JOC Article

Electron-Acceptor-Induced Isomerization of Aryl [6,5] Open Fulleroids to [6,6] Closed Methanofullerenes and the Electrochemical Evaluation of Their Free Energy Difference

Melvin H. Hall*

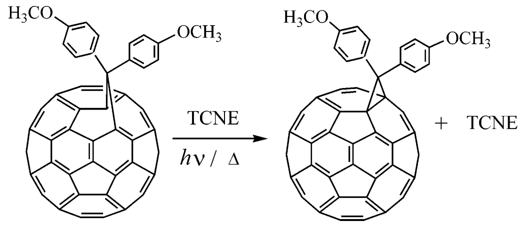
Department of Chemistry and Physics, LaGrange College, LaGrange, Georgia 30240

Philip Shevlin,* Huajun Lu, Anthony Gichuhi, and Curtis Shannon

Department of Chemistry, Auburn University, Auburn, Alabama 36849

mhall@lagrange.edu

Received October 18, 2005



The thermal and photochemical rearrangements of a series of aryl substituted [6,5] open fulleroids to [6,6] closed methanofullerenes are accelerated in the presence in of electron acceptors. These [6,5] open fulleroids, facilitated by electron acceptors, rearrange thermally by a zwitteronic-type intermediate, while the photochemical reactions proceed via an excited-state electron-transfer process. The oxidation potentials of these [6,5] open fulleroids and their corresponding [6,6] closed methanofullerenes isomers have been evaluated. The free energy difference between the [6,5] open fulleroids and their corresponding [6,6] closed isomers have been estimated from the difference in their oxidation potentials.

Introduction

The addition of diazo compounds to C_{60} generates fullerene derivatives with a one-carbon bridge across a carbon−carbon bond.[1] Although there are hypothetically four possible ways to add a one carbon bridge to C_{60}, only the [6,5] open fulleroids, **1**, and the [6,6] closed methanofullerenes, **2**, have been observed experimentally. The [6,5] open fulleroids **1** are the kinetically controlled product, whereas the [6,6] closed methanofullerenes **2** are the products of thermodynamic control.[2] The [6,5] open isomers have been reported to rearrange thermally,[3] photochemically,[4] electrochemically,[5] and under acid catalysis[6] to the methanofullerenes, which have attracted much attention as useful functionalized fullerene derivatives with electronic structures which largely preserve the C_{60} chromophore.[7,8] Although several workers have observed zero-order kinetics for the thermal [6,5] open to [6,6] closed rearrangement,[3,9] we have demonstrated that a photochemical step in the thermal rearrangement is

---

(1) (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, O. *Science* **1991**, *245*, 1186−1888. (b) Vasella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388−1390. (c) Wudl, F. *Acc. Chem. Res.* **1992**, *25*, 157−161.

(2) For reviews, see: (a) Diederich, F.; Isaacs, L.; Philip, D. *J. Chem. Soc. Rev.* **1994**, 243−255. (b) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: Stuttgart, 1994. (c) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317−323. (d) Taylor, R. *Lecture Notes on Fullerene Chemistry*; Imperial College Press: London, 1999. (e) Yurovskaya, M. A.; Trushkov, I. V. *Russ. Chem. Bull.* **2002**, *51*, 367−443.

(3) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; Goldschmidt, R. J.; King, R. C. *J. Am. Chem. Soc.* **1995**, *117*, 5492−5502.

(4) (a) Janssen, R. A. J.; Hummelen, J. C.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 544−545. (b) Ceroni, P.; Conti, F.; Corvaja, C.; Maggini, M.; Paolucci, F.; Roffia, S.; Scorrano, G.; Toffoletti, A. *J. Phys. Chem. A* **2000**, *104*, 156−163.

(5) Eiermann, M.; Wudl, F.; Prato, M.; Maggini, M. *J. Am. Chem. Soc.* **1994**, *116*, 8364−8365.

(6) Gonzalez, R.; Hummelen, J. C.; Wudl, F. *J. Org. Chem.* **1995**, *60*, 2618−2620.

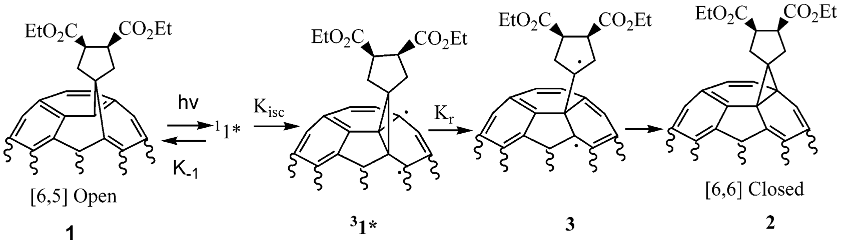
(7) (a) Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 1359−1363. (b) Arias, F.; Echegoyen, L.; Wilson, S. R.; Lu, Q. *J. Am. Chem. Soc.* **1995**, *117*, 1422−1427.

(8) (a) Martin, N.; Sánchez, L.; Illescas, B.; Pérez, I. *Chem. Rev.* **1998**, *98*, 2527−2547. (b) Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593−601.

