Electrochemical Study of γ-Irradiated C$_{60}$ by Hydrodynamic Modulation of a Rotating Disk Electrode

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Electrochemical studies of the products of C$_{60}$ γ-irradiated in cyclohexane were conducted using the frequency response of hydrodynamic modulation at rotating disk electrodes (HMRDE) to determine transport properties by a methodology independent of the concentration of the electroactive species. The diffusion coefficients of C$_{60}$ and its γ-irradiated product were separately determined to be 1.9×10^{-6} and 0.96×10^{-6} cm^2/s, respectively, at 50 °C. The estimated Stokes radius of the radiolytic product of C$_{60}$ approaches twice that of the fullerene itself. Such a result for γ-radiolysis in cyclohexane solution is consistent with the formation of cyclohexane adducts and likely some C$_{60}$ dimer.

Introduction

A C$_{60}$ derivative that was synthesized via γ-irradiation of C$_{60}$ in cyclohexane was initially assumed to be a fullerene dimer based on the nearly 2-fold reduction of the ion mobility of the radiolytic product ion relative to that of unirradiated C$_{60}$ ion.[1] Modeling studies had predicted the stability of C$_{60}$ dimers having a dumbbell shape,[2] and the synthesis of such dimers has been achieved through other routes.[3] Further analysis of the radiolytic product by mass spectral and small-angle X-ray scattering (SAXS),[4] however, indicated that the γ-irradiated products of C$_{60}$ in cyclohexane are cyclohexyl adducts of C$_{60}$, primarily C$_{60}$(C$_6$H$_{12}$)$_{10}$. The SAXS data also indicated that some of the C$_{60}$(C$_6$H$_{12}$)$_{10}$ entities aggregate into dimers in toluene solution, and a more rigorous study of the ion mobilities in γ-irradiated fullerene solutions in several solvents did not definitively identify the product(s).[5] Thus, the identity of the γ-irradiated C$_{60}$ product is somewhat equivocal with questions remaining of the extent to which cyclohexyl radicals add to the C$_{60}$ cage and whether there are dimers of the adducts in solution. We have pursued this subject using an entirely independent electrochemical technique to probe the radiolytic product.

The technique used to assess the mobility of an electroactive species was the frequency response of hydrodynamic modulation at a rotating disk electrode, or HMRDE.[6−10] The frequency response of the limiting current of reduction or oxidation of a given species to sinusoidal modulation of rotation speed is dependent on its diffusion coefficient in the particular medium. In HMRDE, the rotation speed is sinusoidally modulated around a center frequency (speed) and the component of electrode current at the modulation frequency is extracted and measured. The analytical efficacy of such an approach is the removal of all components of the disk current that are independent of mass transport.

The direct determination of the diffusion coefficient of a redox molecule can be performed from the Levich equation for the limiting current at the RDE,

$$i_l = 0.62 nFa\omega^{1/2}D^{2/3}\nu^{-1/6}C \tag{1}$$

where i_l, n, F, a, ω, D, ν, and C are the limiting current, electrons transferred, Faraday's constant, electrode area, rotation speed, the diffusion coefficient of the electroactive species, the kinematic viscosity of the solution, and the bulk concentration of this species in the electrolyte, respectively. For the unknown radiolytic products, however, molecular weight, concentration, and purity are unknown. This difficulty can be circumvented using HMRDE since the diffusion coefficient can be measured independently of the concentration of the redox species (C) and the electrons transferred (n) provided only that the frequency response in HMRDE of the modulated current arises only from a Levich-dependent electron-transfer process of the selected species.

