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Methanofullerenes and Methanofulleroids Have Different Electrochemical Behavior at Negative Potentials

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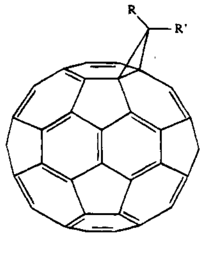
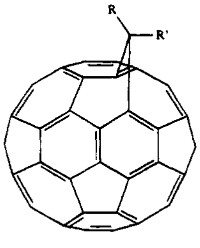
Abstract: Cathodic electrochemistry was performed for two methanofullerene derivatives, **3** and **4**. Since it was possible to isolate the [6,6] closed isomeric forms of these derivatives (called simply methanofullerenes), the electrochemistry of the pure isomers was recorded. The electrochemical behavior of the corresponding mixtures, which also contained the [5,6] open forms (simply referred to as methanofulleroids), was also obtained. In the solvent mixture used, acetonitrile:toluene (1:5), no difference was observed for the potentials of the first four electrochemical waves of the two isomers. However, the methanofulleroid exhibited an anodically-shifted fifth reduction wave, relative to that corresponding to the methanofullerene. This difference in potential was 0.20 V for the fullerene–fulleroid isomers of both **3** and for those of **4**. On the basis of the voltammetric data, the fulleroids behave more as triply degenerate systems, very much like the behavior for C_{60}. This was anticipated, since they are, as is the parent C_{60}, 60 π electron systems. However, the methanofullerenes have 58 π electrons, and part of their conjugated network is destroyed. The fullerenes exhibit what appear to be doubly degenerate LUMOs with a LUMO$^+$ that is some 4–5 kcal/mol higher in energy. The presence of the methanofullerene was confirmed by simultaneous UV–vis spectrophotometry in the case of **3**. Thermalization of isomeric mixtures of **3** and **4** resulted in the quantitative formation of the methanofullerene and the total disappearance of the methanofulleroid, consistent with previous results.

Introduction

The number of synthetic fullerene derivatives continues to increase at a relatively fast pace. A variety of reactions have been employed to prepare monoaddition derivatives of the fullerenes, primarily those of C_{60} and C_{70}.[1] One of the most versatile and best established derivatization reactions involves the addition of diazo compounds directly to C_{60}.[2,3] These reactions result in the formation of isomeric derivatives called either methanofullerenes (**1a**, or simply fullerene) or methanofulleroids (**1b**, fulleroid). The name fulleroid is meant to imply an expanded fullerene system, where the extra methano carbon added does not interfere with the conjugated system of the parent C_{60} moiety. Other possible isomeric structures can be envisioned, those that involve [6,6] open and [5,6] closed arrangements, for a total of four possible isomers.[4] However, it has been experimentally shown that only forms **1a** and **1b** are present.[4,5] To our knowledge, the other two isomers have never been observed. It has been pointed out that the reason why only these two isomers are observed has to do with the preservation of the [5]radialene structure, as in the parent C_{60} molecule.[6,7] It must be pointed out that if the R substituents are different (R and R′), it is possible to obtain other isomeric forms of the fulleroid, since this form lacks a plane of symmetry that bisects the CR_2 adduct.[5]



1a



1b

It has also been shown that the kinetic products of these diazo additions are the fulleroids ([5,6] open),[8,9] but thermalization of these products always affords the thermodynamically more stable fullerenes except when R = R′ = H.[10,11]

Several electrochemical results have been published for some of these methanofullerenes. In the most recent one, we reported the electrochemistry of two methanofullerene derivatives at very negative potentials.[12] Most electrochemical studies have concluded that the electronic structure of the parent fullerene moiety remains essentially unchanged by the adducts. One of the specific structures investigated in ref 12 was **2**(note that only

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(1) (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685. (b) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138 and references therein.

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(8) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301.

