electrochemically generated in deaerated aprotic solvent solutions as well as a large and nearly equal spacing of the formal redox potentials of the consecutive electrode redox processes,¹¹⁻¹⁴ the anions of both fullerenes are promising as selective intermolecular electron-transfer catalysts. Accordingly, Huang and Wayner¹⁵ reported on the electrocatalytic debromination of alkyl bromides and vicinal dibromides by mono-, di-, and trianions of C_{60} . Also, preparative-scale electrolysis, followed by product analysis, of *vic*-dihalides and perfluoroalkyl halides performed by using the C_{60}^{n-} catalysts was reported by Fuchigami et al.¹⁶ Recently, in our systematic study of electrocatalytic reduction of α,ω -diiodoalkanes, $\text{I}(\text{CH}_2)_m\text{I}$ ($m = 2-8$), by the C_{60} anions electrochemically generated in nonaqueous solvent solutions as well as in the C_{60} film-modified electrodes, we demonstrated that the C_{60} anions electrocatalytically deiodinate α,ω -diiodoalkanes.¹⁷ This dehalogenation results in the formation of a range of alkanes, alkenes, and monoiodoalkane derivatives as the reaction products. A competing alkylation involving C_{60} anions and certain α,ω -diiodoalkanes was also observed. Presumably, this is why no systematic trend of changes was found in the determined apparent second-order rate constants

against the alkyl chain length of the α,ω -diiodoalkanes.¹⁷ Importantly, C_{60}^{n-} ($n = 2$ or 3) reacts with *n*-iodoalkanes, yielding a range of alkyl adducts of C_{60} .¹⁸⁻²¹

Although the electrocatalytic properties of C_{60} are now largely revealed,¹⁵⁻¹⁷ no electrocatalytic activity of higher fullerenes has been reported to date. Study of electrocatalytic behavior of higher fullerenes, in comparison to that of C_{60} , is important for the understanding of fullerene reactivity. In the present paper, we report on our cyclic voltammetry (CV) and rotating-disk electrode (RDE) voltammetry study involving electrocatalytic dehalogenation of α,ω -dihaloalkanes in a benzonitrile solution by electrochemically generated di- and trianions of C_{70} . Also, we examine the dependence of the apparent second-order rate constant values, determined by the RDE voltammetry, on the nature of the halogen of the 1,2-dihaloethane as well as on the alkyl chain length of the employed α,ω -diiodoalkanes.

Experimental Section

Chemicals. C_{70} (+99.8% purity by HPLC) was from BuckyUSA (Bellaire, TX). All α,ω -diiodoalkanes, i.e., 1,2-diiodoethane, 1,3-diiodopropane, 1,4-diiodobutane, 1,5-diiodopentane, 1,6-diiodohexane, and 1,8-diiodooctane, as well as 1,2-dichloroethane, 1,2-dibromoethane, tetra-*n*-butylammonium hexafluorophosphate, (TBA)PF₆ (98% purity), and anhydrous benzonitrile (+99% purity, water content < 0.005%) were from Aldrich Chemicals (Milwaukee, WI). All chemicals were used without further purification.

Instrumentation. The CV 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

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chloride saturated Ag/AgCl electrode served as the auxiliary and reference electrode, respectively. The RDE voltammetry experiments were carried out by using a model AFCB1 bipotentiostat, MSRX speed control unit, and 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 about 0.2 mM C_{70} , 0.1 M (TBA)PF₆ in benzonitrile solutions containing 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 experiments were performed at ambient temperature, 20 ± 1 °C, in the dark in order to avoid decomposition of the α,ω -diiodoalkanes. Solutions were deaerated by N₂ purge prior to experiments.

The GC analysis of the bulk electrolysis 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 (Bellofonte, 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 electrolysis products, performed in order to check if any alkyl adducts of C_{70} were formed, was carried out by using an isocratic chromatograph of Perkin-Elmer consisting of a model 250 binary pump and a LC-290 UV-visible spectrophotometric detector set at 340 nm. An analytical Cosmosil Buckyprep column (250 mm \times 4.6 mm) of Nacalai Tesque (Kyoto, Japan) was used with toluene as a mobile phase with a flow rate of 1 mL min⁻¹.