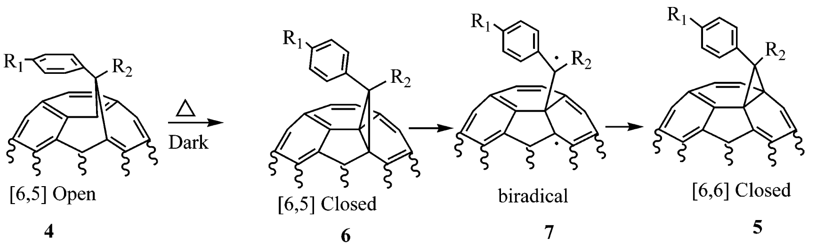
(9) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532−538.

10.1021/jo0521706 CCC: $33.50

SCHEME 1



SCHEME 2



a) R_1=OCH_3; R_2=p-$C_6H_4OCH_3$,

b) R_1=OCH_3; R_2=CH_3

c) R_1=OCH_3; R_2=H

d) R_1=NO_2; R_2=CH_3

e) R_1=H; R_2=CH_3

responsible for the zero-order kinetics.[10] Thus, while the rearrangement of [6,5] open fulleroid **1** to [6,6] closed methanofullerene **2** occurs in 8 h under ambient light at 153 °C with zero-order kinetics, no rearrangement was observed when **1** was heated for 24 h in the dark at 153 °C. The inhibitory effect of oxygen and quenching by triplet sensitizers led us to propose the intermediacy of ^{3}**1*** in which opening to biradical **3** is the step requiring thermal activation (Scheme 1).

We recently reported that [6,5] open fulleroids with radical stabilizing groups, **4**, rearrange to the corresponding [6,6] closed isomers, **5**, both by a zero-order photochemical process and by a higher energy first-order thermal pathway.[11] For example, the rearrangement of the [6,5] open fulleroid **4a** to the [6,6] closed fullerene **5a** occurs in 40 min in the presence of ambient light at 35 °C with zero-order kinetics ($k_0 = 1.38 \times 10^{-6}$ M s^{-1}) with an activation energy of 9.5 kcal/mol by the mechanism in Scheme 1. However, the rearrangement of **4a** occurs over 27 h in the dark at 130 °C with first-order kinetics ($k_1 = 1.63 \times 10^{-5}$ s^{-1}) and an activation energy of 23 kcal/mol. We have proposed that the higher energy unimolecular thermal rearrangement of **4** involves a disrotatory ring closure to the [6,5] closed isomer **6** which subsequently rearranges to the [6,6] closed methanofullerene **5** via a biradical-like intermediate, **7** (Scheme 2).

In this study we report that both the thermal and photochemical rearrangements of these aryl-substituted fulleroids can be facilitated by the addition of electron acceptors to the reaction mixture. To evaluate the mechanism of this unusual reaction, we have measured the kinetics of these thermal and photochemical processes. In addition, we have evaluated the oxidation potentials of a series of [6,5] open fulleroids and their [6,6] closed methanofullerenes isomers and have used the difference in the oxidation potentials of the corresponding isomers to estimate the free energy difference between them.

Results and Discussion

Thermal Rearrangement of Aryl-Substituted Fulleroids in the Presence of Electron Acceptors. When a degassed solution of **4a** in *o*-dichlorobenzene-d_4 (ODCB-d_4) was heated in the dark at 170 °C, it rearranged to **5a** in 2 h. However, when a degassed solution of equal molar amounts of **4a** and tetracyanoethylene (TCNE) in OCDB-d_4 was heated in the dark at 170 °C, the rearrangement of **4a** was too fast to conveniently measure. This TCNE-promoted reaction shows first-order kinetics between 60 and 140 °C with a $\Delta H^\ddagger$ of 6.7 ± 0.4 kcal/mol and a $\Delta S^\ddagger = -58.4 \pm 0.6$ cal/mol-deg (Figure 1). The reaction rate doubles when the amount of TCNE is doubled. The thermal isomerization of **4a** in the absence TCNE has a $\Delta H^\ddagger$ of 23.0 ± 0.3 kcal/mol and a $\Delta S^\ddagger$ of -24.4 ± 0.8 cal/mol-deg. Thus, TCNE lowers the enthalpy barrier by about 16 kcal/mol but

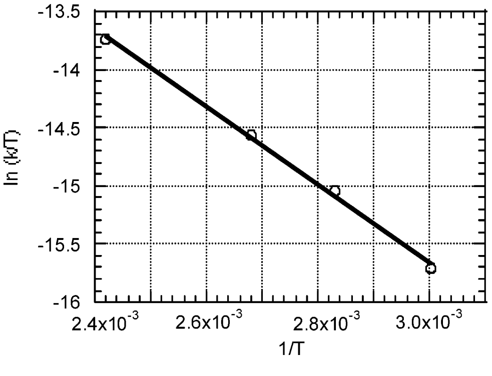


FIGURE 1. Eyring plot of the first-order thermal rearrangement of **4a** to **5a** with TCNE present at 60, 80, 100, and 140 °C in the absence of light. An activation enthalpy of 6.7 ± 0.4 kcal/mol and an activation entropy of -58.3 ± 0.6 cal/mol-deg were measured.

