

Electrochemical and ESR Characterization of C₈₄ and Its Anions in Aprotic Solvents

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Cyclic voltammetry and differential pulse voltammetry studies on the *D*₂ and *D*_{2*d*} isomers of C₈₄ are reported in pyridine, benzonitrile, acetonitrile/toluene (15/85), dimethylformamide/toluene (15/85), and 1,2-dichlorobenzene. The nature of the solvent is found to greatly affect the number and half-wave potentials of the observed redox processes. For example, 10 reduction processes are observed in pyridine, while seven are detected in benzonitrile. The multiple redox processes in pyridine, are taken as evidence for the presence of two isomeric forms of C₈₄ in solution, namely, the *D*₂ and *D*_{2*d*} isomers, each of which has distinct half-wave reduction potentials. A comparison between the electrochemistry of C₆₀, C₇₀, C₇₆, C₇₈, C₈₄, and C₈₆ is presented. ESR studies were performed on solutions containing one or a mixture of the C₈₄ anion(s) and confirmed the presence of two isomers, *D*₂⁻ and *D*_{2*d*}-C₈₄²⁻. Emphasis in this paper is placed on *D*_{2*d*}-C₈₄²⁻; its ESR spectra at different temperatures are discussed and interpreted in terms of a thermally accessible triplet excited state and rotation of the dianion.

Introduction

Few experimental data are available on C₈₄, in large part because of its relative scarcity as compared to the more readily available C₆₀ and C₇₀. The gas phase electron affinity of C₈₄ has been measured as 3.07 eV by Knudsen cell mass spectrometry.¹ This value is larger than the electron affinity measured for C₆₀ (2.65 eV) and C₇₀ (2.72 eV) using the same technique,¹ and it is reflected in electrochemical studies which have shown that C₈₄ is easier to reduce than C₆₀ or C₇₀.^{2,3} Such studies have also revealed that C₈₄, like the other fullerenes investigated to date, can be electroreduced by up to five electrons.³ NMR measurements⁴ and ab-initio calculations^{4c} show that the NMR spectrum of C₈₄ can be accounted for by the coexistence of two isomers, of symmetry *D*₂ and *D*_{2*d*}. The assigned coexistence of these two isomers is further supported by the recent work of Balch *et al.*,⁵ who successfully characterized by X-ray crystallography the organometallic derivatives of the two C₈₄ isomers, (*η*²-C₈₄)Ir(CO)Cl(P(C₆H₅)₃)₂.

We recently reported combined electrochemical and ESR studies which were used to obtain the ESR spectral parameters of anions of each C₈₄ isomer.³ We present here a more extended electrochemical and spectroscopic characterization of C₈₄ in aprotic solvents. The data are first discussed in terms of the solvent effect on the different reduction potentials of C₈₄, after which we describe, in detail, the ESR spectra of the C₈₄ mono-, di-, and trianions in pyridine and DMF/toluene (15/85). The ESR spectrum observed for [*D*_{2*d*}-C₈₄]²⁻ is discussed at length since measurements on this compound provide information related to orbital degeneracy and rotation of C₈₄.

Experimental Section

Chemicals. C₈₄ was produced in a several-step procedure. First, primary extract (BUCKY USA), which has a few percent

of fullerenes which are larger than C₇₀, was selectively extracted with a combination of solvents. This solvent extraction scheme produced a fullerene mix enriched in larger fullerenes, which was then further purified by chromatography using preparative HPLC with a dinitroanilinopropyl (DNAP)-bonded phase column. The fullerene purity of C₈₄ was demonstrated by surface analysis by laser ionization (SALI)—mass spectrometry to be >99.5%. The major impurity peaks were C₈₂ and C₈₆, with no evidence for C₆₀, C₇₀, or C_{2*n*} > C₈₆.

The ¹³C-NMR spectrum of the C₈₄ sample was recorded using a 500 MHz spectrometer (Varian Instruments, Model VXR500). About 10 mg of the sample was dissolved in 5 mL of CS₂, and 0.5 mL of acetone-*d*₆ was added to the solution for locking along with about 5 mg of Cr(acac)₃ to aid relaxation. A total of 60 800 scans were collected with a pulse width of 12 μs (90° pulse width = 16 μs), an acquisition time of 2.1 s, and a cycle time of 5 s. We noticed that a small amount of sample deposited on the tube wall above the liquid meniscus even though the sample was maintained at 15 °C. Therefore, every 24 h, the sample tube was withdrawn and shaken to resuspend (and hopefully redissolve) the sample. The resulting spectrum was virtually identical to those published by Kikuchi *et al.*^{4b} and Taylor *et al.*^{4d} with 31 peaks of nearly equal intensity and one peak about half as intense as the others. The ratio of the sum of intensities for the peaks corresponding to the *D*₂ (21 peaks) and the *D*_{2*d*} (11 peaks) isomers, which is also the molar ratio of the isomers in our sample, is 1.9, in line with the 2/1 mixture of the two isomers reported by previous workers.^{4b,d}

Voltammetric studies were carried out with a C₈₄ suspension of ca. 0.5 mg in 1 mL of a given solvent. Bulk electrolyses were carried out with C₈₄ suspended at a concentration of 0.3–0.5 mg/mL of solvent.

Pyridine (py), acetonitrile (CH₃CN), dimethylformamide (DMF), and *o*-dichlorobenzene (ODCB) were purchased from Aldrich (Sure/Seal quality) and were used as received. Benzonitrile (PhCN) was purchased from Aldrich and distilled over P₂O₅ under vacuum. Toluene was purchased from Mallinckrodt and distilled over CaH₂. Tetrabutylammonium perchlorate (TBAP) was purchased from Fluka, recrystallized from absolute ethanol, and dried in vacuum at 40 °C prior to use.

