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Kinetic Effects in the Electrochemistry of Fullerene Derivatives at Very Negative Potentials

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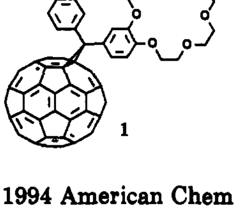
Abstract: Four fullerene derivatives have been synthesized and analyzed using electrochemical techniques at low temperatures and at very negative potentials. Two of these systems are diphenyl methanofullerene derivatives, **1** and **2**, while the others are [4+2] cycloaddition products containing a benzocrown group attached to the resulting cyclohexenyl adduct, structures **3** and **4**. For all four cases, it is possible to observe at least four successive, regularly spaced, chemically and electrochemically reversible waves using cyclic voltammetry. The potential values for these first four waves differ slightly from one compound to the other, reflecting the expected differences in electronic properties of the attached groups. While **1** exhibits potential values that are very similar to those of C_{60}, all other derivatives show waves that are cathodically shifted. In terms of increasing cathodic potential values, the compounds follow the order $C_{60} \simeq \mathbf{1} \leq \mathbf{2} \leq \mathbf{3} \leq \mathbf{4}$. For the first time for any fullerene derivatives, reduction waves beyond the fourth one have been observed for these systems. Interestingly, one of the methanofullerene adducts, **1**, and one of the [4+2] cycloaddition products, **3**, exhibit what appears to be a larger than expected potential gap between the fourth and the next observable reduction wave at room temperature. Either by scanning the potential faster or by lowering the temperature, it was possible to observe an additional redox couple for **1** immediately following the fourth reduction at the expected potential. The same was not true for **3**. Both **2** and **4** exhibit similar voltammetric behavior, which is different from that of **1** and **3** and more in-line with anticipated results, since they exhibit regularly spaced reduction waves, down to the fifth reduction. Compound **4** does not exhibit temperature or scan rate changes of its voltammetric response, while **2** does to some extent. Results are interpreted in terms of homogeneous chemical processes following the electrochemical formation of the tetraanions of **1**, **2**, and **3**, leading to the formation of phenyl-stabilized carbanionic intermediates. In the case of **1** and **2**, another homogeneous chemical process is observed, which is tentatively attributed to an electrochemically induced methanofullerene–fulleroid reaction involving a dinorcaradiene–[10]annulene type equilibrium.

Introduction

Ever since a large scale preparative process for C_{60} was reported in 1990,[1] multiple synthetic modifications of this molecule have been communicated.[2,3] The chemistry is not trivial, since multiple products are typically observed and these are difficult to separate.[3e] The derivative C_{60} compounds have been characterized by a variety of techniques.[2,3] In some cases, electrochemical measurements have been made in addition to the more common spectroscopic UV–vis measurements, which are standard for the characterization of these new compounds.[3] The work of Wudl et al. is particularly noteworthy, since they have explored the rich synthetic chemistry of C_{60} and consistently conducted electrochemical measurements of all of the products.[3] They have found that "azafulleroids are more electronegative than their carbon analogs but not as electronegative as C_{60}, as determined by cyclic voltammetry".[3e] They have found that the cyclic voltammetric pattern for all of these fullerene derivatives (including azafullerenes,[3e] their carbon analogs,[3a–d] and [3+2] and [4+2] cycloaddition products[3f]) is basically the same in THF. Quoting from one of their papers, "The cyclic voltammograms of ... exhibit the four reversible reduction waves observable in all fulleroids C_{60}."[3f] This statement partially summarizes the current state of knowledge of expanded fullerene electrochemistry.

A much more comprehensive account of the effect of derivatization of C_{60} on the electrochemical behavior was very recently published by Suzuki et al.[3g] However, all of the electrochemical results published to date on C_{60} derivatives, including these as well as Wudl's, have been recorded either in THF or in *o*-dichlorobenzene, where it is not possible to scan the potential beyond the fourth reduction wave. The consequence is that, to our knowledge, *there are no reports where the fifth or sixth reduction waves of any C_{60} derivatives have been observed.*

Interested by these reports[2,3] as well as by our own observation of six reversible reduction waves at very negative potentials in the cyclic voltammogram of C_{60} (and also of C_{70}) at low temperatures,[4a] we decided to measure the electrochemistry of four fullerene derivatives, **1–4**, by extending the potential window



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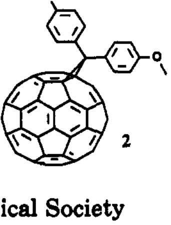

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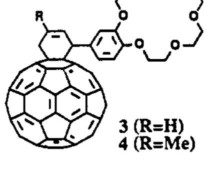

3 (R=H)
4 (R=Me)

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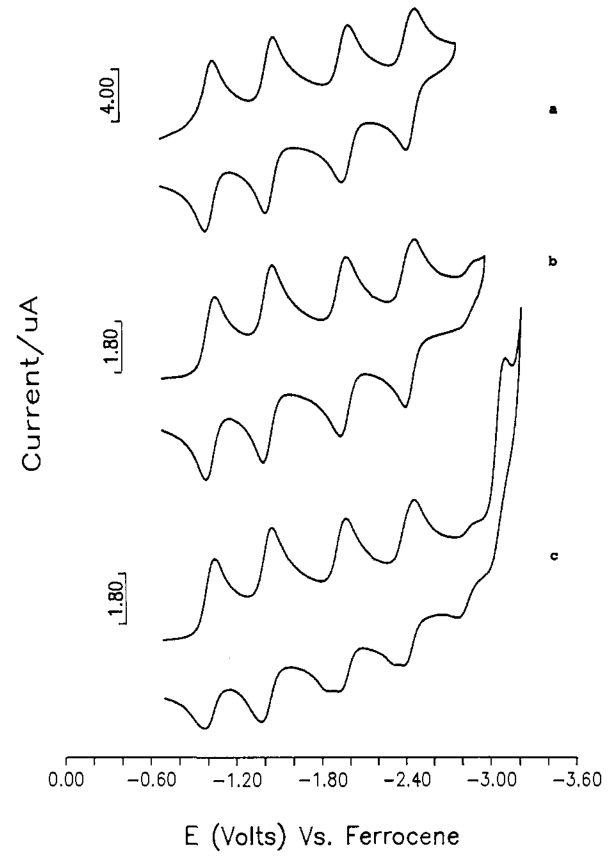