Results and Discussion

Electrocatalytic properties of the $C_{70}^{n-(n+1)-}$ ($n = 0-2$) redox couples with respect to α,ω -diiodoalkanes were qualitatively examined by using CV. Quantitative results, however, were obtained by using the RDE voltammetry because (i) the background currents of the irreversible electroreduction of the α,ω -dihaloalkanes observed in the absence of C_{70} are better discriminated than those measured with CV, and (ii) in contrast to CV, the RDE voltammetry current of the electrocatalytic process corresponding to each $C_{70}^{n-(n+1)-}$ couple is virtually free from the influence of any electrochemical process that would proceed at more positive potentials, since fresh solution containing C_{70} and the substrate is supplied from the bulk solution by forced convection to the electrode surface during the potential scan.

Cyclic Voltammetry. In 0.1 M (TBA)PF₆, benzonitrile, there are four reversible $C_{70}^{n-(n+1)-}$ electroreduction/electro-oxidation peak pairs in the cyclic voltammogram of C_{70} within the accessible potential window of the solvent.¹² Addition of the 1,2-dihaloethanes to the solution has no effect on the $C_{70}^{0/-}$ electroreduction peak (Figure 1). However, the $C_{70}^{-/2-}$ electroreduction peak is increased and the corresponding electro-oxidation peak is gone. Noticeably, the $C_{70}^{-/2-}$ electroreduction peak current markedly increases in the order Cl < Br < I for 1,2-dihaloethanes of the same concentrations. Moreover, there are new CV peaks in the positive potential range produced during the anodic scan that follows the initial cathodic one. Accordingly, in the presence of 1,2-diiodoethane, two new pairs of electro-oxidation and electroreduction peaks are seen during subsequent cycling over the positive potential range (curve 4 in Figure 1). They correspond to the irreversible I^-/I_3^- and quasi-reversible I_3^-/I_2 redox couples, respectively.²² Similarly,

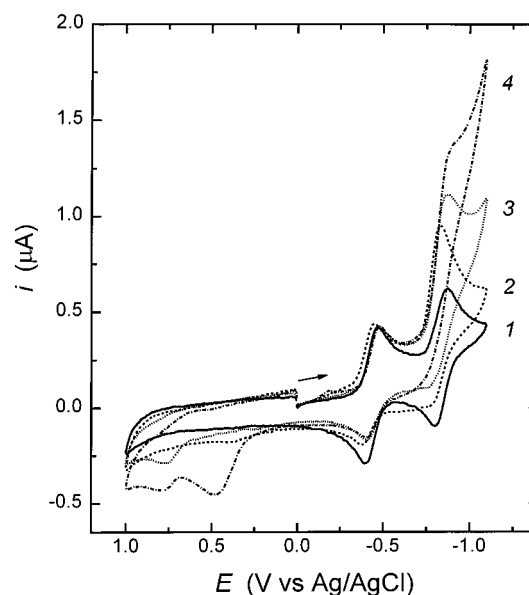


Figure 1. Cyclic voltammograms for 0.1 mM C_{70} (curve 1), 0.1 mM C_{70} and 0.4 M 1,2-dichloroethane (curve 2), 0.1 mM C_{70} and 0.4 M 1,2-dibromoethane (curve 3), as well as 0.1 mM C_{70} and 1.4 M 1,2-diiodoethane (curve 4) in 0.1 M (TBA)PF₆ in benzonitrile, at a Pt electrode. Potential scan rate is 0.1 V s⁻¹.

new electro-oxidation peaks are observed (curves 2 and 3 in Figure 1) in the presence of 1,2-dibromoethane and 1,2-dichloroethane that correspond to the irreversible Br^-/Br_2 and Cl^-/Cl_2 electro-oxidation, respectively.²² These CV results indicate that 1,2-dihaloethanes are reduced and halogens are released in the solution during the initial $C_{70}^{-/2-}$ electro-reduction. Importantly, no additional peaks were observed if reversal of the cathodic scan of potential was set at a value less negative than that of the formal redox potential of the $C_{70}^{-/2-}$ couple. Similar voltammetric behavior is observed for all other α,ω -diiodoalkanes studied.