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Instrumentation and Procedure. All electrochemistry was carried out in a conventional three-electrode cell. A platinum wire served as the counter electrode. A glassy carbon disk electrode purchased from Bioanalytical Systems, Inc., was used as the working electrode. The reference electrode was a saturated calomel electrode (SCE), which was separated from the working solution by a fritted glass bridge. The ferricinium/ferrocene (Fc^+/Fc) couple was used as an internal standard. All potentials are reported as V vs Fc^+/Fc . Cyclic voltammetry (CV), differential pulse voltammetry (DPV), and potential-controlled bulk electrolyses were performed with a BAS 100 electrochemical analyzer (Bioanalytical Systems, Inc.). Thin-layer cyclic voltammetry (TLCV) was performed using a PAR Model 173 potentiostat equipped with a PAR Model 175 universal programmer and a EG&G Model RE0151 X-Y recorder (Princeton Applied Research/EG&G). All experiments were carried out at room temperature (22 ± 1 °C) unless otherwise specified. The solutions for electrochemical measurements carried out outside the drybox were deoxygenated using high-purity nitrogen from TRIGAS.

Controlled potential bulk electrolyses of C_{84} were carried out in an inert atmosphere drybox (Vacuum Atmosphere Co.) using an "H" type cell. Both the working and counter electrodes were made of platinum gauze. The working and auxiliary compartments of the cell were separated by a sintered glass frit. Electroreduction to generate a given anion was performed by setting the potential at a value slightly more negative than the position of the maximum of the DPV peak corresponding to the formation of this anion.

Samples for ESR studies were prepared by potential-controlled bulk electrolyses of a C_{84} suspension. Initially, only a low current was observed due to the low solubility of neutral C_{84} in the utilized solvents. However, as the electrolysis proceeded, all of the C_{84} was eventually reduced to give a bulk solution of the desired anion. Aliquots for ESR studies were then transferred in the drybox from the electrochemical cell to ESR tubes, which were then sealed with septa and Teflon tape. The time between sample preparation and the actual measurement varied from ca. 5 min to ca. 2 h. The C_{84} monoanion was prepared first and stored in the drybox. The C_{84} trianion was prepared last.

The color of the C_{84} solution was green in all of the utilized solvents. No drastic change in color was observed upon electroreduction. All C_{84}^{n-} ($n = 1-3$) solutions have a similar greenish brown color.

ESR measurements were performed at X-band on a Bruker ER 100D spectrometer equipped with a variable temperature apparatus. The maximum available microwave power output was 260 mW. Diphenylpicrylhydrazyl (DPPH) ($g = 2.0037$) was used as the external reference for g values.

Results and Discussion

Electrochemical Characterization of C_{84} in Aprotic Solvents. Figure 1a shows a typical cyclic voltammogram (CV) of C_{84} in PhCN, 0.1 M TBAP. In addition to the five reduction waves already reported^{2,3} for C_{84} and observed here at $E_{1/2} = -0.61$, -0.94 , -1.28 , and -1.63 V vs Fc^+/Fc , a sixth reduction can be distinguished at $E_{1/2} = -2.40$ V vs Fc^+/Fc . However, the position of this redox process at the edge of the solvent potential window makes uncertain an assignment of this electrode reaction to the formation of C_{84}^{6-} . The five reductions of C_{84} are reversible on the cyclic voltammetric time scale, and the peak-to-peak separation of 60–80 mV suggests that each electrode reaction corresponds to a reduction by one electron.

To confirm the stability of the C_{84} anions, thin-layer cyclic voltammetric (TLCV) experiments were carried out on C_{84} in

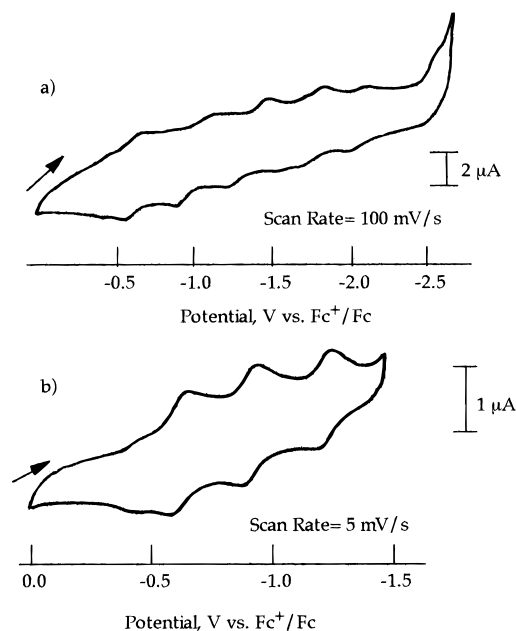


Figure 1. (a) Cyclic voltammogram at a glassy carbon electrode of a saturated solution of C_{84} in benzonitrile, 0.1 M TBAP (ca. 0.5 mg/mL). Scan rate = 100 mV/s. (b) Thin-layer cyclic voltammogram at a platinum grid electrode of a saturated solution of C_{84} in *o*-dichlorobenzene, 0.5 M TBAP (ca. 0.5 mg/mL). Scan rate = 5 mV/s.

o-dichlorobenzene containing 0.5 M TBAP. The resulting voltammogram is shown in Figure 1b. The first three electroreductions are reversible even at a scan rates as low as 5 mV/s. This implies that bulk electrogeneration of solutions of C_{84}^{n-} ($n = 1-3$) will lead to relatively stable species for further spectral characterization. Only the first three anions could be characterized, and all attempts to bulk electrogenerate solutions of C_{84}^{4-} or higher anions were unsuccessful due to the occurrence of a rapid chemical reaction following the electron transfer.