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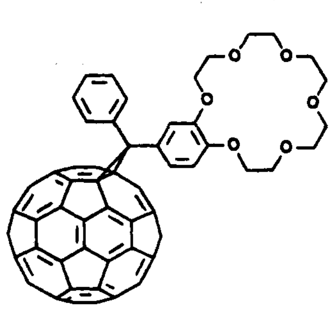
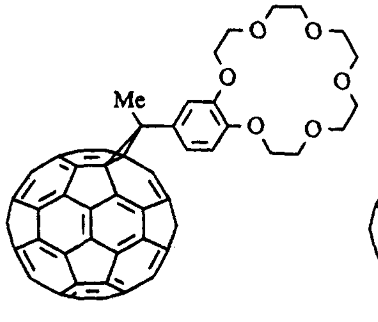


2

the fullerene structure is presented for simplicity and space, but the fulleroid is typically present also). Kinetic effects were noted in this work, and these were probed using a combination of variable temperature and variable scan rates.[12] These effects were observed after the first four reversible cathodic processes, specifically at the fifth reduction leading to the formation of the pentaanionic state.[12] It was concluded that the very small fifth wave observed at −2.84 V vs Fc/Fc$^+$ corresponded to the fifth electron reduction of the intact initial structure, while the sixth wave at −3.04 V arose from a decomposed or rearranged product. The possibility of rearrangement of the tetraanionic form to a [6,6] open fulleroid structure was proposed in this work.[12] At the time, the only pure [6,6] methanofullerene isomer in our hands was that of **2**. The mixture of isomers of this compound contained only a very small amount of the [5,6] isomer.

We now report electrochemical results for two methanofullerene systems, **3** and **4**,for which it was possible to obtain a mixture of the fullerene and fulleroid as well as a pure sample of the corresponding [6,6] fullerene structure. We show here that the fullerene forms of these compounds have a cathodically shifted fifth reduction wave relative to that of the corresponding fulleroid.



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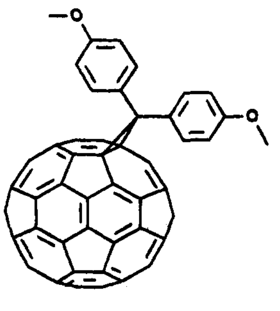

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Results and Discussion

Cyclic and Osteryoung-square-wave voltammetry (CV and OSWV, respectively) of a mixture of the fullerene–fulleroid isomers of compound **3** were recorded in an acetonitrile:toluene solvent mixture.[13] The OSWV is presented in Figure 1. The typical sequential electron transfer series is clearly observed for the first five reduction steps, with relatively constant separation between waves (0.41, 0.50, 0.46, and 0.46 V between the first and second, second and third, third and fourth, and fourth and fifth waves, respectively). Potential values for all of these waves, referenced to internally added ferrocene/ferricinium (Fc/Fc$^+$), are reported in Table 1. Since cyclic voltammograms of all of these samples were also obtained, the values reported in Table 1 correspond to the $E_{1/2}$s determined by this technique, for consistency with prior work.[12] All of these processes were found to be chemically reversible and electrochemically quasireversible by cyclic voltammetry. Notice from Figure 1a that the fifth wave, which appears at a relative potential of −2.88 V, is somewhat smaller in size than the others. If the sixth wave observed at −3.06 V is assumed to correspond to the sixth electron reduction of the same species that underwent the previous five, it would not follow the sequential potential separation scheme since it is only 0.18 V more cathodic than the fifth redox process.

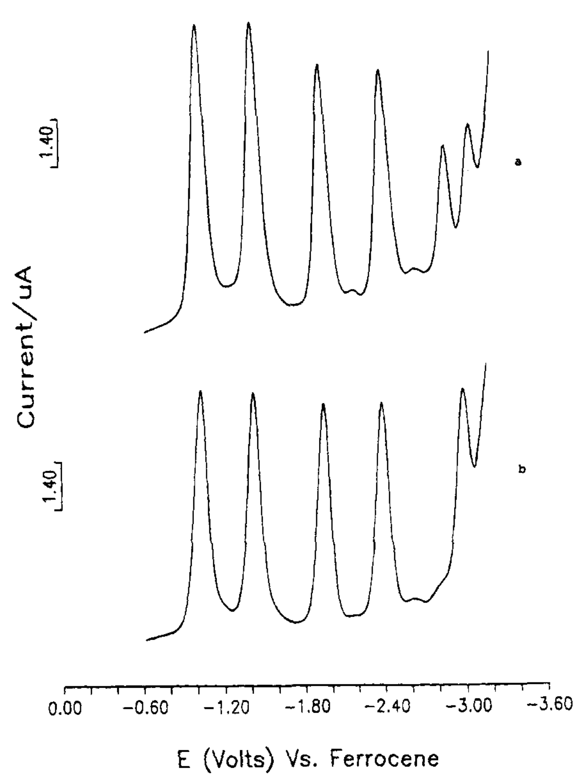

Figure 1. OSWV for compound **3** recorded in 0.1 M TBAPF$_6$ in MeCN:toluene (1:5) at room temperature on a glassy carbon working electrode. The voltammograms were obtained using a sweep width of 25 mV, frequency of 15 Hz, and a potential step of 4 mV. Voltammogram for (a) a mixture of the fullerene and fulleroid isomers and (b) for the pure [6,6] fullerene isomer.