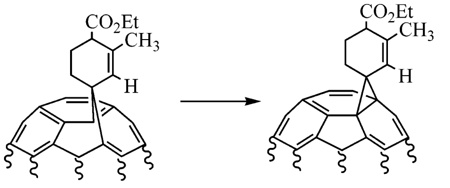
---

[10] Li, Z.; Shevlin, P. B. *J. Am. Chem. Soc.* **1997**, *119*, 1149−1150.

[11] Hall, M. H.; Lu, H.; Shevlin, P. B. *J. Am. Chem. Soc.* **2001**, *123*, 1349−1354.

places a greater entropic demand on the transition state. Since TCNE is a good electron acceptor ($E_{red} = -0.25$ V),[12] there is the possibility that this reaction proceeds by electron transfer. Thus, we have evaluated the rearrangement of **4a** in the presence of other electron acceptors including chloranil ($E_{red} = -0.44$ V),[13] C_{60} ($E_{red} = -0.99$ V),[14] and *p*-dinitrobenzene ($E_{red} = -1.15$ V),[15] with the hope of observing a thermal electron-transfer process. Chloranil and *p*-dinitrobenzene show no effect on the rate of rearrangement of **4a**, whereas C_{60} increases the rearrangement rate by a factor of 1.5 at 170 °C. Since C_{60} is more difficult to reduce than chloranil, it is clear that the effectiveness of the catalysis does not parallel the electrochemical reduction potential of the acceptor.

The rate-accelerating effect of TCNE is not only observed on the fulleroids with aryl substituents on the methano bridge carbon but also manifests itself in the rearrangement of **8** to **9**. We have previously reported that the thermal rearrangement of **8** to **9** is rapid as a result of the favorable prealignment of the π-orbitals of the double bond for stabilization of the allylic radical that develops on the methano bridge carbon.[11] At 80 °C, TCNE increases the rate of rearrangement of **8** to **9** by a factor of 3.



8 **9**

To further consider the possibility that this reaction proceeds by an initial electron transfer from the fulleroid to TCNE, we have measured the electrochemical oxidation potentials of **4a**−**d**, **5a**−**d**, **8**, and **9**. In these cyclic voltammetric studies, double irreversible oxidation peaks were observed for all of the substituted C_{60} adducts (Table 1). However, C_{60} itself shows only a single reversible oxidation peak (+1.26 V).[16]

The first oxidation potentials of **4a**−**d** and **8** are +1.00, +1.06, +1.11, +1.11, and +0.52 V (vs Fc/Fc$^+$), respectively. Thus, the single electron transfers from **4a**−**d** and **8** to TCNE (Scheme 3) are all thermodynamically unfavorable with the calculated free energy changes of +28.50, +30.20, +31.36, +31.36, and +17.74 kcal/mol for **4a**, **4b**, **4c**, **4d**, and **8**, respectively. The fact that the activation free energy for the TCNE-promoted rearrangement of **4a** is 6.7 kcal/mol, whereas the free energy change for the electron-transfer process requires 28 kcal/mol, provides evidence against an electron transfer in this reaction. Furthermore, the $\Delta S^‡$ of -58.4 ± 0.6 cal/mol-deg is far more negative than that for a typical electron transfer, which is usually about −11 to −16 cal/mol-deg[17] and seems to be more characteristic of an addition reaction. For example, the entropy of activation of several Diels−Alder reactions falls between −37 to −45 cal/mol-deg.[18] The unfavorable thermodynamics coupled with the fact that chloranil ($E_{1/2}$ −0.44 V),[13] a better electron acceptor than C_{60} ($E_{1/2}$ −0.99 V),[14] has no effect on reaction rate, whereas C_{60} does, argues against an electron transfer in the mechanism of the TCNE-promoted isomerizations. Reactions in which the rate parallels the electrochemical reduction potential of the acceptors are usually thought to proceed by an electron transfer.[19]

TABLE 1. Potential Values ($E°$) for All Observed Redox Processes measured at 25 °C[a]

	$E°$ (V vs Fc/Fc$^+$)		
	oxidation		reduction
compound	first	second	first
C_{60}	+1.26[b]		−0.99[c]
4a	+1.00	+1.23	−1.28
5a	+1.20	+1.42	−1.17
4b	+1.06	+1.29	−1.28
5b	+1.28	+1.48	−1.25
4c	+1.11	+1.37	−1.16
5c	+1.29	+1.53	−1.02
4d	+1.11	+1.35	−1.22
5d	+1.34	+1.60	−1.13
8	+0.52	+0.79	
9	+0.74	+0.93	

[a] Values were measured in 1.0 mM ODCB/0.15 M TBAPF$_6$ with Ag/Ag$^+$ quasi-reference electrode and reported in volts relative to the potential for internal Fc/Fc$^+$. The scan rate was 40 mV/s. [b] The oxidation potential for C_{60} is reported in ref 16. [c] The reduction potentials for C_{60} are reported in ref 14.

Dilute solutions of **4a** and TCNE in ODCB, when mixed, did not exhibit any color change that is usually observed upon the formation of charge-transfer complexes of aromatic compounds and TCNE.[20] The absorption spectrum of a mixture of the equal molar solutions of TCNE and **4a** is identical with the sum of its individual components at the same concentrations. These results argue against the existence of significant amounts of a charge-transfer complex between **4a** and TCNE under these conditions.