By holding for about 30 s the potential at -1.2 V, i.e., at a value more negative than the $C_{70}^{-/2-}$ electroreduction peak potential and subsequent potential cycling over the $C_{70}^{n-(n+1)-}$ redox couples, we found no new peaks in the voltammograms. Hence, we conclude that no alkyl adducts of C_{70} are formed on the CV experiment time scale.²⁰

Importantly, a step rather than a peak is observed for the $C_{70}^{-/2-}$ electroreduction in excess of the 1,2-diiodoalkane (Figure 2) and the limiting current of this step is proportional to the square root of the 1,2-diiodoalkane concentration (inset in Figure 2). Moreover, the limiting current of this step is virtually independent of the potential scan rate (Figure 3). This is in contrast to the behavior of the $C_{70}^{0/-}$ electroreduction peak current, which is proportional to the square root of the potential scan rate, as expected for a peak whose current is controlled by diffusion (inset in Figure 3). Collectively, the CV results indicate that the $C_{70}^{-/2-}$ redox couple electrocatalytically reduces α,ω -dihaloalkanes and that the $C_{70}^{0/-}$ couple is electrocatalytically inactive. Similar but more pronounced catalytic currents (not shown) are observed for the $C_{70}^{2-/3-}$ redox couple, indicating that the catalytic efficiency increases with an increase of the negative charge of the C_{70} anion.

Rotating-Disk Electrode Voltammetry. Four well-developed cathodic steps corresponding to the first four one-electron $C_{70}^{n-(n+1)-}$ electroreductions are present in the RDE voltammograms of C_{70} in 0.1 M (TBA)PF₆, benzonitrile, for different rotation rates. Limiting currents, i_L , of these steps are controlled by convective diffusion, as verified by the Levich analysis

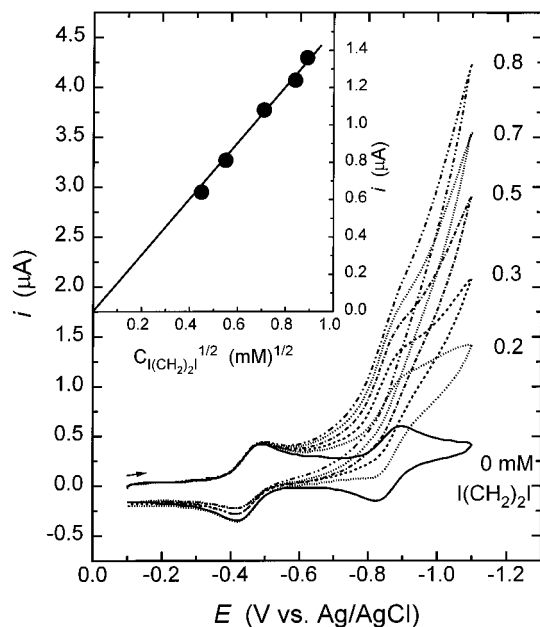


Figure 2. Cyclic voltammograms for 0.1 mM C_{70} in 0.1 M (TBA)PF₆ in benzonitrile and different concentrations of 1,2-diiodoethane indicated at each curve. Potential scan rate is 0.1 V s⁻¹. Inset is the dependence of the C_{70}^{-2-} electroreduction peak current on the square root of the 1,2-diiodoethane concentration.

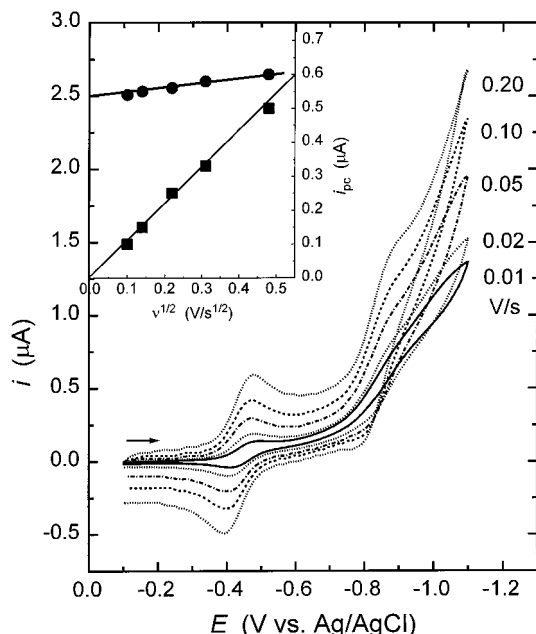


Figure 3. Cyclic voltammograms for 0.1 mM C_{70} , 0.3 mM 1,2-diiodoethane in 0.1 M (TBA)PF₆ in benzonitrile for different potential scan rates indicated at each curve. Inset is the dependence of peak currents of the C_{70}^{0-} and C_{70}^{-2-} electroreductions on the square root of the potential scan rate.