Even though the voltammetric experiments were carried out on saturated solutions, the solubility of C_{84} in the utilized solvents was too low to obtain well-developed cyclic voltammograms. On the other hand, much better developed peaks could be obtained by differential pulse voltammetry (DPV), a technique in which the capacitive background current is largely eliminated. Figure 2 displays examples of differential pulse voltammograms for saturated solutions of C_{84} in solvents containing 0.1 M TBAP. The redox processes can be broken into five groups as indicated in Figure 2. The fifth group has reduction currents that are much smaller than the preceding ones, and this suggests the occurrence of a chemical reaction involving C_{84}^{4-} . This is consistent with the lack of success in electrogenerating bulk solutions of this anion.

Role of the Solvent on the C_{84} Electrochemistry. As shown in Figure 2, there is a striking difference between the differential pulse voltammograms of C_{84} in pyridine, benzonitrile, and DMF/toluene (15/85). Seven redox peaks (including shoulders) are observed in PhCN and DMF/toluene, whereas a total of 10 redox peaks can be distinguished in pyridine. Previous studies have established that the two isomers of C_{84} should coexist in a 2/1 ratio.²⁻⁵ These two isomers were shown to possess the D_2 and D_{2d} geometries with the expected molar ratio of D_2/D_{2d} being 2/1. The voltammogram recorded in pyridine clearly establishes the presence of more than one electroactive species in the C_{84} sample, and these species are assumed to be the D_2 and D_{2d} isomers. Further evidence for the presence of two isomers is provided by the ESR data given in a following section.

TABLE 1: Peak Potentials (V vs SCE) Measured by Differential Pulse Voltammetry for the Reduction of C₈₄ in Various Solvents Containing 0.1–0.15 M TBAP

solvent	1st red.		2nd red.		3rd red.		4th red. ^e	5th red.		
	D _{2d}	D ₂	D _{2d}	D ₂	D ₂	D _{2d}				
pyridine	-0.52	-0.61	-0.84	-0.97	-1.20	-1.30	-1.52 ^d	-1.63	-1.94	-2.07
benzonitrile	-0.43	-0.61		-0.94		-1.28	-1.54 ^d	-1.63		-1.90
CH ₃ CN/toluene ^a	-0.51 ^d	-0.67		-1.00		-1.34	-1.65 ^d	-1.72		-1.99
DMF/toluene ^b		-0.64		-0.96		-1.34	-1.60	-1.76		-2.04
ODCB ^c		-0.61		-0.91		-1.24		-1.56		-1.90

^a CH₃CN/toluene (15/85). ^b DMF/toluene (15/85). Potentials measured at -15 °C. ^c *o*-Dichlorobenzene containing 0.45 M TBAP. ^d The E_p could only be estimated because the corresponding redox process appears as a broad wave which is superimposed on the following process. ^e See text for detail about the lack of assignment.

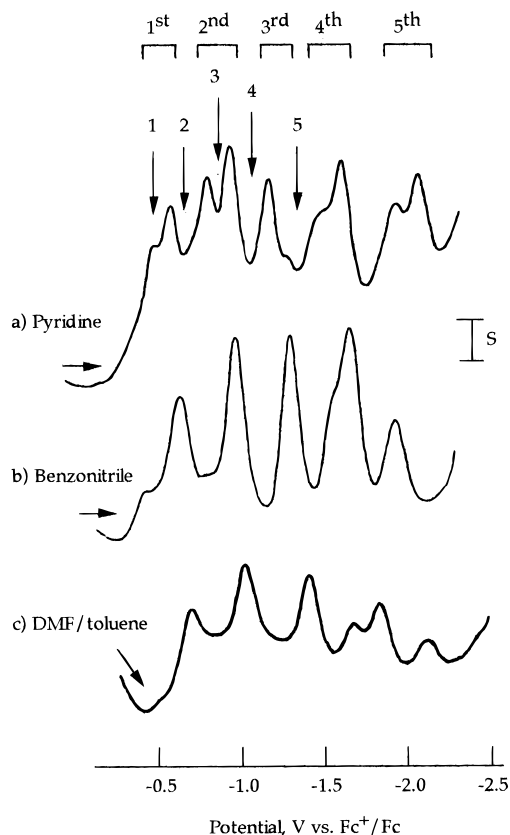


Figure 2. Differential pulse voltammogram at a glassy carbon electrode of a saturated solution of C₈₄ (ca. 0.5 mg/mL) in (a) pyridine (scan rate = 2 mV/s; pulse amplitude = 40 mV); (b) benzonitrile (scan rate = 10 mV/s; pulse amplitude = 50 mV); and (c) DMF/toluene (15/85) (scan rate = 10 mV/s; pulse amplitude = 25 mV). All solvents contained 0.1 M TBAP.