Since the data are not consistent with an electron transfer and the consequent intermediacy of radical ions, we must consider the possibility that the TCNE assists the reaction by first forming a covalently bound adduct that subsequently generates product with the elimination of the TCNE. The first step in the generation of an adduct is likely to be formation of the zwitterion **10**, which could close to **11** or loose TCNE to generate **5** as shown in Scheme 4. Although NMR and MS analysis do not reveal the presence of **11**, it is possible that it is formed reversibly in small quantities during the reaction. However, the simplest explanation for the effect of TCNE is the formation of zwitterion **10**, which provides a low energy pathway connecting **4** and **5**. The anti-Bredt strain energy associated with double bonds at the bridgehead carbons in **4** could provide a driving force for the formation of **10**. The fact that the TCNE-assisted rearrangement of **4a** has a more negative $\Delta S^‡$ than thermal rearrangement in the absence of TCNE is indicative of the associative nature of the former process. Cycloadducts similar to **11** have been observed in the thermal

---

(12) (a) All potentials given in this report are determined to be, or corrected to be, referenced to Fc/Fc$^+$ (b) Peover, M. *Trans. Faraday Soc.* **1962**, *58*, 2370−2374.

(13) Jackman, A. *Adv. Org. Chem.* **1960**, *2*, 329−366.

(14) Arias, F.; Xie, Q.; Wu, Y.; Lu, Q.; Wilson, S. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1994**, *116*, 6388−6394.

(15) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

(16) Xie, Q.; Arias, F.; Echegoyen, L. *J. Am. Chem. Soc.* **1993**, *115*, 9818−9819.

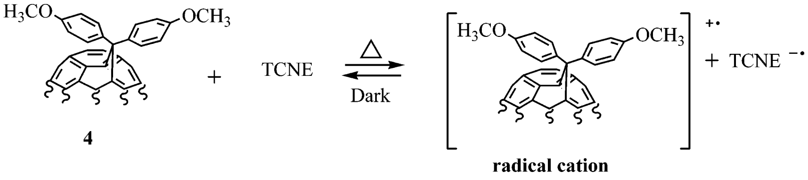
(17) Borchardt, D.; Wherland, S. *Inorg. Chem.* **1986**, *25*, 901−905.

(18) Kiselev, V. D.; Kashaeva, E. A.; Iskhakova, G. G.; Shihab, M. *Tetrahedron* **1999**, *55*, 12201−12210.

(19) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *1056*, 3632−2638.

(20) Kim, E.; Christl, M.; Kochi, J. K. *Chem. Ber.* **1990**, *123*, 1209−1218.

SCHEME 3



$\Delta G_{298} = +28.5$ kcal/mol

SCHEME 4

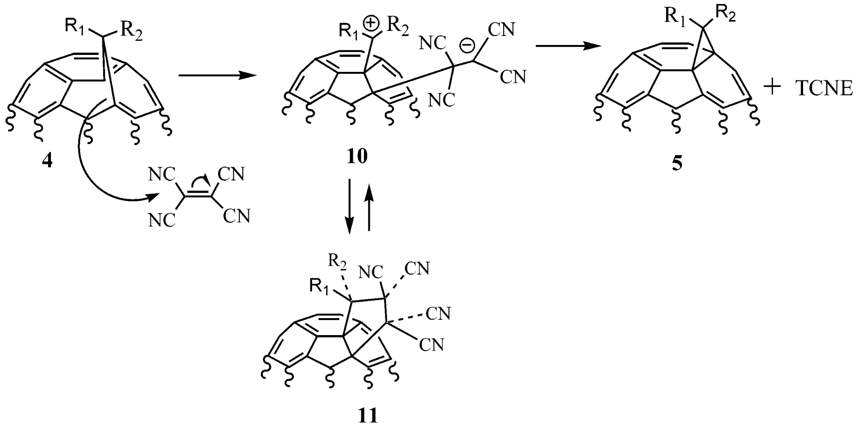


TABLE 2. Rate Constants (s^{-1}) for the Thermal (170 °C) First-Order Rearrangement of [6,5] Open Fulleroids to [6,6] Closed Methanofullerenes

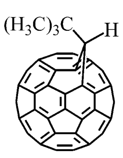
[6,5] open fulleroid	no catalyst[a]	catalyst (TCNE)
4a; $R_1 = OCH_3$, $R_2 = p\text{-}C_6H_4OCH_3$	2.27×10^{-4}	very fast
4b; $R_1 = OCH_3$, $R_2 = CH_3$	2.29×10^{-5}	3.47×10^{-3}
4c; $R_1 = OCH_3$, $R_2 = H$	1.37×10^{-5}	2.10×10^{-4}
4d; $R_1 = NO_2$, $R_2 = CH_3$	1.56×10^{-5}	2.97×10^{-5}
4e; $R_1 = H$, $R_2 = CH_3$	1.03×10^{-5}	3.77×10^{-5}

[a] Values for the noncatalyzed reaction are reported in ref 11.