HMRDE has been applied successfully to many aspects of electrochemical studies,[9−15] such as electrode kinetics, microanalysis, and diffusion coefficient measurements. The frequency response is a function of Sc$^{1/3}$, where Sc is the Schmidt number, given by

$$Sc = \nu/D \tag{2}$$

The kinematic viscosity, ν, is a property of the supporting electrolyte which can be measured by Ostwald viscometry, and D can be either the diffusion coefficient of the electroactive irradiated product, in our case, or that of the original C$_{60}$. This technique was applied earlier to measure the C$_{60}$ diffusion coefficient where direct confirmation using the Levich equation with a pure compound was applicable.[15]

The approximate molecular size of the radiolytic product ion can be estimated using the Stokes−Einstein equation if the diffusion coefficient of the solute molecule is known. When the solute molecule is much larger than the solvent molecule and the solute molecule is spherical, the Stokes−Einstein equation is

$$D = k_B T/(6\pi\eta r) \tag{3}$$

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where D is the diffusion coefficient of the solute molecule of interest in the solvent (our electrolyte), k_B the Boltzman constant, T the temperature, η the viscosity of the electrolyte, and r the effective radius of the solute molecule. The viscosity, η, is related to kinematic viscosity ν by $\nu = \eta/d$, where d is solution density, which we can measure. The diffusion coefficient of the solute molecule can be obtained by eq 2, provided that Sc can be found. In this work, we determine Sc via the HMRDE technique, thence D, so that the approximate size of the radiolytic product can be assessed.

The theoretical frequency response of the modulated current at a potential corresponding to a limiting current is expressed as a set of curves dependent on $Sc^{1/3}$, which allows the determination of D by best fits of the experimental data. The modulation result can be expressed in terms of the dimensionless parameter A[10]

$$A = \Delta i_p / \Delta i_{p \to 0} \qquad (4)$$

where p is the ratio of the frequency of modulation speed (σ) to that of the center rotation speed (ω_0) or $p = \sigma/\omega_0$. Δi_p is the modulation current resulted from the modulated speed component at a certain p value. According to the original work by Tokuda et al.[10] and the extension by Albery et al.[16] to higher Sc values than tabulated in ref 10 and needed here, A is a function of p and Sc. An analytical formula relating A, Sc, and p was given in Albery's paper.[16] We calculated a table of values of A at different p and with a wider range of Sc (from 100 to 20 000) than the original in ref 10 (from 100 to 2100). Since C_{60}, a big molecule, should have a small diffusion coefficient and the solvent we use, *o*-dichlorobenzene, makes for a relatively large ν, it was necessary to anticipate a large Sc value. By fitting experimental data to calculated A values, the Sc number best describing the function was obtained.

Experimental Section

γ-Irradiated C_{60} Source. The γ-irradiation of C_{60}−cyclohexane solutions was performed earlier.[5] Briefly, C_{60} (Hoechst "Gold Grade") was dissolved in 10 mL toluene, and after the C_{60} dissolved, an aliquot of the solution was put into a flask having a volume of 550 mL through which argon was flushed to evaporate the toluene. Cyclohexane was purified and collected in the flask with the C_{60}, argon was bubbled through the solution for 20 min, and the flask was left in the dark for ∼40 h to dissolve the C_{60}. The solution was then sonicated for ∼10 s and bubbled with argon to dissolve any residual C_{60}. The solution was then γ-irradiated to a dose of 50 krad which produced a brown turbid solution that was left in the dark for ∼30 h to permit any postradiolysis reactions to occur. The bulk of the cyclohexane was distilled off the solution while the distillation flask/condenser was swept with argon. When the volume was reduced to ∼20 mL, the dark-brown solution was transferred to a weighed vial in aliquots and evaporated to near dryness using argon and heating to ∼60 °C. The sample was further dried for 18 h in a vacuum oven at 25 °C before being used for the described experiments.

Viscosity and Kinematic Viscosity. The viscosity and kinematic viscosity of the electrolyte 0.5 M tetra-*n*-butylammonium fluoroborate(TBAFB)/*o*-dichlorobenzene(ODCB) used in our modulation experiments were measured by an Ostwald viscometer using water as a reference. The density of the electrolyte was measured by a pycometer with water as a reference. The data are collected in Table 1 with others for 0.5 M tetra-*n*-butylammonium bromide (TBAB)/ODCB.[15]

TABLE 1: Densities (d), Viscosities (η), and Kinematic Viscosities (ν) of Different Solvents

	25 °C			50 °C		
electrolyte	d, g mL^{-1}	η, cP	ν, cS	d, g mL^{-1}	η, cP	ν, cS
H_2O^a	0.99709	0.8904	0.8930	0.98807	0.5468	0.5534
0.5 M TBAB/ODCB		2.60^b	2.0^b			
0.5 M TBAFB/ODCB	1.2587	2.57	2.04	1.2351	1.67	1.35

^{a} d and η of H_2O are taken from ref 17. ^{b} Taken from ref 15.

