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ESR Characterization of Singly-, Doubly-, and Triply-Reduced C_{84} Isomers[†]

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Following C_{60} and C_{70}, C_{84} is one of the more abundant fullerenes. NMR studies[1,2] of C_{84} have shown that two of the possible 24 isomers which obey the isolated pentagon rule[3-10] can be isolated.[1,2,6,11-13] These two isomers have symmetries D_2 and D_{2d} and exist in relative abundances of 2:1. Initial electrochemical studies of C_{84} in benzonitrile (PhCN) and *o*-dichlorobenzene (ODCB)[14] have been reported but did not clearly distinguish between these two isomers. We have reproduced these electrochemical results in benzonitrile[15] (PhCN) as well as carried out new experiments in pyridine and a 15/85 dimethylformamide (DMF)/toluene mixture and have observed that two distinct sets of multiple redox processes can be resolved in the latter solvents, each of which can be associated with reduction of a different isomer. This contrasts with results in PhCN and ODCB, where the two C_{84} isomers apparently have $E_{1/2}$ values too close in potential to be resolved. Combined electrochemical and electron spin resonance (ESR) measurements are now reported in these two new solvents which allow us to assign, for the first time, both half-wave potentials and ESR parameters to a given D_2 or D_{2d} C_{84}^{n-} isomer, where n = 1, 2, or 3.

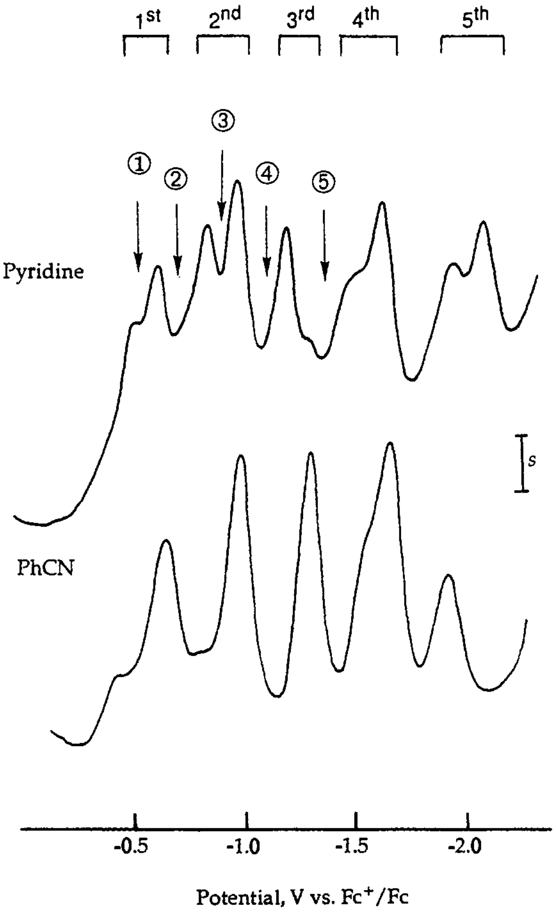

Figure 1. Differential pulse voltammograms obtained at a glassy carbon electrode for saturated solutions of C_{84} in pyridine (pulse amplitude, 40 mV; scan rate, 2 mV/s; *S*, 200 nA) and benzonitrile (pulse amplitude, 25 mV; scan rate, 10 mV/s; *S*, 100 nA). The pulse width and pulse period were kept constant and equal to 50 ms and 1 s, respectively, in both voltammograms.

Figure 1 compares the differential pulse voltammograms (DPVs) of C_{84} in benzonitrile and pyridine containing 0.1 M tetrabutylammonium perchlorate (TBAP).[16] A total of six redox processes are detected in the benzonitrile solution, in agreement with the previous report.[14] In contrast, a total of 10 redox processes are seen in pyridine, which, as shown in Figure 1, can be grouped into five separate sets of two processes.[17] Since two isomers of neutral C_{84} are initially present in solution, one can envision that the first two DPV peaks in pyridine lead to formation of two C_{84}^- isomers, the next two peaks to formation of two C_{84}^{2-} isomers, the next two peaks to formation of two unresolved C_{84}^{3-} isomers, and so on.

In order to examine the ESR properties of each electrogenerated C_{84}^{n-} species, solutions of the different C_{84}^{n-} ions in pyridine or DMF/toluene were generated by stepwise exhaustive bulk electrolysis and their ESR spectra recorded at low temperature (ca. 120 K). The potentials at which the bulk electrolyses were carried out in pyridine are indicated by vertical arrows in Figure 1 and are designated in the text by the notation $x - C_{84}^{y-}$, where x is the number used to differentiate the successive bulk electrolysis, i.e., 1, 2, 3, 4, or 5, and y represents the charge on the C_{84}^{n-} moiety, i.e., 1, 2, or 3. The first three reduction couples (six processes) are all electrochemically and chemically reversible

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(15) The $E_{1/2}$ values which we measured in PhCN are identical within experimental error to the reported values.[14] However, this is not the case for the values measured in ODCB, where the potentials reported in ref 14 are displaced in a negative direction by more than 250 mV due to errors in the reference electrode stability (J. P. Selegue, personal communication).