Figure 1. Cyclic voltammograms for compound **1** recorded in 0.1 M TBAPF$_6$ MeCN/toluene (1:5) at room temperature on a glassy carbon working electrode. The potential scan rate was 100 mV/s, and the reversal scan potential value was (a) −2.75, (b) −2.98, and (c) −3.20 V.

to more cathodic values than those reported by Wudl et al. and more recently by Suzuki et al.[3] If the electronic structure of the parent C$_{60}$ remains essentially unchanged, as reported,[2,3] it should be possible to extend the number of observed sequential reductions beyond four, maybe as far as the sixth, as reported for C$_{60}$.[4] But even if the electronic structures differ upon substitution, waves more cathodic than the fourth one should be observable. Since most of the fullerene derivatives exhibit cathodically shifted peaks (relative to C$_{60}$),[3] it was anticipated that probably only the fifth wave would be observed, but not the sixth, due to the limit in the potential window available.

Results

Cyclic voltammetric analysis of compound **1** in MeCN/toluene (1:5 v/v) shows that this compound exhibits four well-behaved, reversible electrochemical waves, Figure 1a. Although two isomers of this compound were separated by preparative TLC (see the Experimental Section for details), both exhibited identical electrochemical behavior, as shown in Figure 1. These isomers are presumed to be the [6,5]-fulleroid and the [6,6]-fullerene adducts, as described in the Experimental Section. Since no differences in their electrochemical behavior were noted, **1** represents either of the isomers in the present work. Potentials for the electrochemical processes are collected in Table 1 relative to the internal ferrocene/ferricinium (Fc/Fc$^+$) couple. Figure 1b corresponds to a cyclic voltammogram where the potential scan was switched at a slightly more negative value, and it shows the appearance of a much smaller fifth wave. The small current of this wave is indicative of the presence of either a contaminant or some homogeneous chemical reaction following the fourth reduction process. Notice that the anodic waves corresponding to the first four redox processes remain unchanged even after scanning through this fifth (and small) cathodic wave. If the scan is allowed to go even more negative, Figure 1c, still another cathodic wave is observed, one whose intensity is relatively normal. However, after observing this wave, the anodic scan exhibits resolved double waves in the cases of the third and fourth redox processes, Figure 1c. The Osteryoung square wave voltammetry (OSWV)[5] was recorded and is presented in Figure 5 (the OSWV of all compounds are collected together in Figure 5). Notice how much smaller the fifth wave is relative to the others, to the point where it is almost imperceptible. Also notice that there are two additional waves beyond the small fifth wave, for a total of seven. All potential values are presented in Table 1.

Since the voltammetric behavior of **3** is somewhat similar to that of the isomers of **1**, it will be discussed next. Figure 2 shows the cyclic voltammetric behavior of **3**, along with those of all of the other compounds, including C$_{60}$ for comparison. Although the cyclic voltammogram in Figure 2d has relatively low peak currents (due to low concentration of the sample), it can be appreciated that the first four reductions are reversible. As was the case with **1**, a very small wave can be seen following the fourth reduction wave, although for **3** it is almost imperceptible, especially when observing the OSWV (see Figure 5d). It is actually tempting to interpret the OSWV of **3** as consisting exclusively of five waves, with a large potential gap between the fourth and the fifth of 0.72 V. Because of the relatively low concentration, other small waves observed in Figures 2d and 5d could easily be attributed to unidentified impurities in the system. All potential values for these processes are presented in Table 1.

Before the voltammetric behavior of **2** and **4** were recorded, it was thought that the small wave following the fourth one for **1** and **3** was due to some comtamination and that there was indeed a larger than expected separation between the fourth and fifth waves. Discarding the small intermediate wave, the separation between the fourth and the next peaks for **1** (Figure 5b) would correspond to 0.63 V. Such an interpretation would indicate that the LUMOs for these systems have lost the triple degeneracy found in C$_{60}$,[6] giving rise to a doubly degenerate LUMO and a slightly higher LUMO$^+$ as a consequence of their chemical modification.[3g,6] Such an interpretation would be perfectly in-line with the concept of molecular capacitance presented by Weaver and Gao,[7] and their treatment could be applied to calculate the so-called quantum term, or the energy separation between LUMO and LUMO$^+$.[7] Calculated following their equations, these values are 0.17 and 0.21 V for **1** and **3**, respectively.

However, additional experimental results with the other derivatives somewhat contradict this interpretation. The voltammetric behavior of **2**, presented in Figures 2c and 5c, is somewhat different from that of **1**. Besides the anticipated cathodic potential shifts for all waves of **2** due to the electron-donating methoxy groups, there is a fifth wave, which is considerably larger than the corresponding one for **1**. Thus, it is not possible to assign this wave to an impurity and the observation suggests that the same is probably true for the small fifth wave of **1**, *vide supra*. All potential values for **2** are presented in Table 1. Notice from Figure 2c that the potential for the fifth wave follows closely the regular pattern expected for a triply degenerate (or nearly so) LUMO.[7] The separation between the fourth and fifth waves for **2** is 0.43 V, which is essentially the same value as that observed between all other successive pairs of waves, including those of C$_{60}$.[4a] Notice that the anodic waves corresponding to redox processes three and four are again split, as in the case of **1**. It

