Electrocatalytic Dehalogenation of 1,2-Dihaloethanes by the C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} Fullerene Anions: Structure−Reactivity Aspects

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The homogeneous electrocatalytic reduction of 1,2-dihaloethanes by anions of larger fullerenes, C_{76}, C_{78}, and C_{84}, is presented, and structure−reactivity correlations are derived by including our data reported earlier for the C_{60} and C_{70} electrocatalytic process. Cyclic voltammetry measurements indicate that dianions of C_{76} and C_{78}, as well as trianions of C_{76}, C_{78}, and C_{84}, electrochemically generated in 0.1 M $(TBA)PF_6$, in benzonitrile, catalyze dehalogenation of 1,2-dihaloethanes. Values of the second-order rate constant, k, for the electrocatalytic dehalogenation of 1,2-dihaloethanes by the fullerene anions were determined by using the rotating-disk electrode voltammetry under pseudo-first-order conditions with respect to the 1,2-dihaloethanes. For each fullerene anion, k increases in the order: $Cl < Br < I$ for the investigated 1,2-dihaloethanes. Also, $\log k$ linearly increases in the order: $C_{84} < C_{78} < C_{76} < C_{70} < C_{60}$, as a function of respective redox potentials of the fullerene, for each 1,2-dihaloethane. Unlike the $C_{60}{}^{n-}$ electrocatalysis, reported by us earlier to be accompanied by chemical reaction between $C_{60}{}^{n-}$ and certain α,ω-diiodoalkanes yielding alkyl adducts of C_{60}, no reaction between the anions of larger fullerenes and 1,2-dihaloethanes was observed within the voltammetric time scale. Because of the high stability with respect to adduct formation and more positive potentials of the electrocatalyses, the larger fullerenes may be more useful than C_{60} as catalysts, even though the corresponding catalytic rate constants are smaller.

Introduction

Most of the effort on fullerene research has been directed to C_{60} and C_{70} because these compounds can be easily obtained in large quantities.[1] Although the importance of larger fullerenes (C_{76} to C_{120+}) has been recognized, for instance, for endohedral metalation,[1b] the literature on chemical and, particularly, on the electrochemical reactivity of these large carbon cage molecules is scarce.[1,2] This is because only minuscule amounts of larger fullerenes are available in the fullerene soot obtained from the arc-discharged graphite and, as a result, the isolation and the purification of larger fullerenes is tedious and time consuming. Among the different reactivities of fullerenes reported to date, the electrocatalytic properties of fullerenes are important because several chemical reactions can be assisted selectively by the electrode charge transfer to fullerenes.[3] Therefore, electrocatalysis is to find its recognition for the fullerene science and technology.[3−6]

Recently, we reported on the electrocatalytic dehalogenation of α,ω-dihaloalkanes by the C_{60} and C_{70} fullerene anions.[4−6] The α,ω-diiodoalkane substrates do not produce as many catalyst-disabling radicals as mono halogenated alkanes. In our studies, we demonstrated that the fullerene mediated dehalogenation of α,ω-diiodoalkanes results mainly in different alkanes, alkenes, and mono haloalkanes. In a competing reaction, alkyl adducts of C_{60} are also formed in the presence of certain α,ω-diiodoalkanes.[4,6] Advantageously, no alkyl adducts are formed in case of the C_{70} electrocatalysis on the voltammetry time scale.[5] This result suggests that the larger fullerenes may be relatively more stable with respect to derivatization and, therefore, serve as better electrocatalysts than C_{60}. In the present work, we address this issue by performing electrocatalytic study involving larger fullerenes, i.e., C_{76}, C_{78}, and C_{84}, and 1,2-dihaloethanes as substrates, and report on the structure−reactivity aspects of the electrocatalytic processes.