Interestingly, among the fullerenes for which electrochemistry has been described, only C₇₈⁶ and C₈₄^{2,3} are reported to exist in two isomeric forms, namely, C_{2v} and D₃ for C₇₈ and D₂ and D_{2d} for C₈₄. Preliminary studies on C₇₈⁶ have suggested that the two C₇₈ isomers might have different electrochemistries. The variation in relative peak heights assigned to the two C₈₄ isomers in pyridine (Figure 2a) might be interpreted in terms of different solubilities of the neutral and electroreduced species. Such a solubility difference between C₆₀ and its anions is already well established.^{7a,b} ESR studies, described below, led us to assign a given reduction process to a given isomer. The reduction potentials for processes which are well-defined are listed in Table 1 and attributed to a given isomer. In pyridine, the D_{2d} isomer is easier to reduce by one, two, or three electrons ($E_{1/2} = -0.52, -0.84, \text{ and } -1.20 \text{ V vs Fc}^+/\text{Fc}$) as compared to the D₂ isomer ($E_{1/2} = -0.61, -0.97, \text{ and } -1.30 \text{ V vs Fc}^+/\text{Fc}$). In four of the five investigated solvents, the third reduction of each isomer occurs either at a similar potential or at potentials

so close to each other that they cannot be resolved into two distinct processes. The only exception is in pyridine, where the third reduction of the two isomers appears at -1.20 for D₂ and -1.30 V for D_{2d}.

It was not possible to assign the fourth and fifth reduction potentials of C₈₄ to a given isomer because of variation in the heights of the corresponding peaks. This variation can be due to a solubility difference between the two isomers, or it could result from a difference in chemical stability of the reduced D₂ and D_{2d} isomers.

The nature of the solvent is known to markedly influence the electrochemistry of C₆₀.⁷ Changes in solvent are also reflected in the electrochemistry of C₈₄ both in the individual $E_{1/2}$ values and in the overall appearance of the voltammogram. The half-wave potentials for the successive reductions of C₈₄ are also affected. In this part of our studies, we consider only the major redox processes observed in the voltammograms of C₈₄. Even if the major peaks seen in the voltammograms do not correspond to the reduction of the same isomer, we expect the electrochemistry of both isomers to be similarly affected. In the five solvents used in this study (pyridine, benzonitrile, CH₃CN/toluene (15/85), DMF/toluene, (15/85), and *o*-dichlorobenzene), half-wave potentials for reductions of C₈₄ vary by 60 mV as a function of solvent for the first reduction (i.e. from -0.61 to -0.67 V vs Fc⁺/Fc, as seen in Table 1), 90 mV for the second reduction (-0.91 to -1.00 V vs Fc⁺/Fc), and 100 and 200 mV for the third and fourth reductions, respectively. This may be compared with the variation in half-wave potentials for the first four reductions of C₆₀ in the same solvents, that is 200, 160, 100, and 160 mV.^{7a} Thus, the first and second reduction potentials of C₈₄ seem less affected when changing the solvent than do the first and second reduction potentials of C₆₀. However, the higher reductions of C₈₄ are affected by solvent in the same manner as those of C₆₀.

As in the case of C₆₀, there is no apparent correlation between the potentials for reduction of C₈₄ and the polarity or polarizability of the solvent. A similar observation has been made for C₇₆.⁸

The first four reductions of C₆₀ are usually affected in a similar way from one solvent to another, but this is not the case for C₈₄. For example, the first reduction of C₆₀ is easier in DMF/toluene⁹ ($E_{1/2} = -0.82 \text{ V vs Fc}^+/\text{Fc}$) than in CH₃CN/toluene¹⁰ ($E_{1/2} = -0.98 \text{ V vs Fc}^+/\text{Fc}$), and this also the case for the successive three reductions of C₆₀, i.e. $E_{1/2} = -1.24, -1.77, \text{ and } -2.22 \text{ V vs Fc}^+/\text{Fc}$ for DMF/toluene⁹ and $E_{1/2} = -1.37, -1.87, \text{ and } -2.35 \text{ V vs Fc}^+/\text{Fc}$ in CH₃CN/toluene.¹⁰ In the case of C₈₄, the first two reductions are easier in DMF/toluene ($E_{1/2} = -0.64 \text{ and } -0.96 \text{ V vs Fc}^+/\text{Fc}$) than in CH₃CN/toluene ($E_{1/2} = -0.67 \text{ and } -1.00 \text{ V vs Fc}^+/\text{Fc}$), but the order is reversed for the third and fourth reductions, i.e. $E_{1/2} = -1.34 \text{ and } -1.76 \text{ V vs Fc}^+/\text{Fc}$ in DMF/toluene and $E_{1/2} =$

TABLE 2: Half-Wave Reduction Potentials for Fullerenes Measured in CH₃CN/Toluene (20/80), 0.1 M TBAPF₆

C _{2n}	E _{1/2} , V vs SCE						ref
	1st	2nd	3rd	4th	5th	6th	
C ₆₀ ^a	-0.98	-1.37	-1.87	-2.35	-2.85	-3.26	10
C ₇₀ ^a	-0.97	-1.34	-1.78	-2.21	-2.70	-3.07	10
C ₇₆	-0.83	-1.17	-1.68	-2.10	-2.61	-3.04	6
C ₇₈ ^b	-0.72	-1.08	-1.79	-2.18	-2.45	-2.73	6
C ₈₄ ^c	-0.67	-1.00	-1.34	-1.72	-1.99	-2.40 ^e	t.w. ^f
C ₈₆ ^d	-0.58	-0.85	-1.06	-1.96	-2.51		12

^a Measured at -10 °C. ^b Potentials measured for the C_{2v} isomer. ^c Major peaks observed in the differential pulse voltammogram of C₈₄ recorded in CH₃CN/toluene (20/80), 0.1 M TBAClO₄. ^d Measured in *o*-dichlorobenzene, 0.1 M TBAPF₆. ^e Tentative assignment to the 6th reduction of C₈₄. ^f This work.

