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Electrochemically Induced Isomerization of a Fulleroid to a Methanofullerene

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In the rapidly growing field of fullerene functionalization,[1,2] the addition of diazo compounds to buckminsterfullerene, C_{60}, is one of the most useful reactions in terms of versatility, chemical yield, stability, and characterization of the products.[3–5] The reaction of substituted diazo compounds with C_{60} generates a mixture of monoaddition products across the 5,6 (fulleroids, methanoannulene-type bonding) and the 6,6 (methanofullerenes, cyclopropane bonding)[6] ring fusions. With the exception of [5,6] $C_{61}H_2$,[7] all known fulleroids are thermally convertible to their [6,6] isomers.[3–6] In some cases, the thermal isomerization can be very sluggish. Here we show, for the first time, that addition of a third electron to a fulleroid isomerizes it to the methanofullerene.

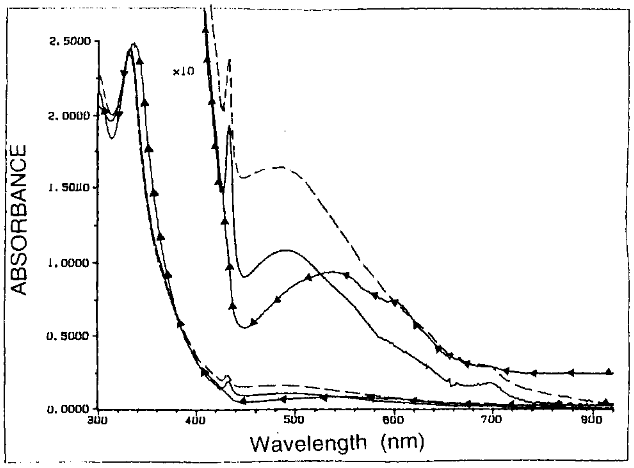
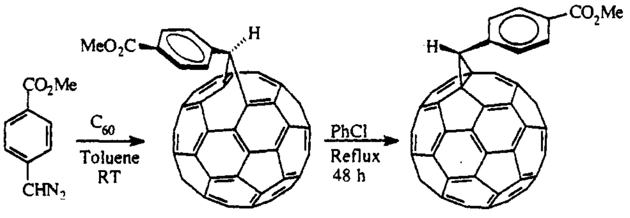


Figure 1. Filled triangles, ultraviolet–visible spectrum of **2** (10^{-4} M) in ODCB/0.15 M TBAF; broken line, ultraviolet–visible spectrum of **3** (10^{-4} M) in ODCB/0.15 M TBAF; full line, ultraviolet–visible spectrum of **2** (10^{-4} M) in ODCB/0.15 M TBAF after electrolysis at −1.5 V vs Ag/Ag$^+$.

Scheme 1



1 **2** **3**

The electronic spectra of C_{60} and the fulleroids are almost superimposable, and those of methanofullerenes are different (cf. Figure 1),[5,6] reflecting the difference in "π" electron count (60 for the former and 58 for the latter).

Though six electrons can be reversibly added to C_{60},[8] the influence of the π-electron count on cyclic voltammetry (CV) has not yet been investigated in detail. Saturation of a double bond of C_{60} in methanofullerenes causes a negative shift of about 50–150 mV for the first three waves.[3] Here we report the synthesis and electrochemical investigation on a *p*-(methoxycarbonyl)-phenyl-substituted fulleroid (**2**) and its methanofullerene isomer (**3**). Further, by a combination of CV and UV–vis spectrophotometry we show that (1) **2** and **3** have only very slightly different electron acceptor character and (2) **2** is converted to **3** upon addition of a third electron to **2**.

The synthesis of **2** and **3** was carried out according to Scheme 1. Equimolar amounts of diazo compound **1** and C_{60} produce, upon chromatographic separation (purity >95% by ^1H NMR), **2** as the main product. On the basis of ^1H–^{13}C J_{C61-H} = 142.5 Hz and UV–vis (Figure 1), the fulleroid structure **2** was assigned to this compound.[6] Heating **2** for 48 h afforded a clean conversion into **3**. Methanofullerene **3** is a cyclopropane, with bridgehead carbons at 74.8 ppm, J_{C61-H} = 163.4 Hz, and a diagnostic UV–vis peak at ca. 430 nm[6] (Figure 1).