Experimental Section

Chemicals. C_{76} (+98% purity), isomeric mixture of C_{78} (98% purity), and isomeric mixture of C_{84} (99% purity) were procured from BuckyUSA (Bellaire, TX). All the 1,2-dihaloethanes, tetra-*n*-butylammonium hexafluorophosphate, $(TBA)PF_6$ (98% purity), and anhydrous benzonitrile (+99% purity, water content < 0.005%) were from Aldrich Chemical Co. (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 chloride saturated Ag/AgCl electrode served as the auxiliary and reference electrodes, respectively. The rotating disk electrode (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 0.05 mM fullerene, in 0.1 M $(TBA)PF_6$, in benzonitrile solutions containing 1,2-dihaloalkanes were carried out by using an EG&G Model 377A Coulometry cell. All potentials cited were measured against the

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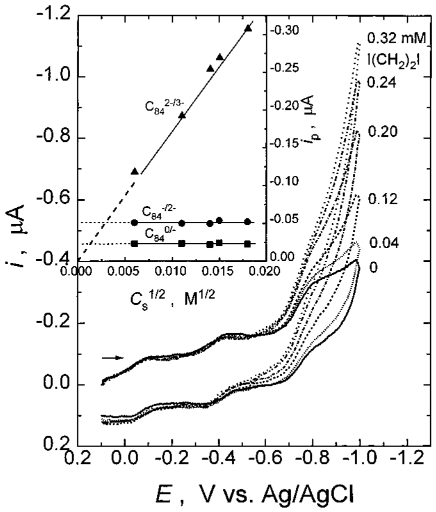

Figure 1. Cyclic voltammograms for 0.02 mM C_{84} in 0.1 M (TBA)-PF_6, in benzonitrile and different concentrations of 1,2-diiodoethane indicated at each curve. Potential scan rate 0.1 V s^{-1}. Inset is the dependence of the $C_{84}{}^{n-/(n+1)-}$ ($n = 0$ to 2) electroreduction current step on the square root of the 1,2-diiodoethane concentration.

Ag/AgCl reference electrode. All experiments were performed at ambient temperature, 20 ± 1 °C, in dark in order to avoid decomposition of the 1,2-diiodoalkanes. Solutions were deaerated by N_2 purge prior to experiments.

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 a FID detector of Hewlett-Packard on a SPB-5 nonpolar phase fused silica capillary column (30 m × 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 × 0.253 mm) operating in an electron ionization mode. The HPLC analysis of the bulk electrolyses products, performed in order to check if any alkyl adducts of larger fullerenes 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−vis spectrophotometric detector set at 340 nm. Analytical Cosmosil Buckyprep column (250 × 4.6 mm) of Nacalai Tesque (Kyoto, Japan) was used with toluene as a mobile phase of the flow rate of 1 mL min^{-1}.

Results and Discussion

The electrocatalytic activity of the fullerene anions toward the 1,2-dihaloethane substrates in benzonitrile solutions was qualitatively studied by using cyclic voltammetry (CV) and, quantitatively, by using the RDE voltammetry.

The qualitative CV investigations indicated that di- and trianions of C_{76} and C_{78} as well as trianions of C_{84} catalytically dehalogenate the 1,2-dihaloethanes. By way of example, Figure 1 illustrates such a behavior for 0.02 mM $C_{84}{}^{n-}$ ($n = 1$ to 3) in the presence of 1,2-diiodoethane of different concentrations in 0.1 M (TBA)PF_6, in benzonitrile. For the third redox couple, $C_{84}{}^{2-/3-}$, a limiting current step of electroreduction is developed rather than a peak and the corresponding electrooxidation peak is vanished. This step increases linearly with the square root of the 1,2-diiodoethane concentration while the first two peaks, corresponding to the $C_{84}{}^{0/-}$ and $C_{84}{}^{-/2-}$ electroreductions, are independent of the 1,2-diiodoethane concentration (Inset in Figure 1). Moreover, it is also observed that the third step is proportional to the C_{84} concentration at constant 1,2-diiodoethane concentration. In excess of 1,2-diiodoethane (10 fold or more) against the fullerene, i.e., under pseudo-first-order conditions with respect to 1,2-diiodoethane, this rather poorly defined current step is potential scan-rate independent from 0.01 to 0.2 V s^{-1}. This behavior indicates that reduction of 1,2-diiodoethane is catalyzed by the $C_{84}{}^{2-/3-}$ couple. Noticeably, the peaks corresponding to the first two ($C_{84}{}^{0/-}$ and $C_{84}{}^{-/2-}$) electroreductions linearly increase with the 1,2-diiodoethane concentration as well as the square root of the potential scan rate. This indicates that they are controlled by diffusion. Additionally, two new pairs of electro-oxidation and electroreduction peaks are observed during subsequent cycling over the positive potential range which followed the initial electroreduction cycling in the presence of 1,2-diiodoethane in the C_{84} solution. Formal redox potentials of these peak pairs are located at about 0.19 and 0.64 V. Apparently, iodide is released during 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 one.[7] Similar voltammetric behavior is seen if 1,2-dibromoethane or 1,2-dichloroethane is used as a substrate and different fullerenes as catalysts. That is, additional peaks corresponding to oxidation of bromide or chloride released into the solution are also observed during subsequent cycling over the positive potential range that follows the initial electroreduction potential scan. These results indicate that 1,2-dihaloethanes are catalytically dehalogenated by fullerene anions under the voltammetric conditions.