-1.34 and -1.72 V vs Fc⁺/Fc in CH₃CN/toluene. In other words, the potential *difference* between two successive reductions of C₆₀ seems solvent independent, while for C₈₄ it is solvent dependent.

Electrochemistry of Higher Fullerenes: A Comparative Study. Electrochemistry can be used as a powerful probe to gain insights into the electronic properties of fullerenes and their anions. However, prior to any comparison between the electrochemical properties of fullerenes, two requirements must be fulfilled. The first is that reduction potentials should be measured in the same solvent and, if possible, using the same supporting electrolyte. The second is that one must utilize data only from reversible electrode processes.

The first requirement is dictated by the dramatic solvent effect on the electrochemistry of fullerenes. Studies have shown that the nature of the solvent is a determining factor in the values measured for the reduction potentials of fullerenes.^{7a,c} The solubility of the fullerene anions with respect to that of the neutral fullerene is also greatly dependent upon the solvent.⁷ The best evidence of this solvent dependence is the successful electrodeposition of C₆₀ⁿ⁻ films using an electrochemical quartz crystal microbalance.^{7b,11} The results described in the present paper are consistent with different solubilities of the two C₈₄ isomers in the same reduced state but may also be accounted for by similar E_{1/2} values for the two isomers in certain solvent systems.

Pure C₆₀ and C₇₀ are now commercially available at relatively low cost. However, it is still painstakingly difficult and expensive to obtain pure samples of higher fullerenes. The difficulty in purifying the higher fullerenes is due in part to the fact that compounds such as C₈₄ and C₇₆ exist as mixtures of isomers. Thus, one must be careful in interpreting results obtained during electrochemical studies. Combining electrochemistry and ESR spectroscopy might help in assigning a particular electrochemical process to the correct fullerene isomers.

Half-wave potentials for the reduction of C₆₀,¹⁰ C₇₀,¹⁰ C₇₆,⁶ C₇₈,⁶ and C₈₄ have been reported in CH₃CN/toluene mixtures containing TBAPF₆ or TBAP as supporting electrolyte. Table 2 summarizes these redox potentials as well as the E_{1/2} values measured for C₈₆¹² in *o*-dichlorobenzene. The larger the fullerene, the larger its electron affinity¹ and the easier it is to reduce. A correlation between the electron affinities and reduction potentials of fullerenes was recently used to calculate the solvation energy of fullerene monoanions in DMF, and a value of ΔΔG_{sol} = -1.76 eV was found.¹³

Of special interest is the potential difference between two successive reductions of the fullerenes listed in Table 2 since these data provide information about the energy needed to add electrons onto an already negatively charged fullerene. This

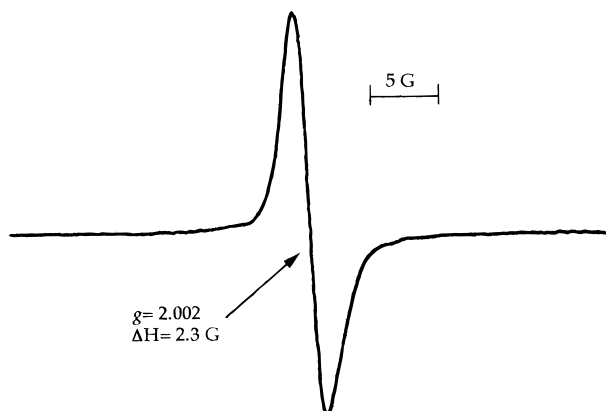


Figure 3. ESR spectrum, at $T = 117$ K and $P = 8.2$ mW, of a frozen pyridine solution of $D_{2d}\text{-C}_{84}^-$ electrogenerated at 1-C_{84}^- .

difference is constant for C₆₀ and is about 500 mV between each two successive processes. In the case of C₇₀ and C₈₄, the absolute potential difference between each two successive reductions becomes smaller as the charge of the anions becomes more negative from -1 to -6. However, this is not the case for C₇₆, where the difference between the second and third reductions is larger than that between the first and second reductions.⁶

Finally, it should be noted that C₇₈ and C₈₆ both display electrochemistry that is markedly different from that of the other fullerenes examined to date. Surprisingly, the third reduction of C₇₈ (-1.79 V) occurs at almost the same potential as the third reduction of C₆₀ (-1.87 V). On the other hand, C₈₆ shows a surprising 900 mV potential difference between the third and fourth reductions.

ESR Characterization of C₈₄ Anions in Aprotic Solvents.

A detailed description of the ESR spectra of the species or mixture of species generated after each of the first five redox processes is given below. The potential at which each anion or mixture of anions was electrogenerated is indicated by a vertical arrow in Figure 2a and is designated as $x\text{-C}_{84}^{n-}$, where x represents the number in Figure 2a and $n = 1, 2, \text{ or } 3$. The differential pulse voltammogram of the species generated after each electrolysis was recorded, and no chemical reactions involving the reduced C₈₄ species were observed on the electrochemical time scale.

After Reduction at 1-C₈₄⁻. The ESR spectrum of a frozen pyridine solution consists of an isotropic 2.3 G wide signal centered at $g = 2.002$ (see Figure 3). The microwave power dependence of the intensity of this ESR signal strongly suggests the presence of one, and only one, paramagnetic species. Saturation of the ESR signal was not observed, even at a maximum microwave power of 260 mW.