(not shown).²³ However, this is not the case for the second, C_{70}^{-2-} , and third, $C_{70}^{2-/3-}$, electroreduction in excess of the α,ω -diiodoalkane (Figure 4). That is, there are positive deviations at smaller rotation rates for the Levich plots of the limiting current versus the square root of the rotation rate, $f^{1/2}$ (inset in Figure 4), indicating that the α,ω -diiodoalkane is electrocatalytically reduced. Values of catalytic limiting current, i_{cat} , were determined by extrapolating the limiting currents to the zero value of the square root of the rotation rate (inset in Figure 4). Under pseudo-first-order conditions with respect to the α,ω -diiodoalkanes, the second-order catalytic rate constant, k , can

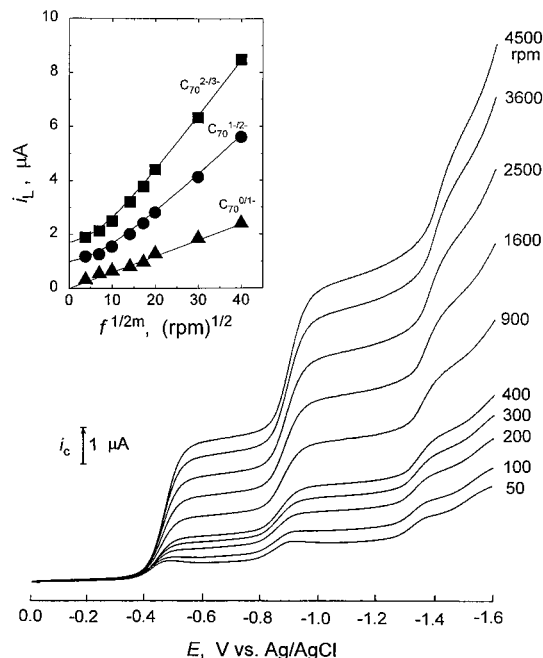


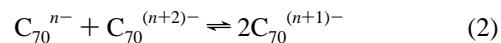
Figure 4. Rotating disk electrode voltammetry curves for 0.05 mM C_{70} , 0.05 M 1,6-diiodohexane in 0.1 M (TBA)PF₆ in benzonitrile for different rotation rates indicated at each curve. Inset is the dependence of the limiting current, i_L , on the square root of rotation rate for the first three $C_{70}^{n-(n+1)-}$ ($n = 0-2$) electroreductions.

be calculated from the determined limiting catalytic currents by using the equation²⁴

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

where D_R and C_R are the diffusion coefficient and concentration of C_{70} , 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 determined i_{cat} values are plotted against the square root of the concentration of each α,ω -diiodoalkane both for the C_{70}^{-2-} and $C_{70}^{2-/3-}$ redox couple in parts a and b of Figure 5, respectively. Noticeably, straight lines with the zero plot intercept are obtained, as eq 1 predicts. The k values calculated from the slopes of these lines by using eq 1 are presented in Table 1.

Because of the dynamic nature of both CV and RDE voltammetry, the α,ω -dihaloalkanes are reduced in the reaction layer by di- and trianions of C_{70} generated at the electrode surface. Accordingly, one would expect that concomitant comproportionation of $C_{70}^{(n+2)-}$ ($n = 0$ or 1), generated at the electrode and C_{70}^n present in bulk solution according to eq 2,



could affect the electrocatalysis. The comproportionation could deplete the $C_{70}^{(n+2)-}$ catalyst in the reaction layer, which might result in overestimation of the determined k values. Obviously, the effect of reaction 2 is more important for slow electrocatalysis, observed for α,ω -dihaloalkanes of a long alkyl chain ($m \geq 5$), than for fast electrocatalysis for α,ω -dihaloalkanes of a short alkyl chain ($m < 5$). Noticeably, the rate of the comproportionation is twice as sensitive to the change of the C_{70} concentration than that of the electrocatalysis because the former reaction is second order and the latter is first order against C_{70} . Therefore, apparent catalytic rate constants for different