Since it was possible to isolate the pure [6,6] fullerene isomer of compound **3** (see details in the Experimental Section), its OSWV was recorded independently, and it is presented as Figure 1b. Notice that within the same potential window used for the mixture, only five waves can be observed. The first four have essentially identical potentials as the corresponding ones for the isomer mixture, but the last one appears to correspond to the sixth wave observed in Figure 1a.

The interpretation of these results is rather evident. The fifth wave observed in Figure 1a must correspond to the fifth reduction of the fulleroid only, while the sixth wave in the same figure must correspond to the fifth reduction of the fullerene, as is evident in Figure 1b. To our knowledge, this is the first time that such a drastic difference in the electrochemical behavior of a fullerene and its isomeric fulleroid is reported. Subtle differences have been previously pointed out,[14] but for the most part the experimental evidence for C_{60} derivatives has been interpreted in terms of preservation of the electronic structure of the parent fullerene. Such electronic similarity of fullerene–fulleroid isomer pairs is somewhat disturbing in view

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[13] Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978.

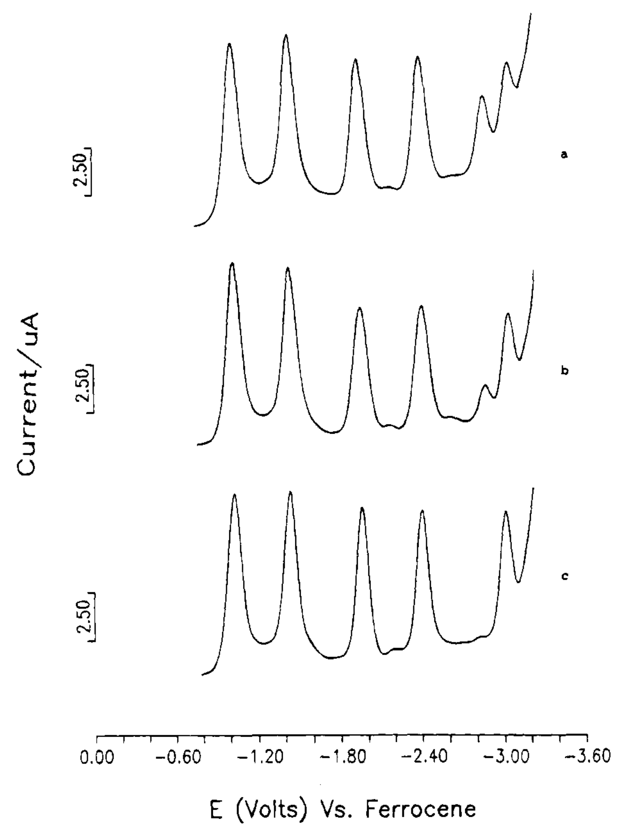

Figure 2. OSWV for an isomer mixture of **3**, recorded using identical conditions to those given for Figure 1 at 25 °C and (a) 0.75 h after preparing the sample, (b) 2.25 h after preparing the sample, and (c) 7 h after preparing the sample.

of the fact that the former is a 58 π electron system, while the latter has 60 π electrons. It must be pointed out that Eirmann et al. (ref 14) also reported that it was possible to convert a fulleroid into a fullerene quantitatively by reducing it coulometrically with 3 electrons.[14]

Confirmation of the results presented above comes from three additional lines of evidence. The first is the room temperature thermalization of a sample containing the fullerene–fulleroid mixture of compound **3** and its voltammetric changes. These OSWV results are presented in Figure 2. This sample was kept in the electrochemical cell under a partial vacuum all the time after the initial voltammogram was recorded, Figure 2a. No special thermal treatment was applied; it was simply allowed to stand at 25 °C and its OSWV was recorded at different intervals on a glassy carbon working electrode. It can be clearly seen that the fifth wave, the one assigned previously to the fulleroid's fifth reduction, decreases in intensity and is completely absent after 7 h, Figure 2c. As mentioned in the Introduction, thermalization of neutral fulleroid isomers is known to result in the formation of the thermodynamically more stable fullerenes, except when R = R' = H in structures **1**.[10,11] Therefore, the explanation for the sequence in Figure 2 is that the fulleroid present in the initial mixture is thermally converted into the fullerene quantitatively and irreversibly. The potentials for the waves in Figure 2c can be found in Table 1, and they correspond closely to those measured for the isolated fullerene sample, those in Figure 1b.