After Reduction at 2-C₈₄⁻. A frozen pyridine solution displays an ESR spectrum which consists, at 8 mW microwave power, of an anisotropic 1.9 G wide signal centered at $g = 2.002$ (Figure 4). This is not the case at lower microwave power (0.82 mW), where a sharp line ($\Delta H = 1.2$ G, $g = 2.003$) superimposed on a broader line is observed. The sharp line saturates at high microwave power (260 mW), and only the broader line ($\Delta H = 2.8$ G, $g = 2.002$) can be detected. The microwave power dependence of the ESR signal of a frozen pyridine solution is shown in Figure 5. The difference in evolution of the two lines upon varying the microwave power clearly indicates the presence of two ESR active species. The broader line in the signal after reduction at 2-C₈₄⁻ is similar to the signal observed after reduction at 1-C₈₄⁻.

After Reduction at 3-C₈₄²⁻. The ESR spectrum of a frozen pyridine solution consists of two sets of resonances that appear

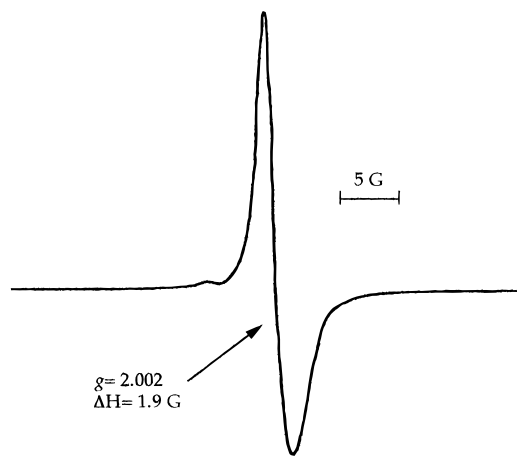


Figure 4. ESR spectra, at $T = 116$ K and $P = 8.2$ mW, of a frozen pyridine solution containing a mixture of $D_{2d}\text{-C}_{84}^-$ and $D_2\text{-C}_{84}^-$ electrogenerated at 2-C_{84}^- .

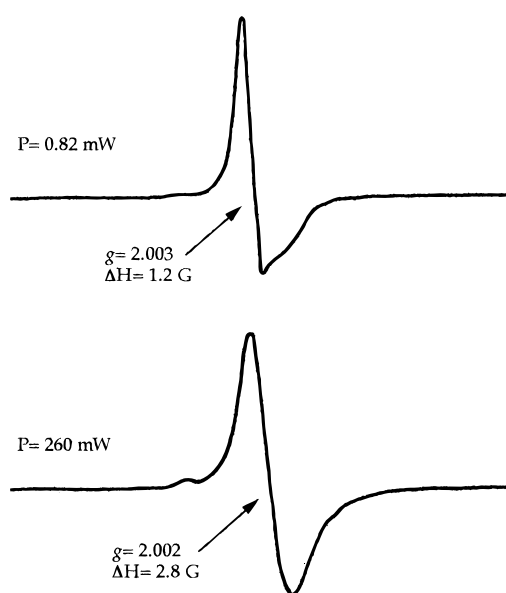


Figure 5. Magnetic power dependence of the ESR spectrum, at $T = 120$ K, of a frozen pyridine solution electrogenerated at 2-C_{84}^- .

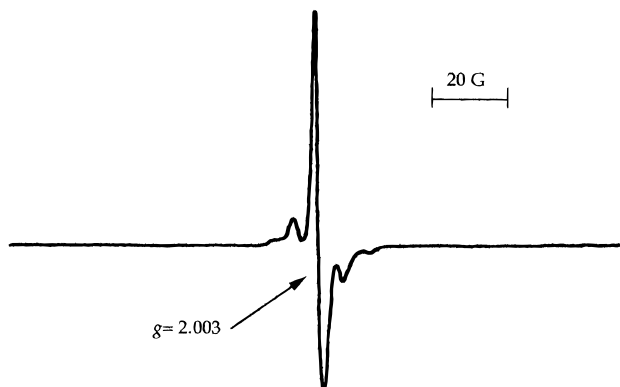


Figure 6. ESR spectrum, at $T = 118$ K and $P = 8.2$ mW, of a frozen pyridine solution containing a mixture of $D_2\text{-C}_{84}^-$ and $D_{2d}\text{-C}_{84}^{2-}$ electrogenerated at 3-C_{84}^{2-} .

as a narrow line superimposed on the spectrum expected for an ESR magnetic triplet state, as shown in Figure 6. The ESR parameters of the narrow line are the same as those for the narrow line that is produced upon reduction at 2-C_{84}^- (see Figure 5). However, microwave power dependence studies indicate that the sharp central line is composed of two underlying lines. At low power, the signal consists of a slightly anisotropic sharp

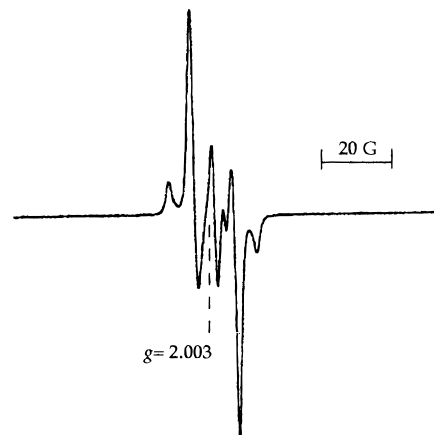


Figure 7. ESR spectrum, at $T = 115$ K and $P = 8.2$ mW, of a frozen DMF/toluene (15/85) solution containing a mixture of $D_{2d}\text{-C}_{84}^{2-}$ and $D_2\text{-C}_{84}^{2-}$ electrogenerated at 4-C_{84}^{2-} .