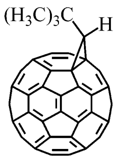
reaction of 1,1-(p-methoxyphenyl)spiropentanes assisted by TCNE, and a zwitteronic intermediate similar to **10** has been proposed.[21]

Table 2 demonstrates that the rate of rearrangement of fulleroids **4a**−**e** in the presence of TCNE decreases with decreasing ability of the substituents to stabilize a positive charge on the bridging carbon. It is interesting to note that **4d**, with its electron-withdrawing *p*-NO_2 group rearranges faster than **4e**, with a *p*-H, in the absence of TCNE but slower in its presence. This is consistent with our postulate that the bridging carbon develops radical character in the absence of TCNE but has cationic character in the lower energy TCNE-assisted pathway. The fact that compounds **8** and **9** are easier to oxidize than **4** and **5**, despite the fact that they bear electron-withdrawing CO_2-Et groups, may be a result of initial stabilization of the radical cation by the prealigned π-orbitals.

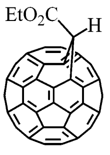
To further investigate the need for positive charge stabilization on the methano bridge in these reactions, we have examined the thermolysis of **12**, **14**, and **15** in the presence and absence of TCNE. Addition of the corresponding tosylhydrazone lithium salt to C_{60} generated **12** with a trace of **13**. There was no evidence for a [6,5] open isomer with the proton over the five-membered ring. This isomer would have a ^{1}H NMR signal further downfield than the corresponding protons in **12** and **13**.[22] Compounds **14**, **15**, and **16** were formed in a 70:20:10 ratio. The thermal rearrangements of **12** to **13**, and **14** and **15** to **16** were not observed upon heating both solutions in the dark at 170 °C for 48 h in the presence or absence of TCNE.



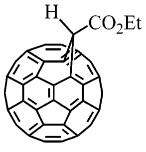
12



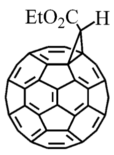
13



14



15



16

The failure of these reactions to proceed is a result of the fact that **12**, **14**, and **15** do not have substituents on the bridging carbon that provide enough stabilization of either a radical or a positive charge. It is interesting to note that the zero-order photochemical rearrangements of both **12** and **14** were observed in 1,2-dichlorobenzene at 170 °C under ambient light.

We have used PM3 computed heats of formation to evaluate the involvement of the [6,5] closed isomer, **6a**, as a viable intermediate in the TCNE-catalyzed rearrangement of **4a** to **5a**. These PM3 calculations, which predict that the [6,5] closed isomer **6a** has a ΔH_f 14.4 kcal/mol higher than that of **4a**,[11] appear to rule out the intermediacy of **6a** in the TCNE-promoted rearrangement, which has an activation enthalpy of only 6.7 ± 0.4 kcal/mol.

---

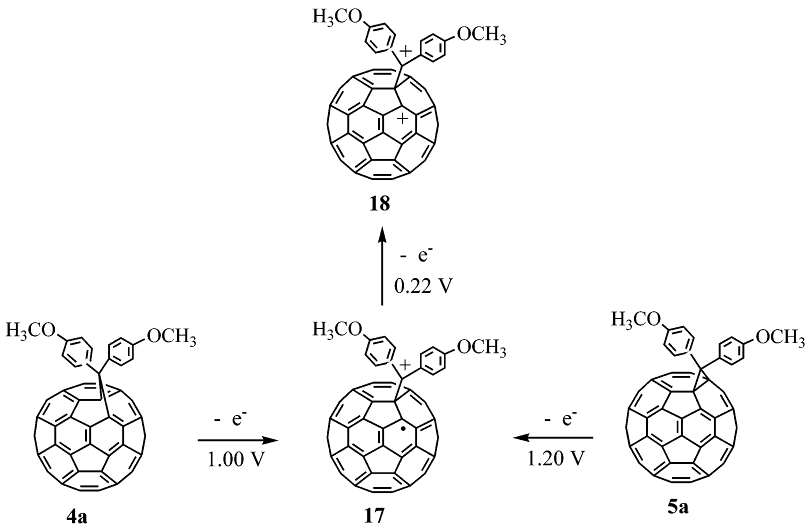
[21] Takahashi, Y.; Ohaku, H.; Morishima, S.; Suzuki, T.; Ikeda, H.; Miyashi, T. *J. Chem. Soc., Perkin Trans. 1* **1995**, 319−325.

[22] Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231−1250.

TABLE 3. Free Energy Difference between the [6,5] Open Fulleroids and the Corresponding [6,6] Closed Isomer as Calculated by PM3 and Estimated from Experimental Oxidation Potentials

	PM3 values				experimental value		
isomer	ΔH_f (kcal/mol)	$\Delta S°$ (kcal/mol)	$\Delta G°$ (kcal/mol)	$\Delta\Delta G°$ (kcal/mol)	E°, ox (V)	$\Delta E°$ (V)	$\Delta\Delta G°$ (kcal/mol)
4a	799.48	0.206	737.68		+1.00		
5a	791.98	0.208	729.83	7.85	+1.20	0.20	4.72
4b	799.98	0.178	746.86		+1.06		
5b	793.72	0.178	740.50	6.36	+1.28	0.22	5.19
4c	801.30	0.172	750.02		+1.11		
5c	798.77	0.172	747.37	2.65	+1.29	0.18	4.25
4d	830.01	0.178	776.72		+1.11		
5d	824.03	0.180	770.30	6.42	+1.34	0.23	5.42
8	730.84	0.192	673.43		+0.52		
9	724.28	0.193	666.63	6.80	+0.74	0.22	5.19

SCHEME 5



The reason for the modest increase in the rate of rearrangement of **4a** in the presence of C_{60} is not clear. It may be that a zwitterion analogous to **10**, with a negative charge on C_{60}, is an intermediate. The fact that such an intermediate is rather sterically unfavorable may account for the small rate increase in this system.