Since a diagnostic absorbance is observed for the fullerene, but not for the fulleroid, around 430 nm,[5,9,14,15] we also monitored the absorbance of the same solution as a function of time. This provided the second line of evidence to support our interpretation. These results are presented in Figure 3. Notice that the absorbance at 430 nm increased monotonically as the fifth reduction wave decreased in the OSWV. Thus the decrease in voltammetric response current for the fifth wave is perfectly matched by the increase in the absorbance at 430 nm, further confirming the nature of the reaction involved.

Table 1. Potential Values for All of the Observed Redox Processes of Compounds **3** and **4**, $E_{1/2}$, at 25 °C. Values Are the Averages of Cathodic and Anodic Peak Potentials from Cyclic Voltammetric Experiments and Are Reported in Volts Relative to the Potential for Internal Fc/Fc$^+$. The Cathodic to Anodic Peak Separations (ΔE) Are Also Reported

	reduction ($E_{1/2}$ (V), ΔE (V))					
compound	1st	2nd	3rd	4th	5th	5th(fullerene)
C_{60}	−0.99	−1.41	−1.90	−2.38	−2.89	−3.26[a]
	0.08	0.08	0.07	0.07	0.08	
3	−1.04	−1.45	−1.95	−2.42	−2.87	−3.07
(from Figure 1a)	0.09	0.08	0.07	0.07	0.09	0.07
3	−1.04	−1.44	−1.96	−2.41		−3.04
(from Figure 1b)	0.06	0.05	0.06	0.04		0.09
4	−1.07	−1.48	−2.00	−2.46	−2.90	−3.10
(from Figure 4a)	0.06	0.06	0.06	0.06	0.10	0.06
4	−1.07	−1.48	−2.02	−2.48	−2.86[b]	−3.11
(from Figure 4c)	0.05	0.06	0.07	0.09		0.08

[a] Value corresponds to the sixth wave of C_{60} and was estimated from OSWV at 10 °C. [b] Cathodic wave was almost imperceptible, so the value reported corresponds to the anodic wave.

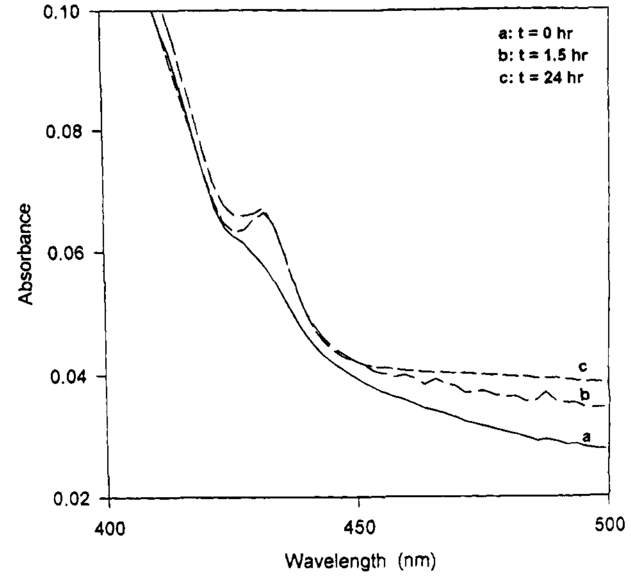

Figure 3. UV–vis spectra for a solution of an isomeric mixture of compound **3** in 0.1 MeCN:toluene (1:5) (no supporting electrolyte) as a function of time. Shown are spectra recorded immediately after preparing the sample, 1.5 h later, and 24 h later. The absorption around 430 nm, corresponding to the fullerene, grows as a function of time.

The third line of evidence was designed to confirm these results. Compound **4** was selected for an additional thermalization experiment using OSWV to detect the changes. The reason for the selection of this compound instead of **2** was the fact that it also presented a relatively large fifth wave, which could be tentatively assigned to reduction of the fulleroid exclusively. This is not the case with compound **2**, which was the main object of our previous work, which shows an almost imperceptible fifth wave, indicative either of a very small amount of the fulleroid in the initial isomeric mixture or of very

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(14) Eirmann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364.