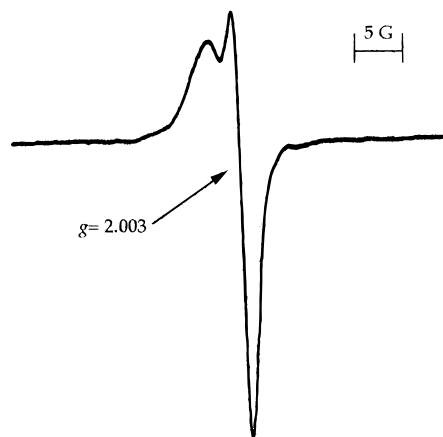


Figure 8. ESR spectrum, at $T = 115$ K and $P = 8.2$ mW, of a frozen pyridine solution containing a mixture of $D_{2d}\text{-C}_{84}^{3-}$ and $D_2\text{-C}_{84}^{3-}$ electrogenerated at 5-C_{84}^{3-} .

line superimposed on a magnetic triplet-like signal. At high power, the signal consists of a isotropic sharp line superimposed on the same triplet-like signal. The narrow line which saturates is believed to be the same line observed following reduction at 2-C_{84}^- .

After Reduction at 4-C_{84}^{2-} . The ESR spectrum of a frozen DMF/toluene solution is shown in Figure 7. This spectrum is similar to that described for a frozen pyridine solution after reduction at 3-C_{84}^{2-} except that the narrow line is no longer seen when the spectrum is recorded at low microwave power. As the microwave power is increased, the triplet state spectrum saturates at ca. 50 mW, and a sharp line appears with increasing power so that at maximum microwave power (250 mW) the ESR spectrum consists of a symmetrical sharp line superimposed on a magnetic triplet signal.

After Reduction at 5-C_{84}^{3-} . The ESR spectrum of a frozen pyridine solution (see Figure 8) clearly suggests the presence of two radicals in that it shows a narrow line superimposed on a broader line. The microwave power dependence of these two lines confirms the presence of two paramagnetic species, neither of which is the triplet system observed after reduction at 4-C_{84}^{2-} . The two redox processes preceding 5-C_{84}^{3-} could not be resolved due to the closeness of the E_p values for both C_{84} isomers.

Tabulation of the ESR parameters for each electrogenerated C_{84}^{n-} anion is given in Table 3. The assignments of the isomer type are based on symmetry considerations which predict a doubly degenerate LUMO for the D_{2d} isomer and a singly

TABLE 3: ESR Spectral Data for the Various C₈₄ Anions in Frozen Pyridine (*T* = ca. 115 K)

anion	symmetry	ΔH (G)	<i>g</i>	comments
C ₈₄ ⁻	<i>D</i> _{2d}	2.3	2.002	no saturation at 260 mW
	<i>D</i> ₂	1.9 ^a	2.003 ^a	saturates at ca. 30 mW
C ₈₄ ²⁻	<i>D</i> _{2d}	<i>D'</i> = 13 G	2.003	saturates at ca. 150 mW
	<i>D</i> ₂	ESR silent		
C ₈₄ ³⁻	<i>D</i> _{2d} ^b	3.9	2.003	no saturation at 260 mW
	<i>D</i> ₂ ^b	1.7	2.002	saturates at ca. 8 mW

^a Measured in frozen DMF/toluene (15/85) at *T* = 112 K. ^b Tentative assignment based on ESR microwave power dependence.

degenerate LUMO for the *D*₂ isomer. The ESR signal of the latter is expected to saturate more easily than the former. With this in mind, one would expect a broader ESR resonance shifted toward higher magnetic fields for the *D*_{2d}-C₈₄⁻ isomer as compared to that of *D*₂-C₈₄⁻. Furthermore, the *D*₂-C₈₄²⁻ isomer is anticipated to be diamagnetic, while the *D*_{2d}-C₈₄²⁻ isomer is expected to display a triplet ESR spectrum, in agreement with our observations.

***D*_{2d}-C₈₄²⁻: Triplet Ground State or Thermally Accessible Triplet State?** As mentioned earlier, the solution generated by bulk electroreduction at 4-C₈₄²⁻ displays a magnetic triplet state ESR spectrum characterized by a zero-field splitting, *D'*, of 13.0 ± 0.3 G (see Figure 7). The zero-field splitting *E'* was found to be 0.36 ± 0.3 G, which is consistent with the symmetry of the *D*_{2d}-C₈₄ dianion, i.e. a molecule which possesses axial symmetry. We were unable to observe an ESR absorbance associated with the “ $\Delta M_s = 2$ ” transition, which would have been additional evidence for the triplet nature of the ESR spectrum of *D*_{2d}-C₈₄²⁻. However, many examples of magnetic triplet systems that do not display a half-field ESR signal have been reported.¹⁴ An average diameter of 13 ± 0.5 Å was estimated for *D*_{2d}-C₈₄²⁻ from the value of the zero field splitting, *D'*, and the central *g* value of the triplet ESR spectrum.^{15,16} This value compares to the 12.6 Å diameter reported for C₆₀²⁻.¹⁷

The temperature dependence of the ESR intensity of the magnetic triplet state was examined in pyridine over the temperature range 110–170 K (below the melting point of the solvent, 230 K) and reveals that the ESR absorption arises from a thermally excited magnetic triplet state with a singlet ground state. The energy separation between the singlet ground state and the thermally accessible triplet state was determined to be 0.022 ± 0.01 eV from an Arrhenius plot of log(χT) vs 1/*T*.