Electrochemical Studies of the Methanofullerenes and Fulleroids. An examination of the oxidation potentials of the fulleroids and methanofullerenes **4** and **5** in Table 1 reveals two interesting trends: (i) As the electron-donating ability of substituents on the phenyl groups of both **4** and **5** decreases, the compounds become harder to oxidize. (ii) The [6,6] closed isomers are harder to oxidize than the corresponding [6,5] open isomers but show the same substituent effect. This behavior is not consistent with the removal of an electron from the benzene moiety in which case the [6,5] open fulleroids and the [6,6] closed methanofullerene would have about the same oxidation potential. Furthermore, a substituted methoxybenzene by itself would probably be slightly harder to oxidize than **4a**. For example, the oxidization potential of 1-methoxy-2,4,6-triethylbenzene has been reported at +1.24 V.[23] Since the ease of oxidation of both **4** and **5** parallels the ability of the groups on the methano bridge to stabilize a positive charge, our results are consistent with formation of a positive charge on the methano carbon upon oxidation in both **4** and **5**. Although the oxidation potentials of the [6,5] open and the [6,6] closed isomers depend on the electron-donating properties of groups on the methano bridge, the difference in oxidation potential between **4** and its corresponding [6,6] closed isomer **5** is always about 0.2 V (Table 3). This observation coupled with the fact that both **4** and **5** develop a positive charge on their methano carbon upon oxidation raises the possibility that oxidation of both **4** and **5** generate the same radical cation **17** (Scheme 5). In this scenario, **4** loses an electron from the π system with concurrent bond formation to give **17**, while removal of an electron from **5** breaks a cyclopropyl bond to form **17**. An analogous opening of a cyclopropyl ring upon electrochemical oxidation followed by rearrangement has been reported in 1,1-(*p*-methoxyphenyl)spiropentene (+0.71 V).[21]

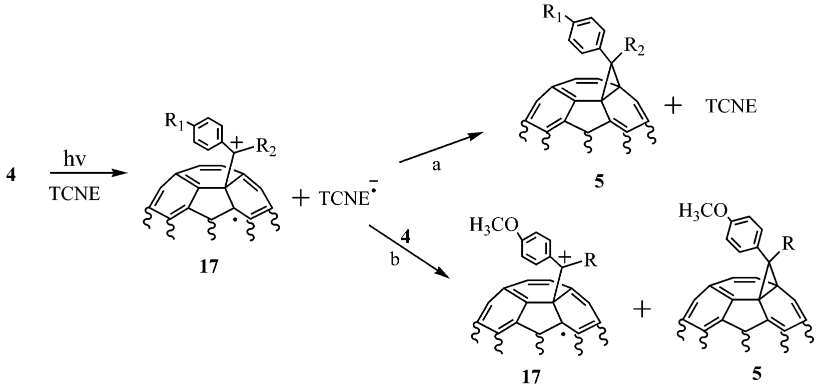
The second oxidation peaks in the cyclic voltammograms of **4** and **5** (Figure 2) are probably due to the loss of an electron from the C_{60} cage in **17** to form the dication **18**. If both **4** and **5** form the same radical cation **17** upon oxidation, the difference between the first and second oxidation peak for a given isomer pair should be the same. Table 1 demonstrates that this difference, which varies from 0.01 to 0.03 V for the isomer pairs **4**, **5a**−**d**, is in fact the same within the experimental error of our measurements.

If our postulate that both the [6,5] open **4** and the [6,6] closed **5** isomers are oxidized to the same radical cation intermediate **17** is correct, the free energy difference between **4** and **5** closed isomers is simply the difference in their oxidation potentials and can be electrochemically measured. To evaluate the validity of this assumption, we have used the PM3 method to estimate

---

(23) Hammerich, O.; Parker, V. D.; Ronlan, A. *Acta Chem. Scand. B 30* **1976**, *1*, 89−90.

SCHEME 6



the free energies of the [6,5] open and the [6,6] closed isomers (Table 3). These semiempirical calculations agree with the experimental observation that the [6,6] closed isomers are more stable than the corresponding[6,5] open isomers. Table 3 demonstrates that calculated free energy differences between **4** and **5** and those derived experimentally by assuming that both isomers are converted electrochemically to **17** are in reasonable agreement. If both **4** and **5** are electrochemically converted to **17**, there is the possibility for electrochemical conversion of **4** to **5** under conditions in which **17** is generated. Accordingly, we have attempted a bulk electrochemical oxidation of **4a** to generate **5a** by holding the potential of a cell containing a 1.0 mmol solution of **4a** at its first oxidation value (1.00 V vs Fc/Fc$^+$) in the absence of light. However, after maintaining potential of the system at 1.00 V for 30 min, the potential abruptly fell to 0.00 V with the development of polymer film on the surface of the glassy carbon electrode that blocked the flow of current. No **5a** was detected. Apparently the radical cation **17** is reactive toward polymerization on the surface of the glassy carbon electrode.