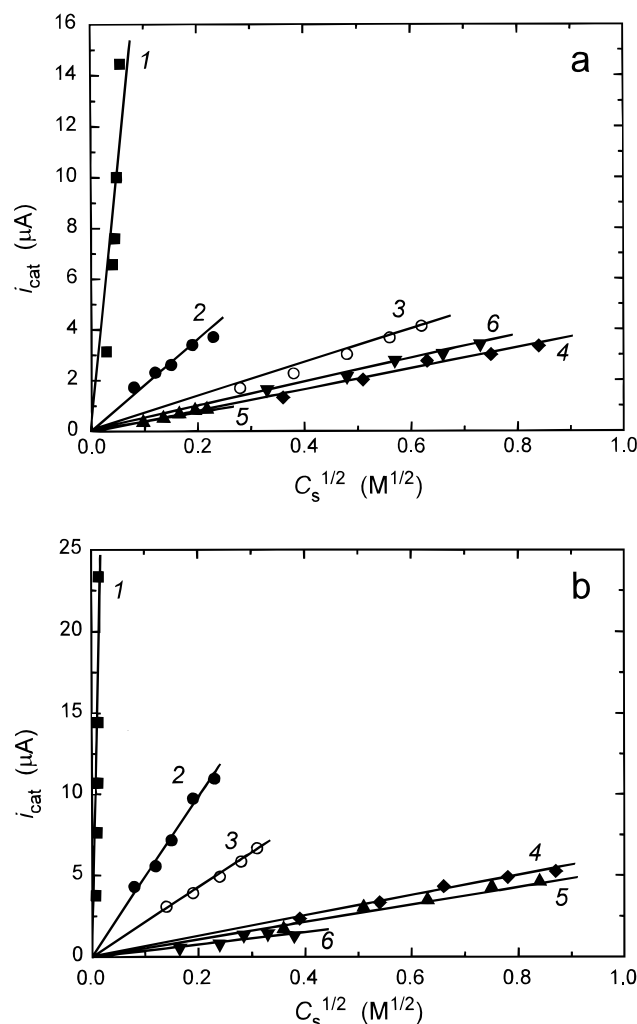


Figure 5. Dependence of the rotation-rate-independent RDE voltammetry catalytic currents, i_{cat} , on the square root of concentration of (1) 1,2-diiodoethane, (2) 1,3-diiodopropane, (3) 1,4-diiodobutane, (4) 1,5-diiodopentane, (5) 1,6-diiodohexane, and (6) 1,8-diiodooctane for the (a) C_{70}^{2-} and (b) C_{70}^{3-} electroreduction for 0.05 mM C_{70} in 0.1 M (TBA)PF₆ in benzonitrile.

TABLE 1: Second-Order Rate Constant, k , for Electrocatalytic Reduction of α,ω -Dihaloalkanes by C_{70}^{n-} ($n = 2$ or 3) Anions, Determined by Voltammetry at the Rotating Pt Disk Electrode in 0.1 M (TBA)PF₆, Benzonitrile