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Table 1. Potential Values for All of the Observed Redox Processes of All of the Compounds, $E_{1/2}$, at 25 °C[a]

compd	$E_{1/2}$(V); ΔE(V) for reductions 1-7 1	2	3	4	5	6	7
C_{60}	-0.99; 0.08	-1.41; 0.08	-1.90; 0.07	-2.38; 0.07	-2.89; 0.08		-3.26[b]
1	-1.02; 0.07	-1.43; 0.07	-1.94; 0.07	-2.41; 0.07	-2.84; 0.07	-3.04; 0.10	-3.23; 0.10
2	-1.07; 0.08	-1.46; 0.07	-1.96; 0.07	-2.42; 0.07	-2.85; 0.11	-3.06; 0.11	-3.33[c]
3	-1.10; 0.05	-1.53; 0.07	-2.09; 0.07	-2.54; 0.08		-3.25; 0.10	
4	-1.14; 0.08	-1.55; 0.08	-2.11; 0.08	-2.56; 0.08	-3.06; 0.09	-3.27; 0.10	

[a] Values are the averages of cathodic and anodic peak potentials and are reported in volts relative to the potential for internal Fc/Fc$^+$. The cathodic to anodic peak distances (ΔE) are also reported. [b] Value was estimated from OSWV. [c] Determined from the -20 °C OSWV.

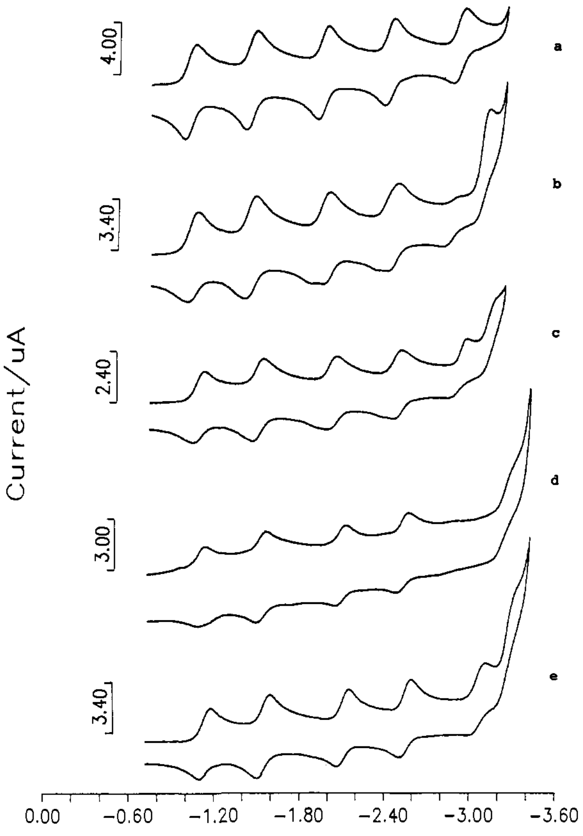


Figure 2. Cyclic voltammograms for all of the compounds studied here and C_{60} in 0.1 M $TBAPF_6$ MeCN/toluene (1:5) at room temperature on a glassy carbon working electrode. The scan rate was 100 mV/s: (a) C_{60}, (b) **1**, (c) **2**, (d) **3**, (e) **4**. All voltammograms are referenced to internal Fc/Fc$^+$.

should again be pointed out that such double anodic waves are only observed if the potential is scanned beyond the sixth reduction, as in the case of **1**; see Figure 1.

Although the intensity of the fifth wave relative to the first hour is much larger for **2** than for **1**, it is still smaller than the others, Figure 5c. Intrigued by this behavior, low-temperature voltammetric experiments were performed.[4a] Figure 3 presents the variable-temperature OSWV for compound **2**. Notice that the fifth wave grows at the expense of the sixth one as the temperature is decreased, and importantly, a seventh wave is clearly observed at the most negative potential of the solvent window. The appearance of seven waves was already described for compound **1** at room temperature, but for the latter the fifth wave was very small, Figure 5b. The pattern observed at -20 °C for **2** in Figure 3c can now be easily interpreted in terms of two overlapping patterns. Wave 6 is clearly decreasing in intensity as the temperature decreases, leaving behind a pattern consisting of six nearly equally spaced waves. The potentials for these waves at -20 °C are -1.04, -1.41, -1.92, -2.37, -2.85, and -3.33 V, with ΔE values for successive pairs of 0.37, 0.51, 0.45, 0.48, and 0.48 V, respectively. Notice that wave 6 at -3.03 V, which decreases in intensity as the temperature decreases in Figure 3c, has been excluded for this series. Upon doing so, the result is a sequence that follows the behavior of C_{60} very closely.