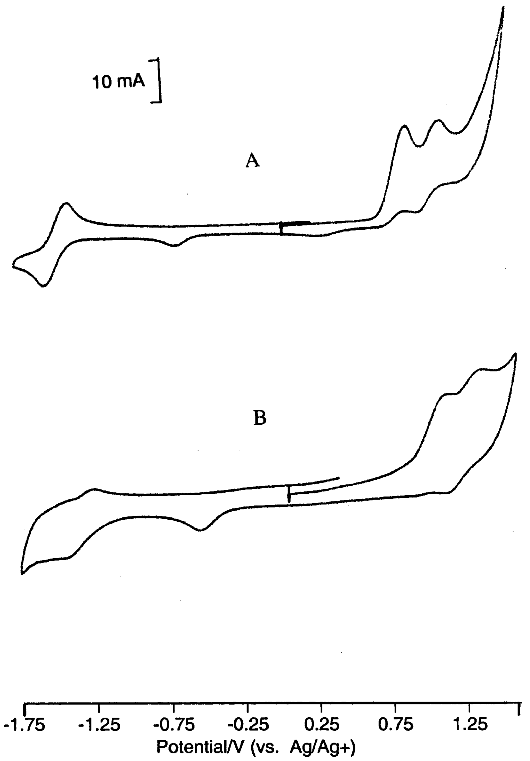


FIGURE 2. Cyclic voltammograms of **4a** (A) and **5a** (B) recorded in 0.1 mM ODCB/0.15 M TBAFP$_6$ at 25 °C on a glassy carbon electrode with Fc/Fc$^+$ as internal standard. The potential scan rate was 40 mV/s.

Photochemical Rearrangement of Aryl-Substituted Fulleroids in the Presence of Electron Acceptors. We have reported that **4a** undergoes a photochemical, zero-order rearrangement to **5a** under ambient light. At 25 °C under ambient light, a degassed solution of 4**a** in ODCB rearranges ($k_o = 1.94 \times 10^{-7}$ M s^{-1}) to **5a** in 3.5 h (Figure 3). However, when 1 molar equiv of TCNE is added to the solution of **4a** under the same conditions at 25 °C, **4a** rearranges ($k_o = 2.10 \times 10^{-5}$ M s^{-1}) to **5a** in 2 min with zero-order kinetics (Figure 4). No cycloaddition products were observed. A degassed solution of **4a** with chloranil (1:1 mole ratio) in ODCB-d_4, when exposed to ambient light, rearranged at 25 °C with a zero-order rate constant of 6.44×10^{-6} M s^{-1} in 20 min. These results appear to be consistent with an excited-state electron-transfer process. It is known that electronic excitation causes an increase in both the oxidizing and reducing potential of a molecule that give rise to electron-transfer reactions.[24] Scheme 6 shows two possible mechanisms in which oxidation of **4** by TCNE leads to ring opening to form **17** and the back electron transfer from TCNE forms the [6,6] closed isomer **5** (pathway a). Our current data does not preclude the involvement of a radical chain process (pathway b). An electron-transfer mechanism has been proposed in the photochemical reactions of 1,1-(*p*-methoxyphenyl)spiropentanes and TCNE to form methylidenecyclobutane.[21]

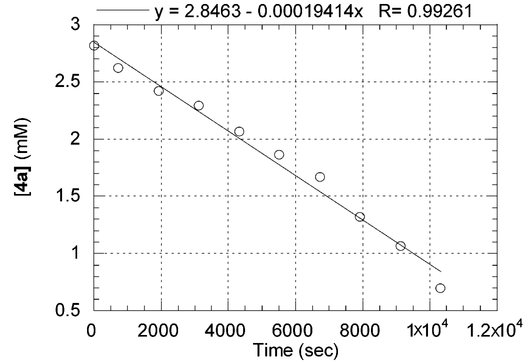


FIGURE 3. Kinetics of the light-promoted rearrangement of **4a** at 25 °C under ambient light; $k_o = 1.94 \times 10^{-7}$ M/s.

---

[24] Masnovi, J. M.; Kochi, J. K. *J. Org. Chem.* **1985**, *50*, 5245−5255.

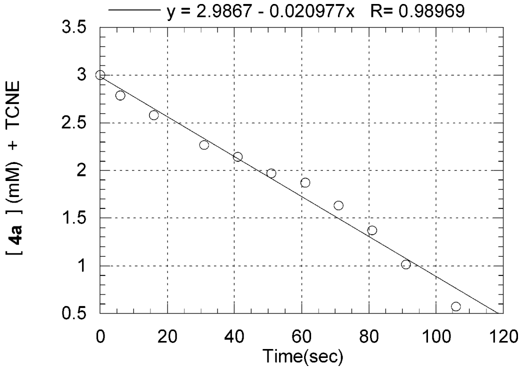


FIGURE 4. Kinetics of the light-promoted rearrangement of **4a** in the presence of TCNE at 25 °C under ambient light; $k_o = 2.10 \times 10^{-5}$ M/s.

Conclusions

These results demonstrate that both the thermal and photochemical rearrangements of aryl-substituted [6,5] open fulleroids are catalyzed in the presence of some electron acceptors. The thermal rearrangement appears to be catalyzed via an zwitteronic-type intermediate, whereas the catalyzed photochemical reaction proceeds via an excited-state electron-transfer process.