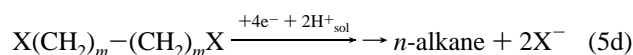
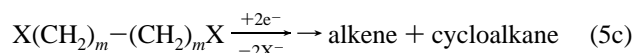
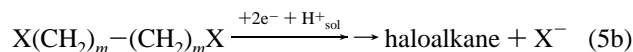
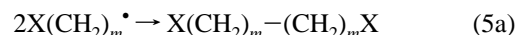
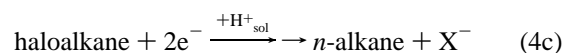
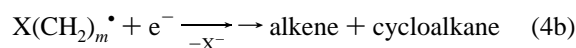
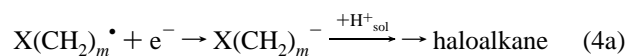
α,ω -dihaloalkane	$k, \text{M}^{-1} \text{s}^{-1}$		
	C_{70}^{2-}	C_{70}^{3-}	C_{70}^{3-}
1,2-dichloroethane	—	2.2 ± 0.1	3.3 ± 0.3
1,2-dibromoethane	—	33.0 ± 1.0	$(1.3 \pm 0.3) \times 10^2$
1,2-diiodoethane	—	$(1.1 \pm 0.1) \times 10^5$	$(5.1 \pm 0.4) \times 10^5$
1,3-diiodopropane	—	40.4 ± 0.3	$(3.6 \pm 0.1) \times 10^2$
1,4-diiodobutane	—	18.7 ± 0.9	65.1 ± 0.2
1,5-diiodopentane	—	10.2 ± 0.3	22.7 ± 0.1
1,6-diiodohexane	—	10.5 ± 0.2	21.1 ± 0.2
1,8-diiodooctane	—	11.7 ± 0.1	19.4 ± 0.8

C_{70} concentrations should be determined in order to evaluate the effect of comproportionation on electrocatalysis. Accordingly, we compared the k values for 0.05 mM C_{70} , presented in Table 1, with those for 0.5 mM C_{70} for the α,ω -dihaloalkanes of a short and long alkyl chain. The rate constants determined for 0.5 mM C_{70} were 10–15% larger than those for 0.05 mM C_{70} . Interestingly, the CV limiting catalytic currents observed in the presence of the α,ω -dihaloalkanes are virtually independent of the potential scan rate (inset in Figure 3), indicating that consumption of the $\text{C}_{70}^{(n+2)-}$ catalyst in the comproportionation reaction 2 is negligibly small. In any case, the determined rate constants for dilute solutions of the $\text{C}_{70}^{(n+2)-}$ catalysts summarized in Table 1 are not overestimated more than by 10–15%.

The calculated k values for the C_{70}^{3-} catalyst are from about 2 (for 1,2-diiodopentane, 1,2-diiodohexane, and 1,2-diiodooctane) to almost 10 (for 1,2-diiodopropane) times larger than those for the C_{70}^{2-} catalyst. The k values both for the C_{70}^{2-} and C_{70}^{3-} catalysts as well as for the C_{60}^{2-} and C_{60}^{3-} catalysts reported previously largely decrease with the increase of heat of formation of the carbon–halogen bond.^{25,26} This behavior was demonstrated in Figure 6 for 1,2-dihaloethanes for which the k values decrease in the order $\text{Cl} < \text{Br} < \text{I}$. This result may indicate that the free energy change of the carbon–halogen bond rupture largely contributes to the activation energy change of the 1,2-dihaloethane reduction. Apparently, the C_{60}^{2-} and C_{60}^{3-} catalysts are more efficient than the C_{70}^{2-} and C_{70}^{3-} catalysts, though the former are known to form alkyl adducts (see below). Moreover, the k values for the electrocatalyses involving C_{70}^{2-} and C_{70}^{3-} , determined in the present study, largely decrease with the increase of the number of carbon atoms in the alkyl chain of the α,ω -dihaloalkanes for $m < 5$ and are virtually independent of m for $m \geq 5$ (Figure 7a). Importantly, this behavior is different from that displayed by either the C_{60}^{2-} or C_{60}^{3-} catalyst (Figure 7b) reported previously.¹⁷ That is, the k value decreases for $m \leq 5$ but there is a maximum for $m = 6$ in the $\log k$ vs m plot for both the C_{60}^{2-} and C_{60}^{3-} catalyst.

The proposed mechanism of catalytic reduction of the α,ω -dihaloethane substrates by the C_{70}^{n-} ($n = 2$ or 3) catalysts is summarized in Scheme 1.

SCHEME 1



where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ and $m = 2-8$.