Electrochemical Experiment. The electrochemical experiments were carried out in a three-compartment thermostated cell. A Pt rotating disk electrode (electrode area 0.165 cm^2) was used as the working electrode, Ag/AgCl/KCl (saturated) as the reference, and a graphite stick as the counter. The same electrolyte, 0.5 M TBAFB/ODCB, was used in both C_{60} and γ-irradiated C_{60} experiments. In the C_{60} experiment, a 1 mM C_{60} solution was used. Rotation speed was controlled by a Pine MSR system, and the potential was controlled by a Pine RDE3 potentiostat.

The modulation experiment setup follows ref 10. A sine wave was generated from a function generator as the modulation signal. The motor programmer input was proportional to the square root of the sum of the amplitudes of center rotation speed and the modulation speed. The center speed, ω_0, was scanned from 400 to 8500 rpm, while the modulation frequency σ was kept fixed at 6 Hz and the modulation amplitude, $\Delta\omega^{1/2}$, was held at 0.5 rpm$^{1/2}$. The output current of the cell was band-pass filtered (0.64 Hz high pass, 32 Hz low pass) to remove the dc Levich component from ω_0, then rectified to recover the peak-to-peak modulation current ΔI_p. For convenience, ΔI_p is simply noted as ΔI in this paper. Also, $\Delta I/\Delta I_{0.05}$ is plotted vs p, the ratio of the frequency of modulation speed to that of the center rotation speed, instead of $A/A_{0.05}$ vs p, as essentially, their relationships with p and Sc are the same. The modulation experimental setup was checked with 2.2 mM Fe^{3+}/1 M H_2SO_4, and results were obtained similar to those in ref 10 in which different equipment was used.

Results

η and n Measurement. The viscosity and kinematic viscosity of 0.5 M TBAFB/ODCB at 25 °C and 50 °C are shown in Table 1. At 25 °C, these values are close to those of 0.5 M TBAB/ODCB.[15] The viscosity drops 35% from 25 °C to 50 °C.

C_{60}. C_{60} shows three reversible redox waves on a Pt electrode in 0.5 M TBAB/ODCB[15] or 0.5 M TBAFB/ODCB (not shown here). The steady-state currents for the first electron transfer are plotted in Figure 1 as a function of rotation speed at 25 °C and 50 °C in 0.5 M TBAFB/ODCB. The Levich plots are in Figure 2, taken from Figure 1 at −0.65 *V*, on the plateau of the first electron transfer. Plugging these slopes into (1) gives D values 1.6×10^{-6} and 2.7×10^{-6} cm^2/s at 25 °C and 50 °C, respectively.