We have proposed that both [6,5] open and the [6,6] closed isomers are oxidized electrochemically to the same radical cation intermediate. If our proposal is correct, then the free energy difference between the [6,5] open and the [6,6] closed isomers is simply the difference in their oxidation potentials and can be electrochemically measured. In all cases studied, the free energy difference between the corresponding isomers is only about 5 kcal/mol.

Experimental Section

We have recently reported the synthesis and characterization of **4a**−**e**, **8**, and **9**.[11] Compound **4a** was synthesized by the reaction of C_{60} with the diazo compound. Compounds **4b**−**e**, **8**, and **9** were synthesized from the general procedure for the reaction of C_{60} with tosylhydrazone lithium salts.

Preparation of Compound 12. The tosylhydrazone of 2,2-dimethylpropanal was prepared by standard procedures. To a solution of the tosylhydrazone (0.1 mmol) in 3 mL of hexane at 0 °C under N_2 in a 250-mL flask was added MeLi (1.4 M, 0.107 mL, 0.15 mmol) using a syringe. A previously prepared solution of C_{60} in toluene (72 mL, 1.4 mM, 0.1 mmol) was added to the flask. The flask was protected from light and heated while the solution refluxed for 30 min. The reaction mixture was monitored by TLC in toluene or hexane/toluene (4:1). The solvent was reduced in vacuo to 20 mL, which was then loaded on a silica gel column and eluted with hexane/toluene. The product was compound **12** with a trace of **13**. There was no evidence for the [6,5] open isomer in which the methine proton is over the five-membered ring [0.039 g, 37% yield]. ^{1}H NMR (ODCB-d_4, 250 MHz): δ 2.49 (s, 1H), 1.56 (s, 9H). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 149.0, 147.3, 146.8, 146.0, 145.0, 144.9, 144.2, 144.0, 143.8, 143.5, 143.2, 142.9, 142.8, 141.9, 141.0, 140.8, 140.3, 140.2, 139.9, 139.1, 138.6, 137.7, 136.6, 134.4, 132.1, 131.1, 130.9, 130.0, 129.7, 128.9, 61.4, 36.7, 30.8. FABMS (NBA): m/s 791 ((M + 1)$^+$), 720 (C_{60}^+).

Compound 13. ^{1}H NMR (ODCB-d_4, 250 MHz): [6,6] closed isomer δ 3.84 (s, 1H) 1.61 (s, 9H). ^{13}C NMR (ODCB-d_4, 100 MHz): δ 148.6, 146.8, 145.8, 145.4, 145.2, 145.0, 144.9, 144.8, 144.5, 144.1, 143.6, 143.5, 143.2, 142.8, 142.6, 142.0, 141.4, 140.5, 140.1, 74.0, 53.6, 36.8, 29.7. FABMS (NBA): m/s 791 ((M + 1)$^+$), 720 (C_{60}^+). Although all of the signals for the ring carbons in **12** and **13** cannot be resolved, signals for the carbons of the bridging groups and the bridgehead carbons are consistent with the structures. The electrochemical synthesis of compound **13** has been reported.[25]

Compounds **14**, **15**, and **16** were prepared as a mixture as previously described, and the NMR spectra data agree with those in the literature.[22]

General Procedure for the Catalyzed Rearrangement of [6,5] Open to the [6,6] Closed Isomer. A 5-mm NMR tube, wrapped with aluminum foil, was charged with the [6,5] open isomer and 0.5 mL of ODCB-d_4 (ca. 3.5 mmol) at room temperature. An equal molar amount of the potential catalyst (TCNE, TNM, C_{60}, Chloranil, *p*-DNB) was added. The NMR tube was degassed, sealed and heated in a temperature controlled jacketed flask. The kinetics were monitored by NMR spectroscopy.

Electrochemistry. Voltammetric experiments were performed on a potentiostat, electroanalytical system equipped with a three-electrode cell, interfaced with a plotter. The glassy carbon working electrode, 3 mm in diameter, was used after being polished with Alpha micropolished alumina (1.0 μm). A silver wire served as a pseudo-reference electrode. 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 recrystallized from an ethanol/H$_2$O (95:5) mixture and dried in vacuo prior to use. The electrochemical measurements were made by dissolving the fullerene sample (1.0 mmol) in 15 mL of ODCB with 0.15 M TBAPF$_6$. The solution was protected from light and placed in the three-electrode electrochemical cell. The cell was degassed for 20 min by bubbling argon gas through the solution. Ferrocene was added as an internal standard. The measurements were made at a scan rate of 40 mV/s.

Computational Studies. Calculations were carried out on a Silicon Graphics Personal Iris workstation. Initial input structures were generated and minimized. Semiempirical PM3 calculations were then preformed using the Spartan 5.0 program to optimize all stationary points. Geometry optimizations of the [6,5] open and the [6,6] closed isomers were carried out on all input structures.

Supporting Information Available: Kinetic data for the rearrangements of **4a**−**d** and **8**; cyclic voltammograms of **4a**−**d**, **5a**−**d**, **8**, and **9**; and the ^{1}H and ^{13}C spectra of **12** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0521706

---

[25] Boulas, P. L.; Zuo, Y.; Echegoyen, L. *Chem. Commun.* **1996**, 1547−1548.