CV measurements of **2** and **3** were carried out in 1,2-dichlorobenzene (ODCB), which allows the detection of four

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[1] (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (d) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423. (e) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213. (f) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050. (g) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630. (h) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (i) Miller, J. S. *Adv. Mater.* **1991**, *3*, 262. (j) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940. (k) Diederich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678. (l) *Acc. Chem. Res.* **1992**, *25*, 1–200. (m) *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters;* Hammond, G. S.; Kuck, V. J., Eds.; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992. (n) Schwartz, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678.

[2] (a) Taylor, R.; Walton, D. R. M. *Nature* **1993**, *363*, 685. (b) Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1138.

[3] (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *254*, 1186. (b) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157. (c) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7300. (d) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301. (e) [5,6]-$C_{61}H_2$ and [6,6]-$C_{61}H_2$ show a very similar relationship of their first and second redox steps. Compound **3**'s behavior is as observed with other methanofullerenes (see refs 3a–d).

[4] (a) Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656. (b) Friedman, S. H.; DeCamp, D. L.; Sijbesma, R.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506. (c) Sijbesma, R.; Srdanov, G.; Wudl, F.; Castoro, J. A.; Wilkins, C.; Friedman, S. H.; DeCamp, D. L.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6510. (d) Prato, M.; Suzuki, T.; Wudl, F.; Lucchini, V.; Maggini, M. *J. Am. Chem. Soc.* **1993**, *115*, 7876. (e) Prato, M.; Bianco, A.; Maggini, M.; Scorrano, G.; Toniolo, C.; Wudl, F. *J. Org. Chem.* **1993**, *58*, 5578.

[5] Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231.

[6] Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479. Cf.: Arnz, R.; Carneiro, J. W. M.; Klug, W.; Schmickler, H.; Vogel, E.; Breuckmann, R.; Klärner, F.-G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 683.

[7] Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829.

[8] Xie, Q.; Perez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, 114, 3978; Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 782.