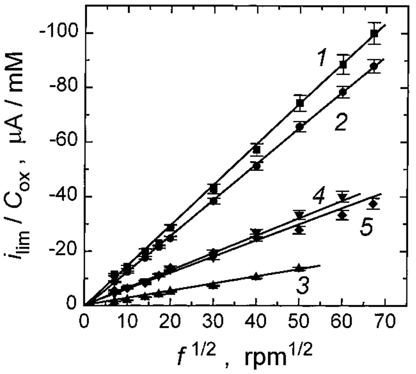

Figure 2. Dependence of the limiting current of the RDE voltammetry, normalized with respect to the fullerene concentration, i_{lim}/C_{ox} on rotation rate for (1) C_{60}, (2) C_{70}, (3) C_{76}, (4) C_{78}, and (5) C_{84} in 0.1 M (TBA)PF_6, in benzonitrile.

Four well developed cathodic steps corresponding to the first four one-electron electroreductions are present in the RDE voltammograms of the investigated fullerenes in 0.1 M (TBA)PF_6, in benzonitrile, for different rotation rates. Levich plots[8] of the limiting current, normalized with respect to the fullerene concentration, i_{lim}/C_{ox}, against the square root of rotation rate, $f^{1/2}$, are linear, as shown for the first electroreduction step of each fullerene in Figure 2. This Levich analysis indicates that all processes are controlled by convective diffusion. Values of the diffusion coefficient, *D*, for neutral fullerenes,[9] determined from slopes of the lines in Figure 2, are summarized in Table 1. Note that the *D* values reported here for C_{78} and C_{84} are the average numbers for more than one isomeric form of these fullerenes.[12,13] Generally, the values of *D* are smaller the larger the fullerene. Surprisingly, the *D* value for C_{76} is smaller than those determined for C_{78} and C_{84}. Presumably, this small value is due to appreciable aggregation of the C_{76} molecules in solution.

As an example of electrocatalytic activity of larger fullerenes toward 1,2-dihaloethanes, the RDE voltammograms are shown in Figure 3 for a 0.1 M (TBA)PF_6 benzonitrile solution of C_{84}

TABLE 1: Values of Diffusion Coefficient *D* for Fullerenes in 0.1 M (TBA)PF$_6$, in Benzonitrile, Determined by the RDE Voltammetry

fullerene	D, $10^6 \times$ cm^2 s^{-1}	ref
C_{60}	3.1 ± 0.2[a]	10
C_{70}	2.7 ± 0.1[a]	11
C_{76}	0.27 ± 0.02	this work
C_{78}[b]	1.0 ± 0.1	this work
C_{84}[b]	0.73 ± 0.03	this work

[a] The *D* values were also determined for C_{60} and C_{70} under the present solution conditions and were found to agree within ±10% with the literature values (refs 10 and 11). [b] Contains more than one isomer (refs 12 and 13).