Once the α,ω -dihaloalkane, $\text{X}(\text{CH}_2)_m\text{X}$, is reduced, the di- or trianion of C_{70} , which acts as a catalyst capable of transferring up to two or three electrons, respectively, repeatedly regenerates its oxidation state in the electrode vicinity provided that sufficiently negative potential is applied. This regeneration is responsible for the observed catalytic currents. The initial electron transfer to $\text{X}(\text{CH}_2)_m\text{X}$, assumed to be the rate-determining step²⁶ governed by an outer-sphere electron-transfer mechanism that was originally proposed for reduction of vicinal dibromoalkanes with aromatic anion radicals,²⁶⁻²⁸ yields a 1-halogenated alkane radical and liberates halide in the solution (eq 3). Possibly, a series of reactions can follow the formation

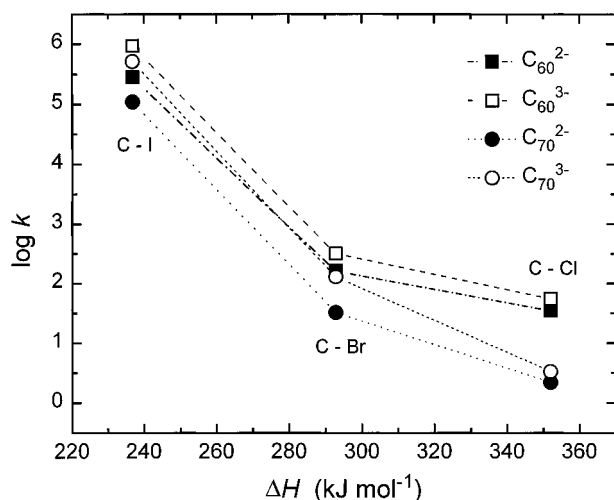


Figure 6. Semilogarithmic dependence of the second-order catalytic rate constants for the reduction of 1,2-haloethanes in 0.1 M (TBA)-PF₆, benzonitrile, by (■) C₆₀²⁻, (□) C₆₀³⁻, (●) C₇₀²⁻, and (○) C₇₀³⁻ on heat of formation of the C-X bond.

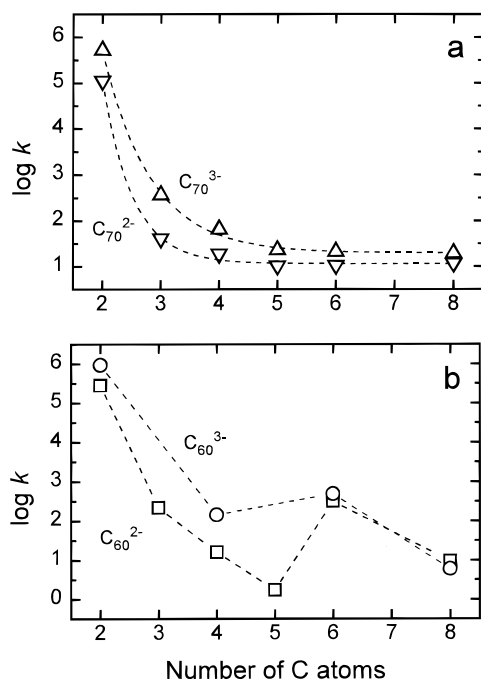


Figure 7. Semilogarithmic dependence of the second-order catalytic rate constant, k , for reduction of α,ω -diiodoalkanes on the number of carbon atoms in their alkyl chains for (a) C₇₀²⁻ and C₇₀³⁻ as well as for (b) C₆₀²⁻ and C₆₀³⁻ catalysts.

of this radical. These are presented in eqs 4 and 5 on the basis of results of the product analysis (see below). These reactions include (i) further electrocatalytic reduction of the radical species to form 1-halogenated alkyl anions followed by a proton abstraction from solvent to yield 1-haloalkanes (eq 4a), (ii) radical pairing to form higher α,ω -dihaloalkanes (eq 5a), (iii) formation of cycloalkanes or alkenes as a result of further reduction of mono-halogenated alkyl radicals in the absence of a proton supply (eq 4b), and (iv) further catalytic reduction of higher α,ω -dihaloalkanes formed in eq 4a to yield 1-haloalkanes (eq 5b), alkenes and cycloalkanes (eq 5c), or alkanes (eq 5d). A radical addition to the catalyst that would result in the C₇₀ alkyl derivatives could also occur besides the radical pairing that would lead to higher α,ω -dihaloalkanes (eq 5a). However, the C₇₀ alkyl derivatives were not detected by the HPLC analysis of the reaction product mixture (see below). This result suggests

that these radical addition reactions are less favored than the radical reduction within the voltammetry time scale.