0002-7863/94/1516-8364$04.50/0

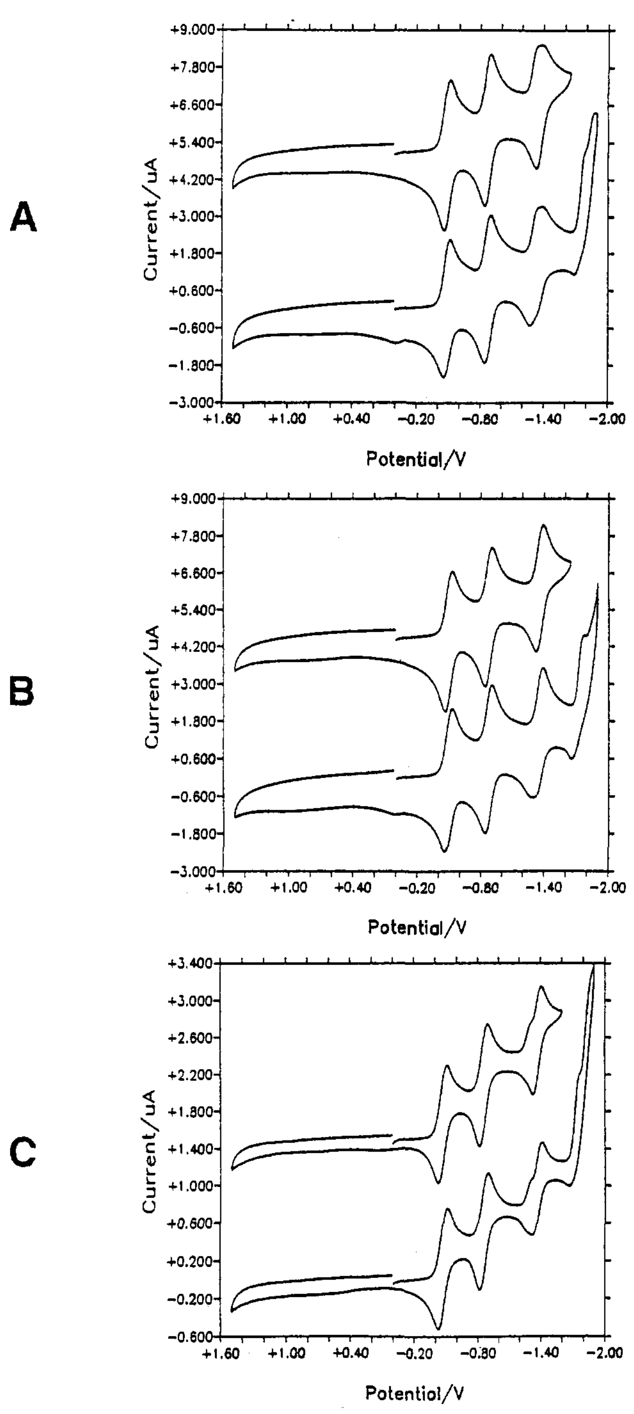

Figure 2. (A) Cyclic voltammogram of **2** (10^{-3} M) at 100 mV/s, ODCB/0.15 M TBAF vs Ag/Ag$^+$; lower scan extended to four waves. (B) Cyclic voltammogram of **3** (10^{-3} M) at 100 mV/s, ODCB/0.15 M TBAF vs Ag/Ag$^+$. (C) Cyclic voltammogram of **2** (10^{-3} M) at 10 mV/s, ODCB/0.15 M TBAF vs Ag/Ag$^+$.

reversible reduction waves, and in 5:1 toluene/acetonitrile, which allows electrochemical studies at more negative potentials.[8]

The strictly reversible[9] first and the second reduction waves in the CVs of compounds **2** and **3**, in line with their electron count, show that **2** is easier to reduce than **3** by 12 mV[3e] (Tables 1, 2; Figures 2, 3), a small number in view of the different electronic character of the two isomers (Figure 2A,B). In scans which extend to the fourth reduction wave, the return signals in both cases appear broadened and slightly shifted (Figure 2A–C, lower scan).

A more dramatic difference occurs at the third reduction step. A simple, reversible behavior of the methanofullerene **3** (Figure 2B) is contrasted by a structured signal for the fulleroid **2** (Figure 2A). In the latter, the reduction signal is composed of two peaks, with scan-rate-dependent relative intensities (Figure 2A,C, same amplitude for both components at 100 mV/s; lower and higher amplitude for the more positive and the more negative component, respectively, at 10 mV/s). The corresponding return wave (reoxidation to the dianion) is not affected, if the scan is restricted to three waves (see above).

The behavior of the third reduction of **2** was investigated by applying multiple sweeps without returning to the neutral species. At 500 mV/s only the more positive signal is observed, and at 100 mV/s the first scan exhibits the same split peak as in the full range scan.

CV in 5:1 toluene/acetonitrile showed that the fourth and fifth reductions of both compounds exhibit nearly identical, scan-rate-independent, structured signals. The fifth waves appear slightly broadened.[10]

The UV–vis spectrum of a sample of electrolysis of **2** at −1.5 V vs Ag/Ag$^+$ (just beyond the third wave) was superimposable with that of a sample of **3**[11] (cf. Figure 1).

We conclude from this that isomerization of **2** into **3** occurs only upon addition of a third electron to **2**; the more positive component of the third wave is the third reduction step of **2**, and the negative component is due to **3**. While one can speculate on a possible isomerization mechanism,[12] it is not surprising that the cyclic voltammograms of both compounds are superimposable in the fourth to fifth wave region due to the electrochemical conversion of the fulleroid **2** into the methanofullerene **3** at the third wave.

The data presented in this communication provide evidence for novel pathways for the isomerization of a fulleroid into a methanofullerene and are part of our current investigations to gain better understanding of the reaction mechanisms involved.[13]

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Supplementary Material Available: Experimental details for the preparation of **2** and **3**, tables of CV peak potentials, a slow scan voltammogram of **2**, and a cyclic voltammogram of **3** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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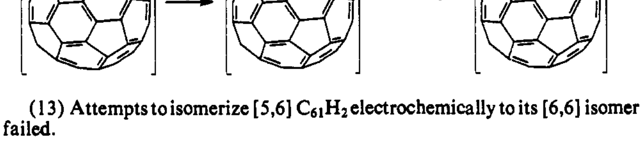
[9] The processes are electrochemically reversible (peak-to-peak separation is 0.06 V) and chemically reversible (area under forward and reverse waves is the same).

[10] Osteryoung square wave voltammetry (OSWV) experiments were also carried out in 5:1 toluene/acetonitrile but did not give additional information: Osteryoung, J.; O'Dea, J. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1986; Vol. 14.

[11] After completion of the bulk electrolysis, the potential was returned to −0.1 V and the sample subjected to UV–vis spectroscopy.

[12] Possible isomerization mechanism:



[13] Attempts to isomerize [5,6] $C_{61}H_2$ electrochemically to its [6,6] isomer failed.