The modulation results for 1 mM C_{60}/0.5 M TBAFB/ODCB are plotted in Figure 3 for both 25 °C and 50 °C. At the more elevated temperature, decreasing viscosity and increasing diffusion coefficient both make Sc smaller and offer relatively better sensitivity for the Sc determination.[10] The best fits of the experimental data to the theoretical curves lead to Sc numbers of 19 000 at 25 °C and 7000 at 50 °C for C_{60}. The diffusion coefficients can be obtained with these Sc numbers, the viscosity values in Table 1, and eq 2. These modulation results are collected in Table 2.
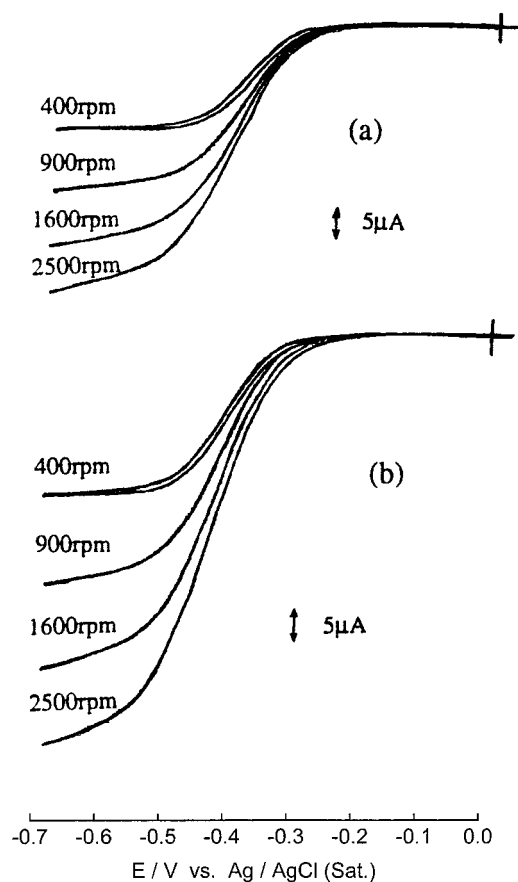
Figure 1. Disk current vs potential at various rotation speeds for 1 mM C_{60}, 0.5 M Bu_4NBF_4/ODCB. $v = 10$ mV/s: (a) 25 °C; (b) 50 °C.
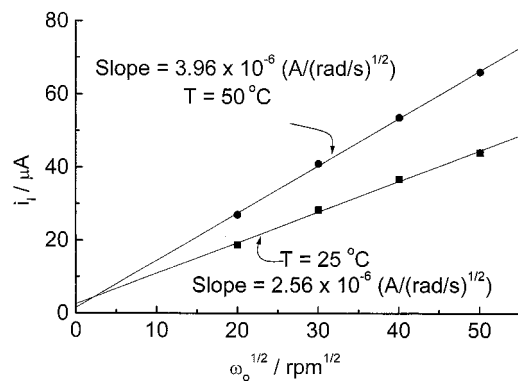

Figure 2. Limiting current vs $\omega_0^{1/2}$ rpm$^{1/2}$ at −0.65 V (plot from Figure 1).

γ-Irradiated C_{60}. The cyclic voltammetry and the steady-state current of the first reduction−reoxidation step of the γ-irradiated C_{60} product in ODCB electrolyte are shown in Figure 4 at 900 rpm. The γ-irradiated C_{60} showed a limiting current region beyond −0.5 V(Figure 4b). Under the same conditions as for C_{60} above, a modulation experiment was carried out and the fit to Sc number 14 000 of the data is given in Figure 5. With Sc = 14 000 and the kinematic viscosity value at 50 °C, we have $D_{irrad−C_{60}} = 0.96 \times 10^{-6}$ (cm²/s), which is approximately half that of C_{60} at the same temperature (Table 2).

Discussion

Diffusion Coefficient. The diffusion coefficients for 0.5 M TBAFB/ODCB in Table 2 show the expected large temperature
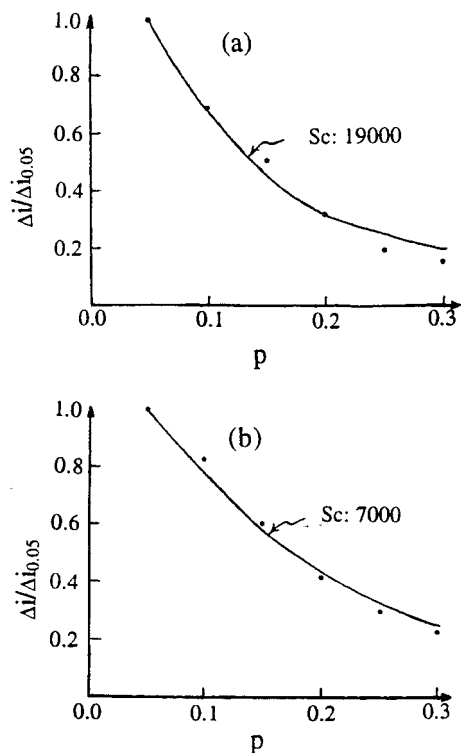

Figure 3. Modulation plots of 1 mM C_{60}, 0.5 M Bu_4NBF_4/ODCB. Solid line for theoretical value, dots for experimental result: (a) at 25 °C; (b) at 50 °C.