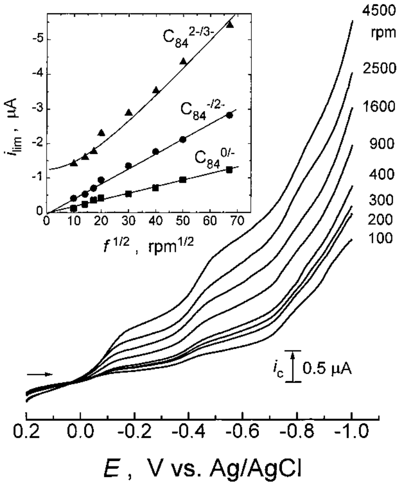

Figure 3. Rotating disk electrode voltammetry curves for 0.01 mM C_{84}, 2.4 mM 1,2-diiodoethane, 0.1 M (TBA)PF$_6$ in benzonitrile for different rotation rates indicated at each curve. Inset is the dependence of the limiting current, i_{lim}, on square root of rotation rate for the first three $C_{84}^{n-/(n+1)-}$ ($n = 0-2$) electroreductions.

and 1,2-diiodoethane. In agreement with the CV results presented above, catalytic currents, enhanced as compared to the limiting currents for small rotation rates, are observed for the third redox couple (Inset in Figure 3). Similar RDE voltammetric behavior is observed for the C_{76} and C_{78} catalysts except that both di- and trianions are catalytically active for these two fullerenes. Values of the second-order rate constant, *k*, were determined by using the RDE voltammetry, under pseudo-first-order conditions with respect to the 1,2-dihaloethane substrate. Under these reaction conditions, *k* is given by[14]

$$k = i_{cat}^{2}/(nFAC_{Ox})^{2}DC_{S} \tag{1}$$

where C_{OX} is the concentration of the fullerene catalyst, C_S is the concentration of the substrate, *F* is the Faraday constant, *n* is the number of electrons transferred, and *A* is the electrode surface area. The values of catalytic current, i_{cat}, were determined by extrapolating to zero abscissa curves of the limiting current versus square root of rotation rate (Inset in Figure 3). Then, these i_{cat} values were plotted against the square root of the 1,2-dihaloethane concentration, both for the second and third fullerene redox couple (Figure 4). As predicted from eq 1, straight lines were obtained. The *k* values calculated from slopes of these lines are presented in Table 2.

To check whether all the isomers of C_{78} and those of C_{84} are involved in the electrocatalysis, control experiments were performed for 0.1 M (TBA)PF$_6$ in pyridine. For this solvent, the voltammograms show different peak potentials for different isomers.[15] Enhanced catalytic currents in the presence of the 1,2-dihaloethane substrates were observed for peaks corresponding to the individual isomers. These results indicate that all isomers of C_{78} and C_{84} are catalytically active. However, we could not quantitate our results with respect to the different isomers primarily due to the close proximity of the voltammetric peaks and also to the variable isomer distribution.[12,13]