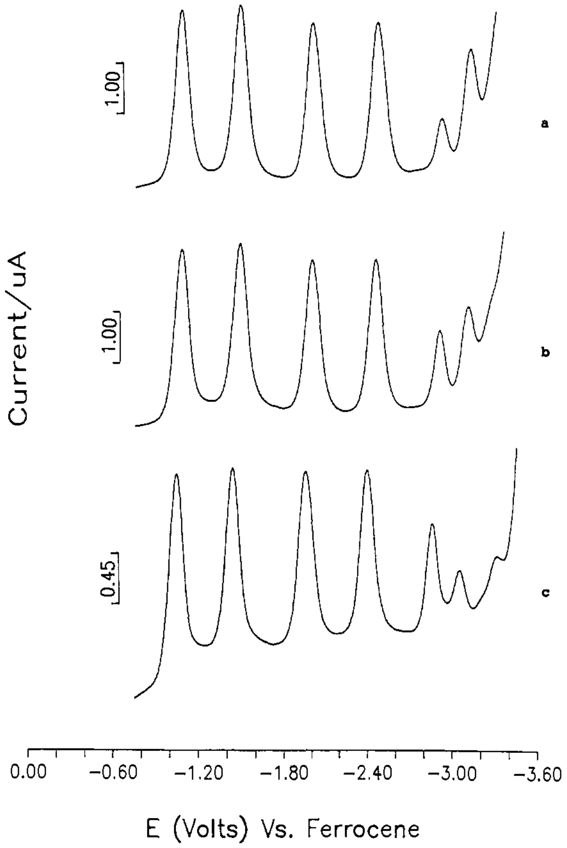


Figure 3. OSWV for compound **2** in 0.1 M $TBAPF_6$ MeCN/toluene (1:5) as a function of temperature. The working electrode was glassy carbon, and the voltammograms were obtained using a sweep width of 25 mV, a frequency of 15 Hz, and a potential step of 4 mV at (a) 25, (b) 15, and (c) -20 °C.

The low-temperature observations with **2** indicate that there must be a chemical step that follows the fourth electrochemical reduction that partially transforms the tetraanion (2^{4-}) to some other species, defined for the moment as (2^{4-})′, and subsequent reduction of the latter is responsible for the observation of wave 6. The slanted prime symbol is used outside the parenthesis to indicate that the tetraanion is transformed via an unspecified chemical, not electrochemical, reaction. Waves 5 and 7 correspond to the subsequent reductions of intact (2^{4-}) to form (2^{5-}) and (2^{6-}), respectively. Lowering the temperature must result in the stabilization of (2^{4-}) relative to (2^{4-})′. In addition to this homogeneous chemical reaction following the first four electron reductions, there must be an additional reaction that takes place after the sixth reduction, which results in the observation of the double anodic waves. Before offering possible structural suggestions and reaction schemes to explain these observations, additional experimental results are presented now.

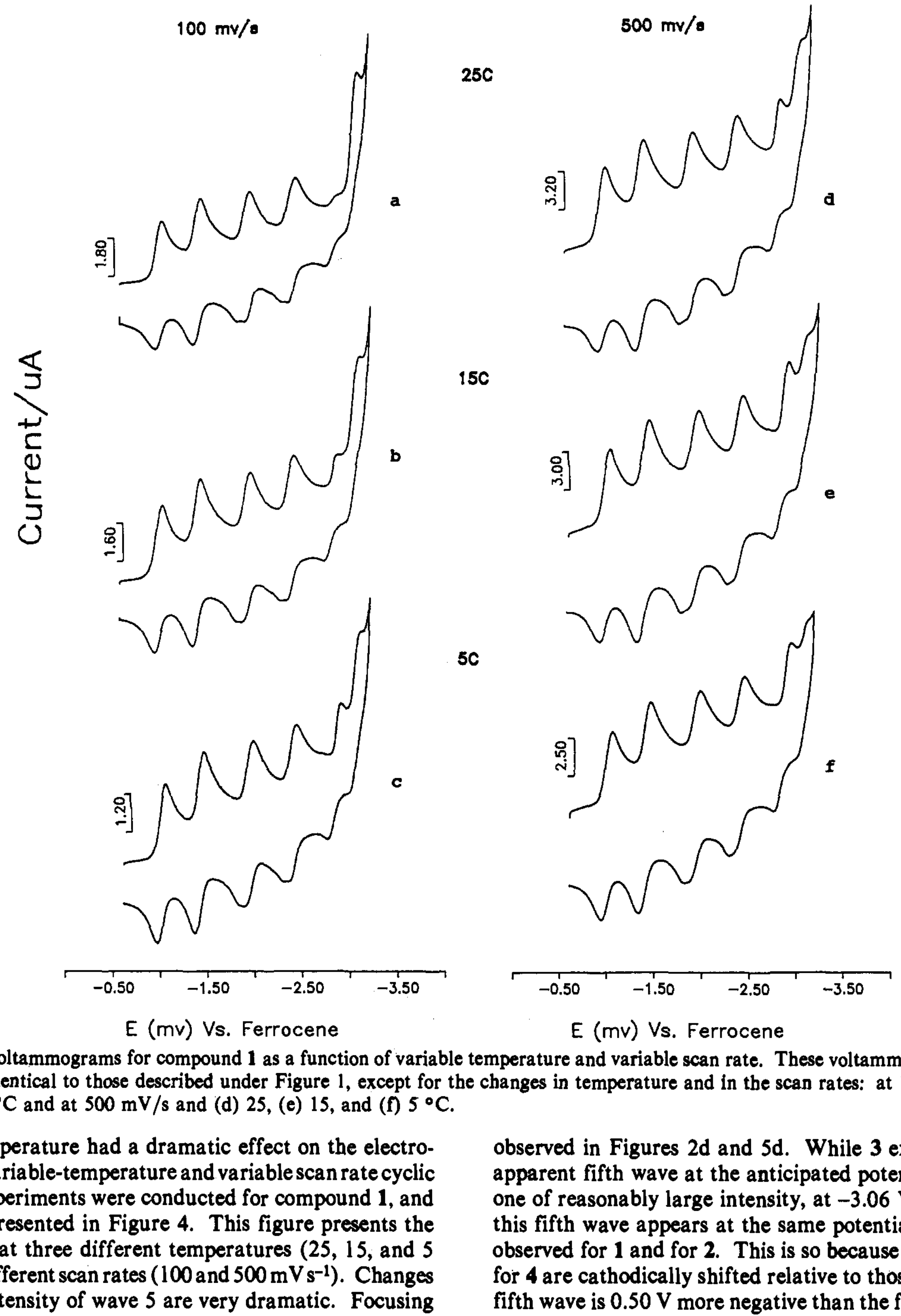


Figure 4. Cyclic voltammograms for compound **1** as a function of variable temperature and variable scan rate. These voltammograms were recorded using conditions identical to those described under Figure 1, except for the changes in temperature and in the scan rates: at 100 mV/s and (a) 25, (b) 15, and (c) 5 °C and at 500 mV/s and (d) 25, (e) 15, and (f) 5 °C.