TABLE 2: Schmidt Numbers (Sc), Diffusion Coefficients (D), and Stokes Radii (r_s) for C_{60} or Irradiated C_{60} in Different Eletrolyte/Solvent Systems

solute/electrolyte/ solvent	$D \times 10^6$ (25 °C)			$D \times 10^6$ (50 °C)		
	Sc	cm² s⁻¹	r_s Å	Sc	cm² s⁻¹	r_s Å
C_{60}/0.5 M TBAB/ ODCB	17400[a]	1.1[a]	7.6			
C_{60}/0.5 M TBAFB/ ODCB	19000	1.1	7.7	7000	1.9	7.3
irrad-C_{60}/0.5 M TBAFB/ODCB				14000	0.96	14.8
C_{60}/0.1 M (TBA)ClO₄/PhCl		3.7[b]	7.4[b]			

[a] Taken from ref 15. [b] Taken from ref 18.

dependency. At 25 °C, the diffusion coefficient of C_{60} in 0.5 M TBAFB/ODCB obtained here, 1.1×10^{-6} cm² s⁻¹, is consistent with the result from ref 15 for C_{60} in 0.5 M TBAB/ODCB (see Table 2), a similar electrolyte, though Sc at 25 °C is slightly greater. The diffusion coefficient is smaller than that given by Kadish and co-workers,[18] possibly because of a more concentrated and more viscous electrolyte.

Stokes Radii of C_{60} and C_{60} Radiolytic Product in ODCB. From D and η, the Stokes radii of C_{60} and the γ-irradiated C_{60} in ODCB were estimated from eq 3, shown in Table 2. At 25 °C, the r_s value obtained here for C_{60} in 0.5 M TBAFB/ODCB is 7.7 Å, which is close to that of C_{60} in 0.5 M TBAB/ODCB, 7.6 Å, estimated from the previous HMRDE result.[15] At 50 °C, the modulation gives 7.3 Å for C_{60}/0.5 M TBAFB/ODCB. A value $r_s = 7.4$ Å for C_{60} in 0.1 M (TBA)ClO₄/PhCl, obtained by Kadish and co-workers from Levich plots, is close to ours and reflective of similar solvation. The r_s for the irradiated C_{60} in 0.5 M TBAFB/ODCB is 14.8 Å, twice as large as C_{60} in the same solvent, indicating molecules much larger than C_{60} in the C_{60} radiolysis product.
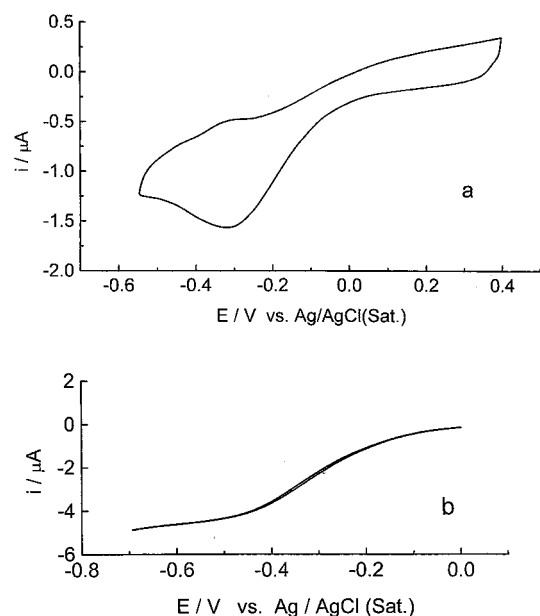
Figure 4. CV and steady-state currents of γ-irradiated C_{60} in 0.5 M Bu_4NBF_4/ODCB; $T = 25$ °C: (a) $v = 100$ mV/s; (b), $v = 10$ mV/s, $\omega_0 = 900$ rpm.
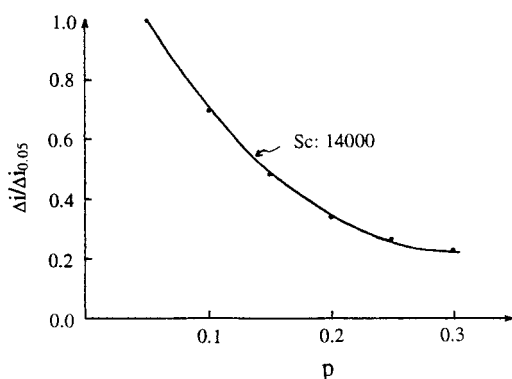