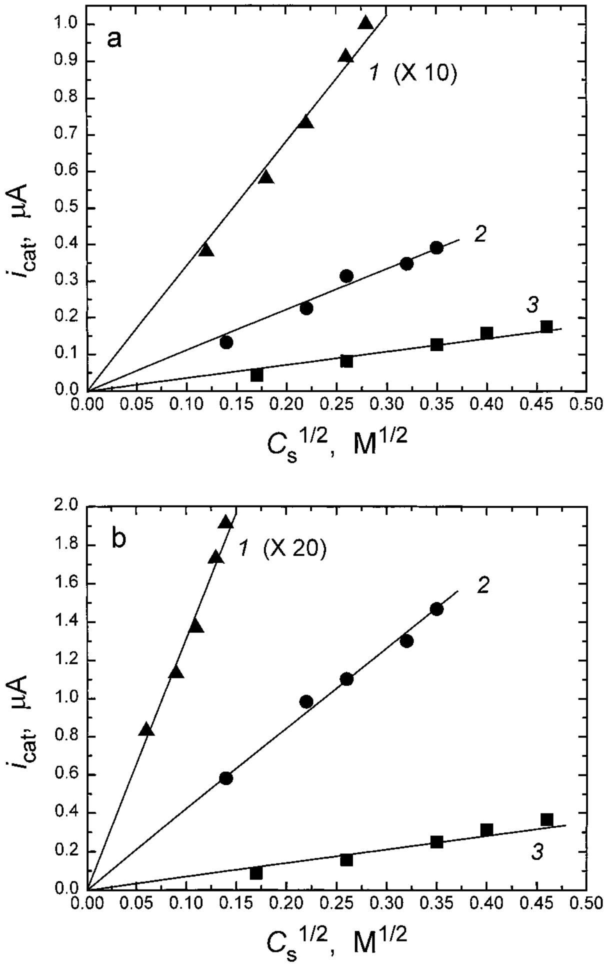

Figure 4. Dependence of the rotation rate independent RDE voltammetry catalytic current, i_{cat}, on square root of concentration of (1) 1,2-diiodoethane, (2) 1,2-dibromoethane, and (3) 1,2-dichloroethane, for the (a) second and (b) third electroreduction of C_{76} (0.06 mM) in 0.1 M (TBA)PF$_6$, in benzonitrile.

TABLE 2: Values of the Second-Order Rate Constant, *k*, for Electrocatalytic Reduction of 1,2-Dihaloethanes by C_m^{n-} (m = 60, 70, 76, 78, 84, and n = 2 or 3) in 0.1 M (TBA)PF$_6$, in Benzonitrile, Determined by the RDE Voltammetry

fullerene redox couple	$E_{1/2}$[a] V vs Ag/AgCl	k,[b] M^{-1} s^{-1}			ref
		Cl(CH$_2$)$_2$Cl	Br(CH$_2$)$_2$Br	I(CH$_2$)$_2$I	
$C_{60}^{-/2-}$	−0.86	3.5 × 10	1.6 × 10^2	2.8 × 10^5	*c*
$C_{70}^{-/2-}$	−0.82	2.2	3.3 × 10	1.1 × 10^5	*d*
$C_{76}^{-/2-}$	−0.63	2.1	2.5 × 10	3.3 × 10^4	*e*
$C_{78}^{-/2-}$	−0.47	0	10	9.8 × 10^3	*e*
$C_{84}^{-/2-}$	−0.42	0	0	0	*e*
$C_{60}^{2-/3-}$	−1.34	5.5 × 10	3.2 × 10^2	9.4 × 10^5	*c*
$C_{70}^{2-/3-}$	−1.26	3.3	1.3 × 10^2	5.1 × 10^5	*d*
$C_{76}^{2-/3-}$	−1.12	3.2	8.3 × 10	5.1 × 10^4	*e*
$C_{78}^{2-/3-}$	−0.84	0	8.9	1.6 × 10^4	*e*
$C_{84}^{2-/3-}$	−0.78	0	1.7	1.9 × 10^2	*e*

[a] The $E_{1/2}$ values determined in the present work agree with the literature values (ref 2d and e). For the Fc$^{+/0}$ couple, $E_{1/2}$ = 0.45 V vs Ag/AgCl under the present solution conditions. [b] The estimated error of the *k* values is ±15% (standard deviation). [c] From ref 4. [d] From ref 5. [e] Present work.

The rate constants presented in Table 2 may be somewhat overestimated due to the dynamic nature of both the CV and RDE voltammetry. That is, a concomitant comproportionation of $C_m^{(n+2)-}$ (m = 76, 78, and 84, and n = 0 or 1), generated at the electrode surface and C_m^{n-} present in bulk solution, according to eq 2,