Since low temperature had a dramatic effect on the electrochemistry of **2**, variable-temperature and variable scan rate cyclic voltammetric experiments were conducted for compound **1**, and the results are presented in Figure 4. This figure presents the results obtained at three different temperatures (25, 15, and 5 °C) and at two different scan rates (100 and 500 mV s^{-1}). Changes in the relative intensity of wave 5 are very dramatic. Focusing on the lowest temperature and the fastest scan rate voltammogram (Figure 4f), it is evident that redox pair 5 is essentially reversible under these experimental conditions. It is thus possible to approximate the behavior of **2** by simply lowering the temperature and/or increasing the scan rate while recording the voltammogram of **1**. These observations are perfectly consistent with the occurrence of a homogeneous chemical reaction of the tetraanion (1^{4-}) to another species, (1^{4-})$'$, which is inhibited at lower temperatures and delayed by fast potential scanning. Thus, it is fair to state that both **1** and **2** behave similarly, with the only difference that **2** seems to be more stable than **1** after multiple electron reductions. However, both systems undergo similar homogeneous chemical reactions, but at slightly different rates.

Finally, the cyclic and OSWV behavior of **4** is presented in Figures 2e and 5e. Notice how different its behavior is compared to that of **3**. It should be added here that the cyclic and OSWV behavior of **3** does not change when the temperature is decreased nor if the potential is scanned faster. It remains identical to that observed in Figures 2d and 5d. While **3** exhibits a lack of an apparent fifth wave at the anticipated potential, **4** does exhibit one of reasonably large intensity, at −3.06 V. Serendipitously, this fifth wave appears at the same potential as the sixth wave observed for **1** and for **2**. This is so because all reduction waves for **4** are cathodically shifted relative to those for **1** and **2**. This fifth wave is 0.50 V more negative than the fourth wave at −2.56 V, as anticipated for a regular sequence. Therefore, it is assigned to reduction process 5 in Table 1. The last wave observed at −3.27 V falls almost at the exact potential as the last one observed for **3** (−3.25 V). Interestingly, neither **3** nor **4** exhibits the doubly split anodic waves that were observed for both **1** and **2**.

A summary of the results now follows. Compounds **2** and **4** exhibit fifth reduction waves at potentials that follow a reasonably regular pattern and thus behave much more as underivatized C_{60}. However, the fifth wave is never as intense as the previous four, not even at very low temperatures and using fast scan rates. There is a sixth wave in both cases which is very close to the fifth one. Compounds **1** and **3** exhibit either very small (**1**) or almost imperceptible (**3**) fifth waves at the expected potential. Lowering the temperature and/or scanning the potential faster results in a larger fifth wave for **1**, but not for **3**. In the case of **1** and **2**, it is possible to identify a seventh wave at very negative potentials along with some split anodic waves when the potential is scanned beyond the sixth reduction. From the variable-temperature

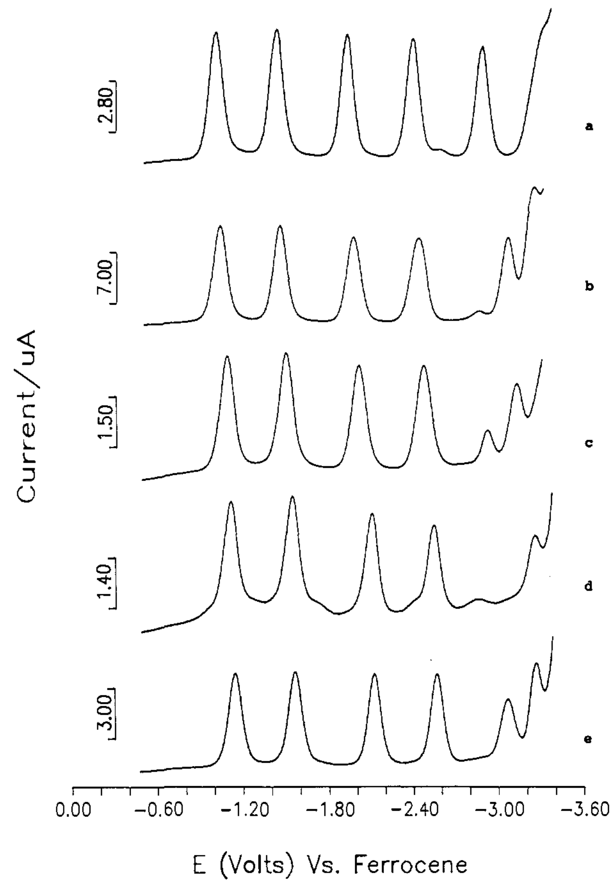
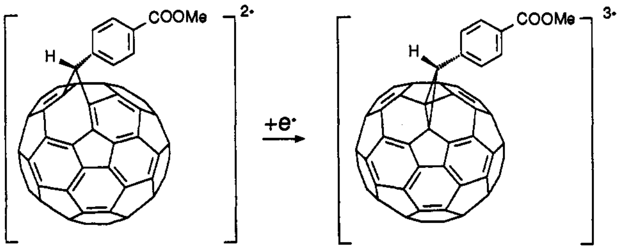


Figure 5. OSWV for all of the compounds studied here and for C_{60} at room temperature. All other conditions are identical to those described under Figure 3: (a) C_{60}, (b) **1**, (c) **2**, (d) **3**, (e) **4**. All voltammograms are referenced to internal Fc/Fc^+.