Figure 5. Modulation plots for γ-irradiated C_{60} in 0.5 M Bu_4NBF_4/ODCB; $T = 50$ °C.

TABLE 3: Radii of C_{60}, C_{60} Derivatives, and Their Stokes Radii in ODCB Solution

M	r (Å)	M(ODCB)x	r_s (Å)
C_{60}	3.5–5.0[a]	C_{60}(ODCB)x	7.3[d]
C_{60}–C_{60}	7.8[b]	$(C_{60})_2$(ODCB)x	~11[e]
$C_{60}(C_6H_{12})_{10}$	~7.0[c]	$C_{60}(C_6H_{12})_{10}$(ODCB)x	~10[e]
$[C_{60}(C_6H_{12})_{10}]_2$	~14[c]	$[C_{60}(C_6H_{12})_{10}]_2$(ODCB)x	~17[e]
		irrad–C_{60}(ODCB)x	14.8[d]

[a] C_{60} has a radius of 3.5 Å in the solid state and a van der Waals radius 5.0 Å. [b] According to ref 20. [c] from ref 5. [d] Stokes radius from modulation experiment. [e] Estimated assuming the same solvation shell contribution to Stokes radius as in C_{60} (the first row in the table), i.e., ~3 Å.

Previous studies on the γ-radiolytic product of C_{60} by mass spectrum and small-angle X-ray scattering (SAXS)[4] indicated there is a cyclohexane adduct of C_{60}, i.e., C_{60} $(C_6H_{12})_{10}$ (monomer). The SAXS data[4] and mobility investigation[5] also suggested the possible existence of a dimer of the hexane adduct of C_{60}, namely, $[C_{60}$ $(C_6H_{12})_{10}]_2$. Model calculations[5] give the radii of the dimer and the monomer of hexane adducts as 14 Å and 7 Å, respectively. Table 3 lists the radii of C_{60} and derivatives and their corresponding Stokes radii. The solvation shell contribution of ODCB of about 3 Å[19] in our experiment to the Stokes radii measured for pure C_{60} ought to be similar

for the radiolysis product. On this basis, the Stokes radii for the dimer $[C_{60}(C_6H_{12})_{10}]_2$, monomer $C_{60}(C_6H_{12})_{10}$, and dimer C_{60}–C_{60} would be approximately ~17, ~10, and ~11 Å, respectively (Table 3). Our experimental Stokes radius for the radiolytic product, 14.8 Å, suggests that the radiolytic product of C_{60} may contain both the monomer and the dimer of the C_{60}–cyclohexane adduct and possibly the C_{60}–C_{60} dimer as well. It is claimed by Wang et al.[20] that the four-member ring dimer of C_{60} splits into monomers upon cathodic electron uptake. Dimer connective diffusion is the transport mechanism, in our case, so that we can still detect them by HMRDE.

We have earlier pointed out that the use of the Levich equation directly to obtain D requires knowledge of n and C. With the radiolysis product, measurements of the Levich limiting current for the process we studied in modulation give D values that straddle the value of 0.96×10^{-6} cm^2/s at 50 °C, depending on assumptions concerning n and C which we did not have to make with modulation. The Levich data are, however, consistent with a product that contains significant dimer (if $n = 1$), as we conclude from modulation results. If $n > 1$ for a dimer, we would have to conclude our product has some inert components or ones not reduced at the wave seen. Our best estimate is thus what we conclude from modulation. If there is a mixture of monomer and dimer, a fit of the modulation behavior is not strictly correct. However, analysis of the determining equations indicates that monomer content would be overestimated and this effect strengthens our conclusions relative to the product containing a significant amount of dimer.