$$C_m^{n-} + C_m^{(n+2)-} \leftrightarrow 2C_m^{(n+1)-} \qquad (2)$$

could affect the electrocatalysis. As discussed earlier,[3a,5] the comproportionation could deplete the $C_m^{(n+2)-}$ catalyst in the reaction layer which, in turn, might result in overestimation of the determined k values. Noticeably, the rate of the comproportionation is twice as sensitive to the fullerene concentration than that of the electrocatalysis because comproportionation is the reaction of the second order while electrocatalysis is of the first order against the fullerene. Therefore, apparent catalytic rate constants for different fullerene concentrations had to be determined in order to estimate the effect of the comproportionation on electrocatalysis. Control experiments indicated that the rate constants were larger by 10−15% for the concentration of fullerenes larger by an order of magnitude. Importantly, the CV catalytic currents in the presence of 1,2-dihaloethane are virtually independent of the potential scan rate indicating that consumption of the fullerene in the comproportionation reaction 2 is insignificant. Hence, the rate constants for dilute solutions of the fullerene catalysts summarized in Table 2 are not overestimated more than by 10−15%.

For better understanding of conceivable electrocatalysis routes, we determined, by both GC-MS and HPLC, the products of bulk electrolyses performed at constant potentials in solutions containing the fullerene and one of the 1,2-dihaloethane. That is, in independent bulk electrolysis experiments, either the dianion (in case of C_{76} and C_{78}) or trianion (in case of C_{76}, C_{78}, and C_{84}) of the fullerene was electrochemically generated in a 0.1 M $(TBA)PF_6$ benzonitrile solution of the 1,2-dihaloethane. In agreement with the results reported earlier for the C_{60} and C_{70} catalysts for the 1,2-diiodoethane substrate,[4,6] ethane and ethene were the major electrolysis products. In the presence of the 1,2-dibromoethane or 1,2-dichloroethane substrate, only bromoethane or chloroethane was the major reaction product, respectively. A HPLC chromatogram of the reaction product mixture obtained after bulk electrolysis revealed no new peaks which would correspond to the formation of alkyl adducts of larger fullerenes.

The present results indicate that the initial electron transfer to $X(CH_2)_2X$, assumed to be the rate determining step[16] governed by an outersphere electron-transfer mechanism that was originally proposed for reduction of vicinal dibromoalkanes with aromatic anion radicals,[16−18] yields a 1-halogenated ethane radical and liberates halide in the solution. On the basis of our previous and present[5] results of product analyses, we can postulate a series of reactions that could follow the formation of this radical and result in formation of ethane (in the presence of trace amounts of water in the solvent), ethene, and/or mono halogenated ethane as reaction products. Moreover, the radical might be added to the catalyst resulting in the fullerene alkyl adducts. However, fullerene alkyl derivatives were not detected by the HPLC analysis of the reaction product mixture. The HPLC analysis suggests that these radical additions to the fullerene cages are less favored than the radical reduction or, less plausible, that the larger fullerene alkyl derivatives are less stable.

Our earlier[4−6] and present results show that all the di- and trianions of C_{60}, C_{70}, C_{76}, and C_{78} as well as trianions of C_{84} electrocatalytically dehalogenate 1,2-dihaloethanes and the potential of this dehalogenation is governed by the values of the formal redox potential $E_{1/2}$ of the fullerenes. Importantly, the larger the fullerene, the more positive the $E_{1/2}$ values of the consecutive electroreductions[2d] (Table 2). Also, the larger the fullerene the more positive is the $E_{1/2}$ value for electrocatalytic reduction of 1,2-dihaloethanes. For instance, the gain in the overpotential is as large as nearly 500 mV for $C_{84}^{n-/(n+1)-}$ as compared to $C_{60}^{n-/(n+1)-}$ (n = 1 or 2). However, the rate constants of electrocatalysis are smaller the larger the fullerene. Figure 5 shows the Brønsted type dependence of log k versus $E_{1/2}$ of the fullerenes for electrocatalytic reduction of 1,2-dihaloethanes. For each fullerene anion, k increases in the order: Cl < Br < I, as predicted from Savéant's theory of dissociative reduction.[17]