Scheme 1

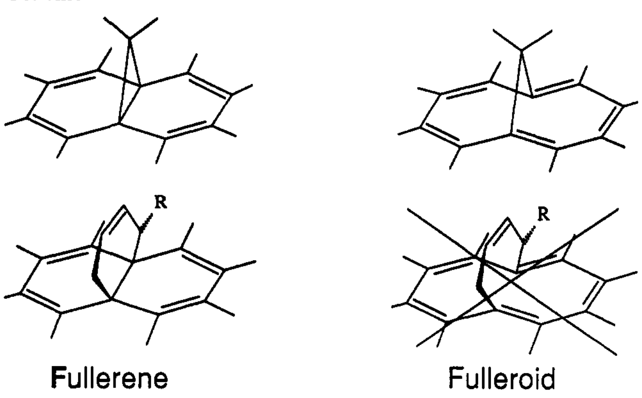


experiments of **1** and **2** it is possible to identify reduction wave 6 with an electrochemical process that is not connected with either reduction steps 5 or 7.

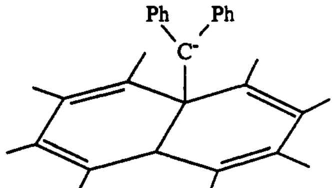
Discussion

After considerable debate over the correct bond structure of diazomethane-derivatized C_{60}'s, the question seems to have been finally resolved recently.[8] The original issues revolved around the possible formation of [5,6] and [6,6] adducts and also around the question of whether the derivatives could be properly described as methanofullerenes or as expanded fulleroids; see Schemes 1 and 2 for explanations of the nomenclature.[8] The conclusion seems to be that all possible modes of attack do exist [5,6] and [6,6] adducts) and that all of the possible isomers do form.[8] However, after thermalization the methanofullerene form attached to a [6,6] bond always seems to predominate.[8]

Scheme 2



Scheme 3



(Charge on fullerene = no. e transferred -1)

Recent results from Wudl et al., published only in preliminary form as an abstract, seem to suggest it is possible, under certain circumstances, to synthesize and to isolate [5,6]-expanded fulleroids; see Scheme 1.[9] In this abstract,[9] the authors claim that the [5,6]-expanded fulleroid adduct can be irreversibly converted to a [6,6] methanofullerene by electrochemical reduction with three electrons, Scheme 1. Further details of this work must await full publication of the results.

For simplicity in the presentation and discussion of the results, only that part of the fullerene derivative structures involving the [6,6] juncture will be presented in subsequent arguments, Scheme 2. The presence of a fulleroid structure is not possible in the case of compounds **3** and **4**. These must have the fullerene structure depicted in Scheme 2, since a delocalized annulene structure is not possible. Furthermore, Diels–Alder adducts have only been reported to form at [6,6] junctures, so the structure of **3** and **4** must be the one depicted in Scheme 3.[2]

It seems instructive to begin with a discussion, *a priori*, concerning some possible chemical transformations that might take place in these systems, especially after several electron transfers. It has already been established in the Results section that some homogeneous chemical reactions are occurring after the electrochemical reductions of all of these systems.

One immediate possibility that comes to mind is the formation of a carbanion intermediate, the product of bond breakage, as shown in Scheme 3. Such a stable diphenylcarbanion would result directly from bond breakage of a multiply reduced methanofullerene or fulleroid structure. Only the broken methanofullerene structure is presented in Scheme 3, but it must be kept in mind that it is also possible to have the analogous carbanion of the fulleroid, if the latter form is present to any extent, *vide infra*. Such carbanions should be favored after multiple reductions of the fullerene derivative. If carbanion formation occurs after say, the fourth reduction, then the charge remaining on the fullerene sphere would equal -3. It has been shown via theoretical calculations that π- and σ-donors, as well as π-acceptors, on a cyclopropane ring favor this kind of bond breaking, as opposed to breaking of the bond that is opposed to the substituted

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[8] (a) Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eirmann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479. (b) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231. (c) Osterodt, J.; Nieger, M.; Windscheif, P.-M.; Vögtle, F. *Chem. Ber.* **1993**, *126*, 2331.

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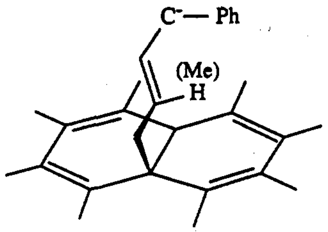
Scheme 4



(Charge on fullerene = no. e⁻ transferred -1)

bridgehead carbon.[10] The additional Coulombic strain imposed on the overall molecule upon multiple electron transfers should favor the formation of such diphenylcarbanions of **1** and **2**. However, **2** should exhibit a more destabilized intermediate carbanion than **1** because of the location of the two methoxy substituents on the *para* positions of the phenyl groups. Another way of stating this is to say that **2** should be less susceptible than **1** to form a carbanion after multiple electron transfers and should thus retain its integrity better.

Formation of similarly stabilized carbanions is also possible for **3** and **4**. The resulting carbanions would be stabilized by a phenyl group and by a vinyl substituent, Scheme 4. It would be anticipated that the extra methyl group found on the cyclohexenyl ring of **4** would again lead to destabilization of the intermediate carbanion. Again, stating it in reverse, the methyl group would stabilize the original structure and disfavor its breakage to form the intermediate carbanion.

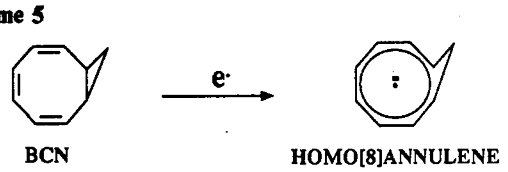
We believe that formation of such a carbanion structure could be responsible for the voltammetric observations after the fourth electron reductions of **3** and **4**. In the case of **3**, there seems to be a total absence of a reduction wave that corresponds to $3^{4-} \rightarrow 3^{5-}$, Figures 2d and 5d. Thus the last wave observed at −3.25 V must correspond to the reduction of the carbanionic product, $(3^{4-})'$, the structure of which is presented in Scheme 4. It was not possible to see the fifth reduction even after decreasing the temperature and increasing the scan rate. Thus, chemical conversion of 3^{4-} to a modified form, $(3^{4-})'$, must be very fast and thermodynamically favored.