Conclusions

The diffusion coefficients of C_{60} and γ-irradiated C_{60} were measured by the HMRDE technique at 50 °C in 0.5 M TBAFB/ODCB solution. The diffusion coefficient of the irradiated C_{60} product is about half of that measured for C_{60} in the same electrolyte at the same temperature. The Stokes radius of the radiolytic product of C_{60} is thus nearly twice as big as that of C_{60}. The experimental results are consistent with the existence of both monomer C_{60} $(C_6H_{12})_{10}$ and dimer $[C_{60}$ $(C_6H_{12})_{10}]_2$ in the radiolytic product of C_{60}.

References and Notes

(1) Bakale, G.; Lacmann, K.; Schmidt, W. F. *ICDL Proceedings*; Fuhr, J., Biller, P., Eds.; IEEE Publisher: Piscataway, NJ, 1993; p 131.

(2) Gal'pern, E. G.; Stankevich, I. V.; Chistyakov, A. L.; Chernozatonskii, L. A. *Chem. Phys. Lett.* **1997**, *269*, 85.

(3) (a) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Am. Chem. Soc.* **1992**, *114*, 5454. (b) Burger, B.; Winter, J.; Kuzmany, H. *Z. Phys. B* **1996**, *101*, 227. (c) deLucas, Al.; Martin, N.; Sanchez, L.; Seoane, C. *Tetrahedron Lett.* **1996**, *37*, 9391.

(4) Henderson, S. J.; Hettich, R. L.; Compton, R. N.; Bakale, G. *J. Phys. Chem.* **1996**, *100*, 5426.

(5) Bakale, G.; Lacmann, K.; Schmidt, W. F. *J. Phys. Chem.* **1996**, *100*, 12477.

(6) Miller, B.; Bruckenstein, S. *J. Electrochem. Soc.* **1970**, *117*, 1032.

(7) Miller, B.; Bellavance, M. I.; Bruckenstein, S. *Anal. Chem.* **1972**, *44*, 1983.

(8) Miller, B.; Bruckenstein, S. *Anal. Chem.* **1974**, *46*, 2026.

(9) Miller, B.; Bruckenstein, S. *J. Electrochem. Soc.* **1974**, *121*, 1558.

(10) Tokuda, K.; Bruckenstein, S.; Miller, B. *J. Electrochem. Soc.* **1975**, *122*, 1316.

(11) Bruckenstein, S.; Miller, B. *Acc. Chem. Res.* **1977**, *10*, 54.

(12) Miller, B.; Rosamilia, J. M. *Anal. Chem.* **1983**, *55*, 1281.

(13) Rosamilia, J. M.; Miller, B. *Anal. Chem.* **1983**, *55*, 1142.

(14) Rosamilia, J. M.; Miller, B. *Anal. Chem.* **1984**, *56*, 2410.

(15) Miller, B.; Rosamilia, J. M.; Dabbagh, G.; Muller, A. J.; Haddon, R. C. *J. Electrochem. Soc.* **1992**, *139*, 1941.

(16) Albery, W. J.; Hillman A. R.; Bruckenstein, S. *J. Electroanal. Chem.* **1979**, *100*, 687.

(17) *CRC Handbook of Chemistry and Physics.* Weast, R. C., Astle, M. J., Ed.; CRC Press: Boca Raton, FL, 1981.

(18) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 7137.

(19) This is estimated from the Stokes radius of C_{60} in ODCB solution, $\sim$7.3 Å (see text) and the van der Waals radius 5.0 Å or radius of C_{60} in solid state 3.5 Å.

(20) Wang, G. W.; Komatsu, K.; Murata, Y.; Shiro, M. *Nature* **1997**, *387*, 583.