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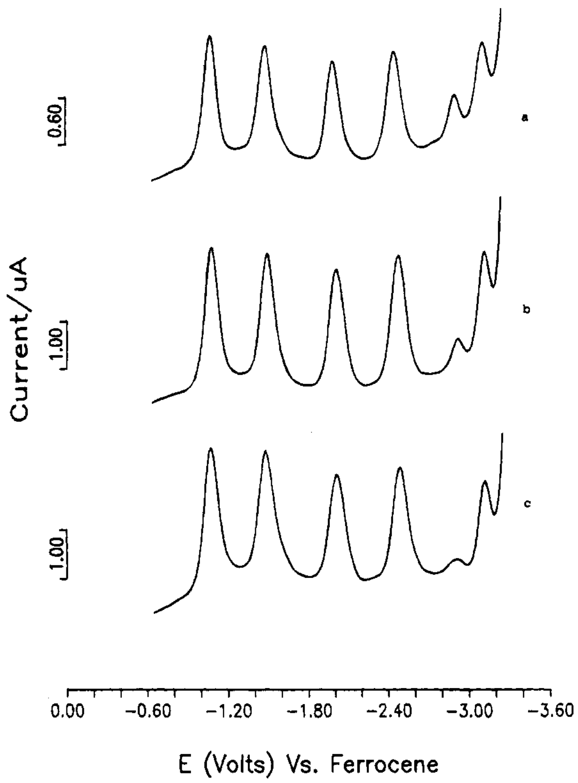
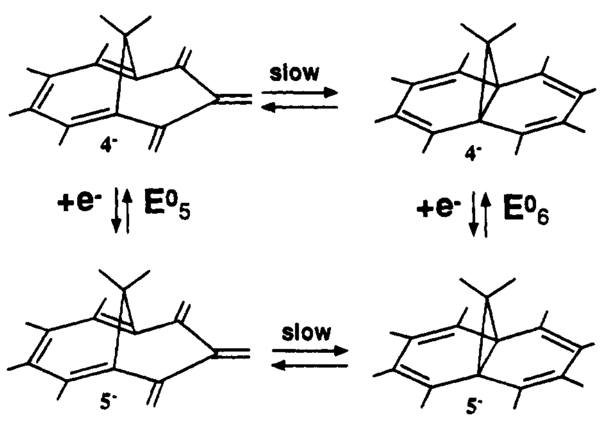


Figure 4. OSWVs for an isomer mixture of compound **4**: (a) at 25 °C immediately after preparing the sample, (b) after equilibrating the sample at 45 °C (approximately 15 min to heat from 25 to 45 °C), and (c) 11 min after recording 4b. Note the decrease in intensity of the fifth wave. Conditions were similar to those used to obtain Figure 1.

efficient conversion of the fulleroid into the fullerene upon electrochemical reduction, *vide infra.*[12] Figure 4 shows the OSWV results for the thermalization experiment for the fullerene−fulleroid mixture of compound **4**. In this case, no voltammetric changes were detected when the sample was kept at 25 °C for several hours. It was necessary to heat the sample to 45 °C to detect a change in the OSWV. Figure 4a corresponds to the OSWV at 25 °C, 4b is the corresponding one at 45 °C (it took approximately 15 min to attain equilibrium after heating the sample from 25 to 45 °C), and 4c is still at 45 °C but recorded 11 min after the one in 4b. It is evident that the fifth wave, at −2.85 V, decreases in intensity, as expected. The change in intensity that was observed, as in the case of **3**, was irreversible. Interestingly, the fifth wave did not disappear completely as it did in the case of **3**. These results indicate that the fulleroid to fullerene conversion requires more energy for **4** than for **3**.

The new results presented here clearly show that pure [6,6] methanofullerene isomers exhibit electrochemical behavior that is different from that of the corresponding [5,6] fulleroid isomers. Since the first four reductions of these isomers have similar potentials and since these follow a regular successive electron transfer sequence with nearly constant separations (*vide supra*) it can be safely concluded that both isomers have at least a doubly degenerate LUMO of very similar energy. It has been pointed out by Weaver and Gao that successive electron transfer sequences on spherical or nearly spherical molecules can be accounted for by assuming that the molecules act as a simple capacitor.[16] Thus the potentials for successive electron transfers to C_{60} leading to its corresponding hexaanion, C_{60}^{6-},[12] follow a linear correlation when plotted vs the state of reduction of the C_{60}.[17] A simple way to express these observations is to say that successive electron transfers, in the absence of quantum or other effects,[16] will exhibit equally spaced waves, with typical separations between 0.4−0.5 V, depending on the dielectric constant of the medium. Such is the behavior exhibited by C_{60} and by C_{70}. Thus the almost constant separation in potential of the first four waves of the fullerene and fulleroid isomers of compounds **3** and **4** indicate that the LUMO is at least doubly degenerate.