For better understanding of the different possible reaction routes, we analyzed the products of bulk electrolyses performed at constant potentials in solutions containing C₇₀ and one of the α,ω -dihaloalkanes by both GC-MS and HPLC. That is, in independent bulk electrolysis experiments, either the dianion or trianion of C₇₀ was electrochemically generated in a benzonitrile solution of the α,ω -dihaloalkane. For the 1,2-diiodoethane substrate, ethane and ethene were the major electrolysis products. The yield of the former increased with the increase of the water content in the solvent needed as a proton supply. However, in the presence of the 1,2-dibromoethane or 1,2-dichloroethane substrate, only bromoethane or chloroethane was the major reaction product. In the case of α,ω -diiodoalkanes of the long alkyl chains ($m > 3$), the major reaction products were 1-iodoalkanes and trace amounts of alkenes. An HPLC chromatogram of the reaction product mixture obtained after bulk electrolysis revealed no new peaks that would correspond to the formation of alkyl adducts of C₇₀. This result is in contrast to our former results on the C₆₀ electrocatalytic reduction of α,ω -diiodoalkanes, where substantial amounts of alkyl adducts of C₆₀ were found both for the 1,3-diiodopropane and 1,5-diiodopentane substrates.

The results presented above indicate that the C₇₀^{*n*-} ($n = 2$ or 3) catalysts are more stable than the C₆₀^{*n*-} ($n = 2$ or 3) catalysts with respect to the alkyl adduct formation that would deplete the effective catalyst concentration in the electrode vicinity. This lack of the adduct formation could be also a reason why the determined $\log k$ decays monotonically with the number of carbon atoms of the α,ω -diiodoalkane for the C₇₀^{*n*-} catalysts (Figure 7a) and could be accounted for by only the inductive effects of the halogen substituents. Apparently, this effect is the less pronounced the longer the alkyl chain. This result is in contrast to that obtained previously¹⁷ for the C₆₀^{*n*-} catalysts where maximum in plots is seen (Figure 7b). This maximum could be due to the competing alkylation of C₆₀^{*n*-} observed for I(CH₂)_{*m*}I ($m = 3$ and 5), which would decrease the effective C₆₀^{*n*-} concentration in the reaction layer at the electrode and, hence, decrease the apparent rate of catalysis.

Conclusions

Electrocatalytic reduction of a homologous series of α,ω -dihaloalkanes, X(CH₂)_{*m*}X (X = Cl, Br, I), is catalyzed by both di- and trianions of C₇₀ in 0.1 M (TBA)PF₆, benzonitrile, at a platinum working electrode. By use of the RDE voltammetry, the second-order rate constants for electrocatalytic dehalogenation of the α,ω -dihaloalkanes by the C₇₀^{*n*-} ($n = 2$ or 3) catalysts are determined under pseudo-first-order conditions with respect to the α,ω -dihaloalkanes. The k values increase in the order Cl < Br < I for the investigated 1,2-dihaloethanes. The calculated k values for C₇₀^{*n*-} ($n = 2$ or 3) catalysts are generally smaller than those for the C₆₀^{*n*-} ($n = 2$ or 3) catalysts. For the C₇₀^{*n*-} catalysts, there are monotonic decays of $\log k$ with the number of carbon atoms of alkyl chains of the α,ω -diiodoalkanes. The GC-MS and HPLC analyses of the reaction products, obtained by the constant potential bulk electrolyses, revealed a mixture of alkanes and alkenes as major reaction products for 1,2-diiodoethane and 1,3-diiodopropane substrates while monohalogenated alkanes were major reaction products for other α,ω -dihaloalkanes. No reaction between C₇₀^{*n*-} ($n = 2$ or 3) and the α,ω -diiodoalkanes leading to alkyl adducts of C₇₀ was observed neither on the CV or RDE voltammetry time scale nor under the bulk electrolysis conditions. This is unlike

the results for the C_{60}^{n-} catalysts reported earlier,¹⁷ where corresponding electrocatalytic reductions are accompanied by chemical reaction between C_{60}^{n-} and certain α,ω -diiodoalkanes yielding alkyl adducts of C_{60} .

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