On the other hand, the intermediate fifth wave at −3.06 V was clearly visible for compound **4**, Figures 2e and 4e, although its intensity was not as high as that for the previous four waves. It is therefore possible to observe the reduction of 4^{4-} to 4^{5-}, before it has enough time to open up completely to form $(4^{4-})'$. As stated above, the extra methyl group must destabilize the formation of the carbanion, thus inhibiting the homogeneous decomposition reaction and leading to partial observation of this wave.

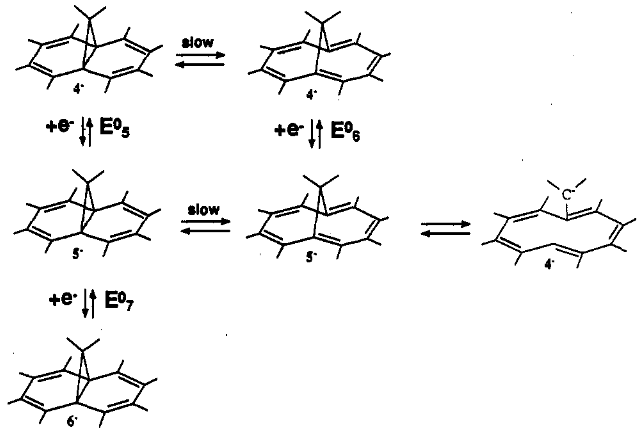
It has already been pointed out that **1** and **2** exhibit at least two independent homogeneous chemical reactions. These are reflected in (1) the small size of the fifth wave for both compounds and (2) in the observation of a double anodic wave for redox processes 3 and 4, Figures 1, 2, and 5. These processes have been shown experimentally to be independent. The small size of the fifth wave is more pronounced in **1** than in **2**. It can be increased by lowering the temperature and/or by increasing the scan rate, Figures 3 and 4. The other observation, the double anodic waves, is only present if the potential is scanned past the sixth reduction wave, Figures 1 and 2.

The only other homogeneous chemical reaction that could play an important role is relevant only for compounds **1** and **2**. That reaction is the methanofullerene–fulleroid equilibrium that has been described by Wudl et al.[9] This reaction is analogous to the dinorcaradiene–1,6-methano[10]annulene equilibrium, which has been extensively investigated.[11] The question is particularly relevant in the present discussion because the methanofullerenes **1** and **2** are related to their corresponding fulleroids by the same bond-shifting reaction as in the case of the dinorcaradiene–annulene; see Scheme 2. It can be immediately appreciated that a methano-bridged [6,6] juncture on C_{60} will be more rigidly held out of planarity (and thus favor the methanofullerene form) than in the model methano[10]annulene, where there is more flexibility. Indeed, it has been shown that the equilibrium is shifted to the homoaromatic annulene species in the case of 1,6-methano[10]annulene.[12] As already mentioned, the reverse is true in the case of the fullerene derivative.

Scheme 5



Scheme 6



An important point to probe is how are these equilibria affected by electron reductions, if at all. Since **1** and **2** are successively reduced with multiple electrons, this question is particularly germane. The one-electron reduction of 1,6-methano[10]-annulene is known to result in the formation of an anion radical where the unpaired electron occupies a HMO orbital of ψ-symmetry.[13] This observation is consistent with a planar, homoaromatic anion radical. A similar observation has been made with bicyclo[6.1.0]nona-2,4,6-triene (BCN), which upon reduction, is transformed from BCN into the homo[8]annulene anion radical, Scheme 5.[14] However, the BCN anion radical was also found to be present simultaneously, using ESR spectroscopy.[14] Thus, an equilibrium between the closed and the open (homoaromatic) forms was detected, which favored the latter.[14]

On the basis of our observations, it is not possible to assign the two observed homogeneous chemical processes unequivocally in the cases of **1** and **2**. However, one can speculate that the fullerene–fulleroid equilibrium is displaced toward the latter species after the fourth electron reduction and that both forms open up to the intermediate carbanion after they are further reduced. It is also possible that the sequence is actually reversed, that is, that carbanion formation precedes bond shift isomerization. One of these reaction sequences is represented in Scheme 6. Probably the sixth reduction corresponds to the formation of the pentaanionic fulleroid, while the seventh reduction wave could be a final electron transfer, leading to the formation of the intact hexaanion. The observed split anodic waves, which are very close in potential, could arise from oxidation of the open carbanionic and from the intact closed forms of the reduced compounds.

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Further studies involving ion-pairing effects and other spectroscopic techniques are currently underway to assign the mechanistic details of these homogeneous reactions. Of particular interest is the question of whether it is possible to generate a multiply reduced, highly negatively charged open form of these compounds, which might be important in the preparation of endohedral metallic complexes.

Experimental Section

Electrochemical Measurements. Studies were performed using a BAS-100W electrochemical analyzer, interfaced with a Hewlett-Packard ColorPro plotter. The working glassy carbon electrode was 3 mm in diameter and was polished with 1/4 μm diamond polishing compound (Metadi II) from Buehler using a polishing microcloth from the same manufacturer.

A silver wire was used as a pseudoreference electrode, and it was cleaned by direct immersion into dilute nitric acid for approximately 3 min and then polished with a razor blade prior to usage. The platinum wire used as the counter electrode was cleaned by heating in a flame for approximately 30 s.

The supporting electrolyte ($TBAPF_6$) was purchased from Fluka (>99%) and was recrystallized twice from an ethanol/H_2O (95:5) mixture and dried in vacuo prior to use.