Scheme 1



Analysis of the reduction waves beyond the fourth one indicates that the fulleroid has a fifth reduction that follows the regular sequence predicted for a molecular capacitor using Weaver and Gao's treatment, with a separation of 0.46 V from the fourth reduction wave, *vide supra*. Although the sixth electron reduction of the fulleroid was not detected in these experiments, the fact that the fifth one follows the regular sequence indicates that its LUMO is approximately triply degenerate.

The case of the fullerene isomer is different. Its fifth reduction wave occurs some 0.65 V more negative than its fourth reduction, or 0.20 V more negative than the corresponding reduction of the fulleroid in the case of **3**. In the case of **4**, this difference is also 0.20 V. This larger potential gap between the fourth and fifth reduction waves of the fullerene isomers, relative to that of the fulleroids, indicates that there is a quantum effect, following the terminology of Weaver and Gao.[16] Therefore, the 58 π electron fullerenes have doubly degenerate LUMOs with a LUMO$^+$ which is some 200 mV higher in energy (about 4−5 kcal/mol). On the other hand, the fulleroids have approximately triply degenerate LUMOs and their energy is close to that of the fullerene's LUMO.

At this point only one question remains. Are the new results in contradiction with previous reports?[12] The answer is no, but the interpretation does change. In our previous paper[12] we assigned the sixth wave to an unspecified "decomposition product" (we proposed an "open" version of the fullerene isomer on Scheme 6) and the fifth to the "intact" fullerene derivative. We now identify the "intact" fullerene derivative with the corresponding fulleroid form, and the "decomposed product" with the corresponding [6,6] fullerene. Thus in Scheme 6 of ref 12, the interconversion between the tetrareduced forms should involve the fulleroid and the fullerene, not an "open" version of the fullerene. For clarification, we present Scheme 1 with the new structural assignments. It is important to note that the relative increase in the intensity of the fifth wave relative to that of the sixth as the scan rate was increased and/or the

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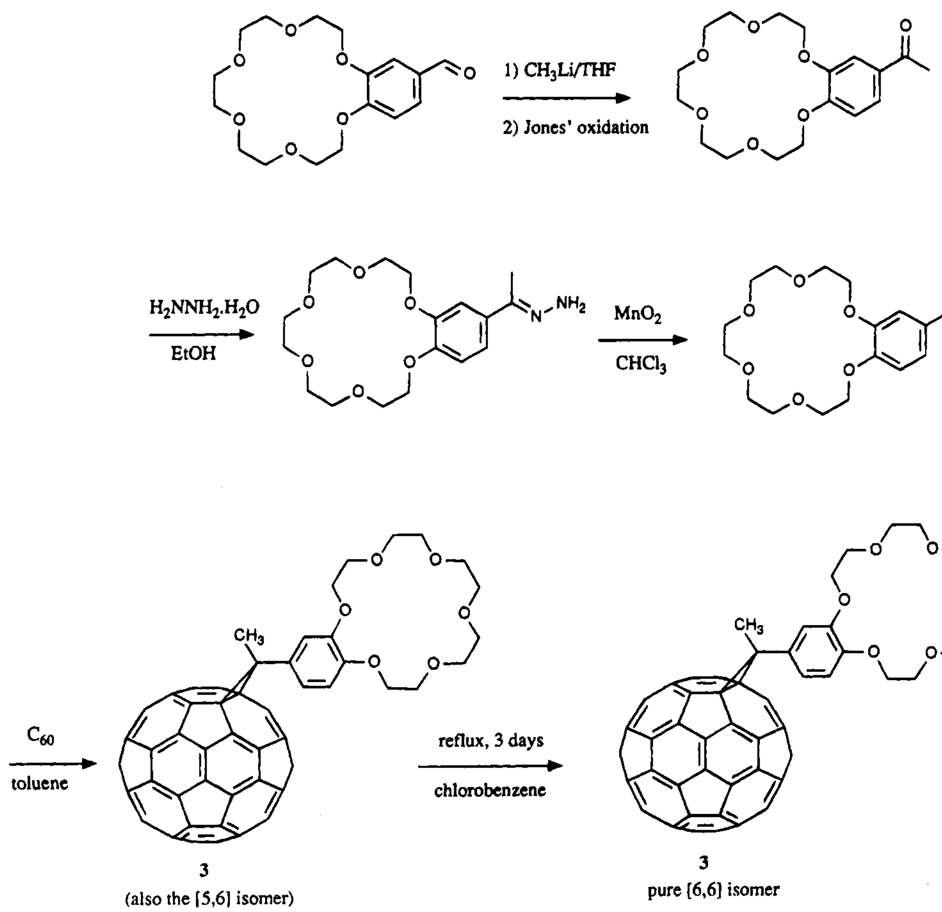
(16) Weaver, M. J.; Gao, X. *J. Phys. Chem.* **1993**, *97*, 332.