Rotation of *D*_{2d}-C₈₄²⁻. As the temperature of the sample is increased, the positions of the inner and outer pairs of lines move toward the center of the spectrum and, at about 200 K, merge to yield a single isotropic ESR line (see Figure 9). The changes observed in the spectrum when the temperature is increased can be understood in terms of an increasing rate of rotation of the *D*_{2d}-C₈₄²⁻ molecules in the softened, and then melted, solvent matrix. To analyze the rate of rotation, we used modified Bloch equations¹⁸ for slow rotation to evaluate the activation energy of the rotational frequency changes. The relevant equation is given in eq 1:

$$\gamma^2(d_0^2 - d^2) = 2\omega^2 \quad (1)$$

where *d* and *d*₀ are the measured values of the apparent and real zero-field splittings in gauss from points of extreme slope of the derivative of the absorption spectrum in the presence and absence of rotation, respectively; ω is the exchange frequency in radians; and γ is the gyromagnetic ratio of the electron. The inner pair of lines were used because they are more sensitive to rotation at lower rotation frequencies. A value of *d*₀ = 15.07 G was measured at *T* = 94 K, before the inner pair of lines

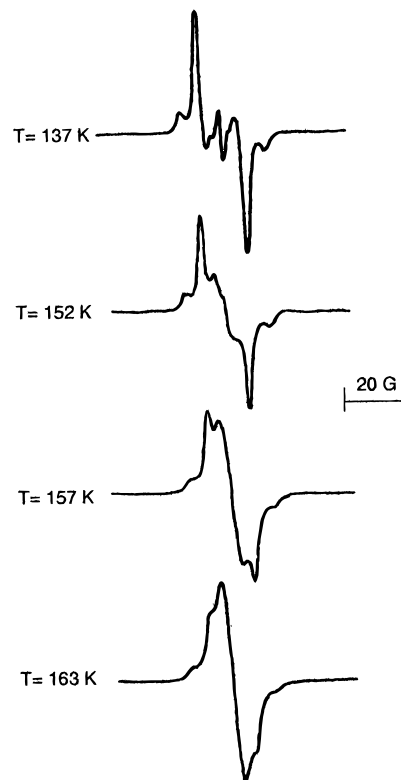


Figure 9. Temperature dependence of the ESR spectrum, *P* = 8 mW, of the frozen DMF/toluene solution electrogenerated at 4-C₈₄²⁻.

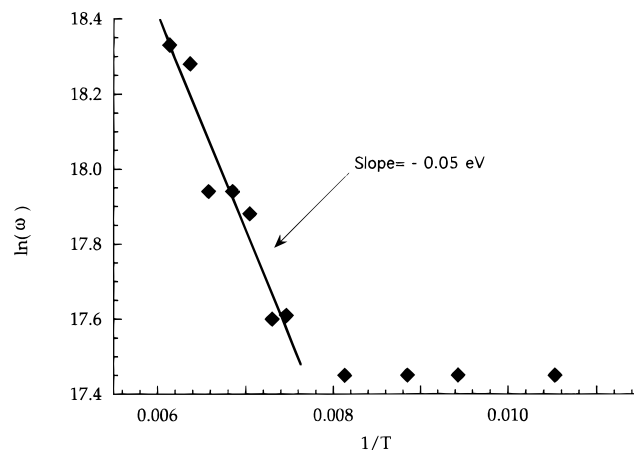


Figure 10. Plot of ln(ω) vs 1/*T*. ν was calculated using eq 1 (see text for details).

start moving toward the center of the spectrum. Figure 10 shows the plot of ln(ω) versus 1/*T* over the temperature range from 94 to 163 K. The portion of the curve that corresponds to the higher temperatures (*T* ≥ 130 K) can be fitted by a straight line of slope 0.05 ± 0.02 eV, which gives an estimate of the activation energy of the rotation which is responsible for the line narrowing and ultimate collapse.

Summary and Conclusion

C₈₄ can be reversibly electroreduced by at least five electrons. Thin-layer cyclic voltammetric measurements confirmed that the first three C₈₄ anions are stable enough to allow for ESR characterization of these species. The electrochemistry of C₈₄ is highly solvent dependent; in pyridine, the two C₈₄ isomers detected by ¹³C-NMR show distinct redox waves, whereas in DMF/toluene or benzonitrile, mainly one set of redox processes is observed. This is interpreted in terms of different solubilities

between the two reduced C₈₄ isomers but may also be due to an incomplete resolution of the reduction waves associated with each isomer in these solvents.

ESR spectroscopy was used to establish the presence of two C₈₄ isomers as proposed by electrochemistry (and confirmed by NMR measurements). The assignments of the isomer type are based upon symmetry considerations which predict a doubly degenerate LUMO for the D_{2d} isomer and a nondegenerate LUMO for the D₂ one. A temperature dependence study of the ESR signal intensity of D_{2d}-C₈₄²⁻ reveals that the ESR absorption arises from a thermally accessible triplet state with a singlet ground state. The singlet-triplet energy separation was determined to be 0.022 eV. Temperature dependence studies give an estimated 0.05 eV for the activation energy of rotation of the D_{2d}-C₈₄ isomer dianion.

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