All cyclic voltammograms, unless otherwise specified, were run at a scan rate of 100 mV/s, and all OSWV were obtained using a sweep width of 25 mV, a frequency of 15 Hz, and a step size of 4 mV.

The electrochemical cell that was used for all of these experiments is similar to that previously described.[4a] It was designed and constructed in-house from Pyrex glass using tungsten-glass seals to make all electrochemical connections. The cell was initially charged with the supporting electrolyte and the fullerene sample (typically 1 mg of the latter) and pumped to approximately 10^{-5}–10^{-6} mmHg for 5 h. Then 3 mL of the MeCN/toluene solvent mixture (1:5) was vapor transferred directly through the vacuum line and into the cell. The solvent mixture was also prepared by direct vapor transfer of the components after three freeze–pump–thaw cycles were applied to each, while pumping the individual solvents down to 10^{-5}–10^{-6} mmHg for approximately 15 min.[4a] After direct solvent transfer into the electrochemical cell, the whole ensemble was disconnected from the vacuum line and allowed to warm to room temperature. Therefore, all electrochemical measurements were obtained while the cell was kept at the vapor pressure of the prevailing solvent.

Synthesis. The preparation of compound **1** has already been reported,[15] but the procedure for its separation into two isomers has not been described. Compounds **3** and **4** were prepared by the Diels–Alder reaction of the corresponding 4′-(benzo-18-crown-6)buta-1,3-diene and C_{60}, and this is described in detail.

Compound 1. Compound **1** was prepared in 42% yield as previously described.[15] Two closely spaced bands were separated by preparative TLC on silica gel using toluene/methanol, 2:1. The two compounds showed almost identical ^{1}H-NMR spectra and ES-MS molecular ions. On the basis of ^{1}H-NMR assignments,[1] these isomeric compounds correspond to the [6,6]-fullerene and the [6,5]-fulleroid addition products, and these were found to be in an approximate ratio of 1:1.

Compound 2. 4,4′-Dimethoxybenzophenone hydrazone (51 mg, 0.2 mmol) was oxidized with MnO_2 (100 mg, 1.15 mmol) in 10 mL of THF in the usual way to give the corresponding diazo compound (0.2 mmol), which was used without further purification. The diazo compound solution was added to a purple solution of C_{60} (144 mg, 0.2 mmol). After stirring overnight, TLC of the reaction mixture showed two spots, with $R_f = 0.40$ and 0.79 (using 7:1 hexane:toluene). The product mixture was worked up in the usual manner and chromatographed in two portions (silica gel, hexane/toluene) to yield 84 mg of compound **2** (two isomers) and 32 mg of recovered C_{60}. A small amount of a more polar material (probably a bis-adduct) was also obtained. ^{1}H-NMR in ppm: 6.71, 6.9, 7.2, 7.9 (m, aromatic H's), 3.75, 3.84, 3.86 (methoxy groups). MS: (crown ether tagged as described in ref 15) m/z for MX = 1387. Thermalization of the expected [6,6] and [6,5] isomer mixture (toluene, reflux for 2 days) gave a single isomer. The product used for the electrochemical experiments is probably a mixture of [6,6] and [6,5] isomers.

4′-(Benzo-18-crown-6)buta-1,3-diene. Allyltriphenylphosphonium bromide (1.05 g, 2.75 mmol) was stirred with freshly distilled ethyl ether (15 mL) under nitrogen at room temperature while 1.8 M phenyllithium in cyclohexane and ethyl ether (2.2 mL, 3.96 mmol) was added dropwise. After 4 h a solution of 4′-formyl-benzo-18-crown-6 (0.77 g, 2.26 mmol) in ether/THF was added, and stirring was continued for an additional 3.5 h. The mixture was then treated with water (18 mL). The two layers were separated, and the aqueous layer was extracted with ether (4 × 20 mL). The combined organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to yield a brown residue. It was then chromatographed on neutral alumina and eluted with petroleum ether/2-propanol (10:1) to give the corresponding diene as white crystals (0.40 g, 49%). Mp: 77–79 °C. ^{1}H-NMR ($CDCl_3$): 7.0–6.1 ppm, m, 6H; 5.4–5.1, m, 2H; 4.2–3.6, m, 20H. ESI-MS (in KOAc) $m/e = 4.04$. Anal. Calcd for $C_{20}H_{328}O_6$ with 0.05 equiv of NaCl: C, 65.39; H, 7.68. Found: C, 65.72; H, 7.27.

Compound 3, To C_{60} (70.10 mg, 0.023 mmol) in toluene (6.5 mL) was added the diene (8.44 mg, 0.023 mmol) in toluene (1.0 mL) at room temperature. The resulting mixture was warmed to 70 °C for 22 h under nitrogen. Column chromatography on silica with toluene/chloroform/ethanol (absolute) (10:10:1) yielded **3** as a dark brown solid (7.37 mg, 30%). EIS: (K^+), m/z 1124. ^{1}H-NMR (CS_2–acetone-d_6) in ppm: 7.28–7.13, m, 3H; 6.89, d $J = 8.2$ Hz, 1H; 5.34, bs, 1H; 4.37, ABX $J = 14.3$, 7.1 Hz, 2H; 4.10–4.07, m, 2H; 4.04–4.01, m, 1H; 3.85–3.78, m, 4H; 3.66–3.58, m, 13H.

Compound 4: 25% yield. EIS: (K^+), m/z 1138. ^{1}H-NMR (CS_2–acetone-d_6) in ppm: 7.20–6.80, m, 4H; 5.23, bs, 1H; 4.45, d $J = 14$ Hz, 1H; 4.07–3.90, m, 5H; 3.82–3.73, m, 4H; 3.62–3.55, m, 12H; 2.50, s, 3H.

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