(17) Echegoyen, L.; Arias, F.; Xie, Q. Electrochemical Properties of Fullerenes and Fullerene Derivatives at Very Negative Potentials: A Possible Route to Endohedral Complexes in *Molecular Engineering for Advanced Materials*, NATO ASI Series; Becher, J., Ed.; Kluwer Academic Publishers, in press.

Scheme 2 Synthetic Route for 3



temperature was decreased (Figures 3 and 4 in ref 12) was due to kinetic inhibition of the conversion of the fulleroid to the fullerene. In other words, it does not really grow, it simply does not disappear as quickly as at the higher temperatures and slower scan rates. This is in perfect agreement with the proposed electrochemical conversion of a fulleroid into a fullerene form by Eirmann et al.[14] It could very well be that this interconversion begins at an earlier reduction stage, say 2 or 3 electrons in our systems, but it cannot be detected until after the fourth since the potentials for the fourth reduction of both isomers are nearly the same. Thus the absolute intensity of the fifth wave is not a direct measure of the bulk concentration of the fulleroid form but includes a kinetic factor, which is precisely the one detected at faster scan rates and lower temperatures. In Figure 4 of ref 12, it was evident that a small amount of the fulleroid was present, which became more evident at the lower temperatures and faster scan rates. After the fulleroid is converted into the fullerene quantitatively, either thermally or via electrochemical reduction, the fifth wave is never again observed, not by increasing the scan rate nor by decreasing the temperature to −25 °C. This is true for all of the compounds studied: **2**, **3**, and **4**. In a particular experiment, a mixture of the isomers of **3** was studied by OSWV. Initial temperature decrease resulted in the relative increase of the fifth wave, just as previously described for **2** and **4**.[12] After thermalization for 7 h at room temperature, which led to the complete disappearance of the fifth wave (see Figure 2), decreasing the temperature again did not result in the observation of the fifth wave again.

Thus the new results are in perfect agreement with the previous ones if the voltammetric behavior is assigned by taking into consideration a chemical step that involves the isomerization of the fulleroid into the corresponding fullerene polyanion, as first suggested by Eirmann et al.[14] The kinetic effects observed are precisely due to this interconversion. Our previously observed seventh wave in ref 12 was not observed here, maybe due to a slightly narrower potential window for the solvent system.

Experimental Section

Electrochemical Measurements. Details of the electrochemical measurements can be found in refs 12 and 13. Briefly, a BAS-100W electrochemical analyzer was used to record the voltammetric experiments, interfaced with a Hewlett−Packard ColorPro plotter. A glassy carbon working electrode (3 mm in diameter) was used after being polished with $^1/_4$ μm diamond polishing compound (Metadi II) from Buehler. A silver wire served as pseudo-reference electrode. The platinum wire used as the counter electrode was cleaned by being heated in a flame for approximately 30 s.

The supporting electrolyte (TBAPF$_6$) was purchased from Fluka (>99%), recrystallized twice from an ethanol:H$_2$O (95:5) mixture, and dried in vacuo prior to use.

OSWVs were obtained using a sweep width of 25 mV, a frequency of 15 Hz, and a step size of 4 mV.

The electrochemical cell used for all of these experiments was also described.[12] The supporting electrolyte was initially placed in the cell along with the fullerene sample (typically 1 mg of the latter), and the system was evacuated to approximately 10^{-5}−10^{-6} mmHg for 5 h. Three milliliters of the MeCN:toluene solvent mixture (1:5) was then vapor transferred directly through the vacuum line. After the solvent was transferred, the cell was removed from the vacuum line and the electrochemical experiments were performed. All electrochemical measurements were obtained while the cell was kept at the vapor pressure of the prevailing solvent.