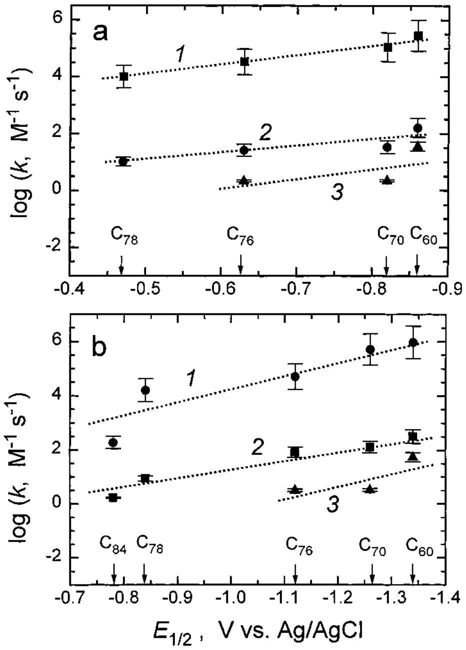

Figure 5. Dependence of log k versus $E_{1/2}$ for (a) the second electroreduction, and (b) the third electroreduction of the C_{60}, C_{70}, C_{76}, C_{78}, and C_{84} fullerenes for (1) 1,2-diiodoethane, (2) 1,2-dibromoethane, and (3) 1,2-dichloroethane.

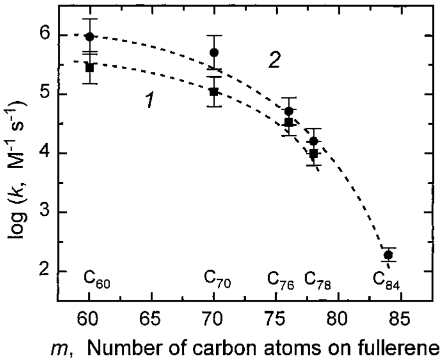

Figure 6. Dependence of log k versus number of carbon atoms of the fullerene cage for the fullerene (1) dianions and (2) trianions, in the presence of 1,2-diiodoethane in 0.1 M $(TBA)PF_6$, in benzonitrile.

From Table 2, it also follows that the k values increase in the following order: $C_{84} < C_{78} < C_{76} < C_{70} < C_{60}$ for each 1,2-dihaloethane. Figure 6 shows this trend of the log k against the number of carbon atoms on the fullerene cage. Apparently, the rate of electrocatalysis for di- and trianions is smaller the larger the fullerene. This rate decrease can be rationalized in terms of thermodynamics. Most likely, the free energy difference corresponding to the difference of formal redox potentials of the fullerene and the 1,2-dihaloethane largely contributes to the activation energy of reduction of 1,2-dihaloethanes by the fullerene anions. Noticeably, the larger fullerenes are more stable than C_{60} with respect to the alkyl adduct formation. That is, no reaction between the anions of larger fullerenes and 1,2-dihaloethanes yielding alkylated products was observed. Thus, anions of larger fullerenes are better catalysts for electrode-assisted chemical reactions in terms of the overpotential and catalyst stability, although the corresponding electrocatalytic rate constants are much smaller than those for the C_{60} anions.

In summary, the anions of larger fullerenes, C_{76}, C_{78}, and C_{84} electrocatalytically reduce 1,2-dihaloethanes. The dianions of C_{76} and C_{78}, as well as trianions of C_{76}, C_{78}, and C_{84}, electrochemically generated in 0.1 M $(TBA)PF_6$, in benzonitrile, catalyze dehalogenation of 1,2-dihaloethanes. The second-order rate constant for the electrocatalytic dehalogenation of 1,2-dihaloethanes by the fullerene anions, determined by the RDE voltammetry under pseudo-first-order conditions, increase in the order Cl < Br < I for the investigated 1,2-dihaloethanes and in the order $C_{84} < C_{78} < C_{76} < C_{70} < C_{60}$ for each 1,2-dihaloethane. No chemical reaction between the anions of larger fullerenes and 1,2-dihaloethanes resulting in formation of alkyl adducts of fullerenes is observed. Because of the high stability with respect to the adduct formation and more positive $E_{1/2}$ values of the electrocatalyses, the larger fullerenes may be more useful than C_{60} as catalysts, even though their corresponding catalytic rate constants are smaller.

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