UV−vis Measurements. These were made using a Hewlett-Packard 8452A diode array spectrophotometer, interfaced with a Leading Edge computer and a Hewlett-Packard Desk Jet 500 printer.

Synthesis. The general preparative methods used to prepare compound **3** are presented in Scheme 2.

Preparation of Crown Ether Ketone. To a solution of 1.05 g (3.08 mmol) of the crown ether aldehyde (prepared by formylation of benzo-18-crown-6) in 50 mL of freshly distilled THF under N_2 was added 7 mL of a 1.4 M methyllithium ether solution (9.80 mmol) at −78 °C. The dry ice/acetone bath was removed, and the mixture was stirred at room temperature for 30 min. The reaction was quenched with 20 mL of 10% HCl. The mixture was concentrated to 30 mL and extracted with CH_2Cl_2. The combined organic extracts were washed with saturated $NaHCO_3$ and NaCl, dried over Na_2SO_4, and concentrated to give an oily residue. The residue was dissolved in 15 mL of acetone and 5 mL of Jones reagent was added into the solution slowly. The mixture was stirred for another 30 min, and 2-propanol was added to stop the reaction and to dissolve the solid. Water and CH_2Cl_2 were added, and the layers were separated. The aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with saturated $NaHCO_3$ and NaCl, dried over Na_2SO_4, and concentrated to give a yellow solid. The crude product was purified by flash chromatography (eluant: ligroin (35−60 °C)/2-propanol/CH_2Cl_2 8/1/1) to afford 156 mg of the pure product (white solid). ESI-MS (KOAc/MeOH) *m/z*: 393 ($M + K^+$). ^1H NMR (200 MHz, $CDCl_3$) δ: 7.55 (dd, J = 1.94, 7.85 Hz, 1H), 7.50 (d, J = 1.94 Hz, 1H), 6.86 (d, J = 7.85 Hz, 1H), 4.21 (m, 2H), 3.94 (m, 2H), 3.74 (m, 2H), 3.68 (s, 14H), 2.54 (s, 3H).

Preparation of Crown Ether Hydrazone. A solution of 400 mg (1.13 mmol) of crown ether ketone and 550 μL (11.3 mmol) of hydrazine monohydrate in 15 mL of absolute ethanol was refluxed under N_2 for 24 h. Removal of solvent gave 410 mg (99%) of a yellow oil which was used directly for the next reaction without further purification. ESI-MS (KOAc/MeOH) *m/z*: 406 ($M + K^+$).

Preparation of Crown Ether Fulleroid−Fullerene Mixture and Pure Fullerene (3). A solution of 250 mg (0.347 mmol) of C_{60} and 100 mg (0.273 mmol) of crown ether diazomethane in 250 mL of toluene under N_2 was stirred overnight at room temperature. Then the solvent was removed in vacuo, and the crude product was purified by flash chromatography (eluant: toluene, then methanol/toluene 1/8), affording 155 mg (42%) of **3**, a mixture of [5,6] and [6,6] isomers (dark solid). ESI-MS (KOAc/MeOH/toluene) *m/z*: 1097 ($M + K^+$). ^1H NMR (200 MHz, $CDCl_3/CS_2$) δ: 7.51 (dd, J = 2.20, 8.15 Hz, 1H), 7.44 (d, J = 2.20 Hz, 1H), 7.03 (d, J = 8.15 Hz, 1H), 4.23 (m, 2H), 3.96 (m, 2H), 3.75 (m, 2H), 3.69 (s, 14H), 3.21 (s, 1.5H), assigned to the [5,6] isomer, 2.53 (s, 1.5 H), assigned to the [6,6] isomer. This mixture was refluxed for 3 days in 250 mL of chlorobenzene to yield the [6,6] isomer quantitatively. ^1H NMR (200 MHz, $CDCl_3/CS_2$) δ: 7.45 (d, J = 8.10 Hz, 1H), 7.43 (s, 1H), 6.99 (d, J = 8.10 Hz, 1H), 4.23 (m, 2H), 3.96 (m, 2H), 3.75 (m, 2H), 3.69 (s, 14H), 2.53 (s, 3H).

Preparation of Compound 4. Compound **4** was prepared in 45% yield as previously described.[12] The [6,6] and [5,6] isomers were refluxed in toluene for 72 h to yield the pure [6,6] isomer quantitatively. ^1H NMR (300 MHz, $CDCl_3/CS_2$): δ 8.03 (d, J = 8.03 Hz, 4H), 7.00 (d, J = 8.7 Hz, 4H) 3.08 (s, 6H).

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