(16) C_{84} was produced in a several-step procedure. First, primary extract (BUCKY USA) (which has a few percent of fullerenes which are larger than C_{70}) was selectively extracted with a combination of solvents. The solvent extraction scheme produced a fullerenes mix enriched in larger fullerenes which was then further purified by chromatography with a preparative HPLC "DNAP" column. The mass purity of the C_{84} sample was demonstrated by surface analysis by laser ionization (SALI) mass spectrometry to be >99.5%. The major impurity peaks were C_{82} and C_{86}, with no C_{60}, C_{70}, or $C_{2n} > C_{86}$ evident.

(17) Similarly, two sets of redox processes are also observed in the DPV of a saturated solution of C_{84} in DMF/toluene (15/85).

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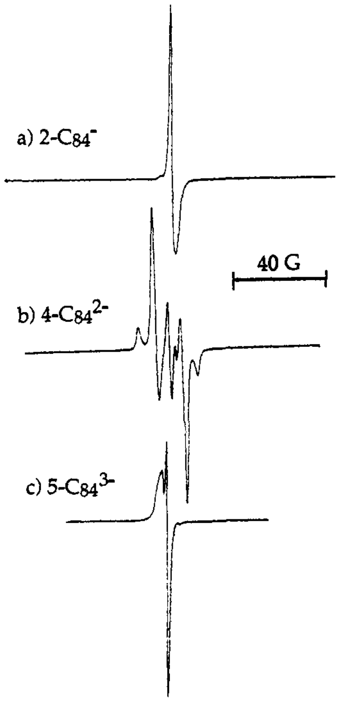

Figure 2. ESR spectra, at $T = 115$ K and $P = 8.2$ mW of frozen solutions of the appropriate C_{84} anion(s) in DMF/toluene (15/85) containing 0.1 M TBAP after electrogeneration at (a) 2-C_{84}^-, (b) 4-C_{84}^{2-}, and (c) 5-C_{84}^{3-} (see Figure 1 for the potentials).

as ascertained by reversing the potential scan at −1.3 V. This was not the case for the latter two sets of redox processes, and attempts to generate C_{84}^{4-} or C_{84}^{5-} by bulk electrolysis at potentials more negative than −1.3 V failed due to the fact that these species are unstable in the utilized solvent systems on the time scale of the experiment.

An isotropic 2.3 G wide ESR signal centered at $g = 2.002$ is observed for the frozen pyridine solution obtained after the first bulk electroreduction at 1-C_{84}^-. The microwave power dependence of the intensity of this ESR signal strongly suggests the presence of one, and only one, paramagnetic species in solution. Saturation of the ESR signal was not observed, even at a maximum microwave power of 260 mW. The second bulk electrolysis at 2-C_{84}^- leads, both in pyridine and in the DMF/toluene mixture, to an ESR spectrum which consists, at 8 mW microwave power, of an anisotropic 1.9 G wide signal centered at $g = 2.002$ (Figure 2a). 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 distinguished. This 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-C_{84}^- is similar to the signal observed after reduction at 1-C_{84}^-.

The ESR spectrum obtained after electrolysis at 3-C_{84}^{2-} consists of two sets of resonances that appear as a narrow signal superimposed on an ESR magnetic triplet state signal. The ESR parameters of the narrow line are the same as those given in Table 1 for the narrow line that is produced upon reduction at 2-C_{84}^-. The narrow ESR signal disappears after electrolysis at 4-C_{84}^{2-}. The line which disappears at 3-C_{84}^{2-} is the line that was produced at 1-C_{84}^-. The spectrum of the magnetic triplet state which remains (see Figure 2b) is characterized by zero-field splittings, $D' = 13.0 \pm 0.3$ G and $E' = 0.36 \pm 0.3$ G, which confirm that the magnetic triplet is axially symmetric as expected. 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. This single motionally narrowed line of the magnetic triplet continues to be observed after the solvent melts completely.

Table 1. ESR Spectral Data for the Various C_{84} Anions in Frozen Pyridine (T = ca. 115 K)

anion	symmetry	ΔH (G), g	comments
$(C_{84})^-$	D_{2d}	2.3, 2.002	no saturation at 260 mW
	D_2	1.9, 2.003[a]	saturates at ca. 30 mW
$(C_{84})^{2-}$	D_{2d}	D', 13 2.003 E', 0.36	saturates at ca. 150 mW
	D_2	ESR silent	
$(C_{84})^{3-}$	D_{2d}[b]	3.9, 2.003	no saturation at 260 mW
	D_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.

An average diameter of 13.0 ± 0.5 Å is estimated for C_{84}^{2-} from the value of the zero-field splitting, D', and the central g value of the triplet ESR spectrum,[18,19] and this value compares to the 12.6 Å diameter reported[20] for C_{60}^{2-}. The larger diameter of C_{84}^{2-} is consistent with the relative molecular diameters of C_{84} and C_{60}. Also of interest is a comparison with the diameters of the photoexcited triplets of C_{60} and C_{70}, which are reported to be 6.1 and 7.9 Å respectively.[21] Again, one expects the photoexcited triplet to be smaller in size than a dianion triplet on the same molecular frame because electrostatic repulsion between the two unpaired electrons of the dianion increases the size of the triplet.

The temperature dependence of the ESR intensity of the magnetic triplet state was examined in pyridine over the temperature range 110–170 K, all values below the melting point of the solvent (230 K), and revealed 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 eV from an Arrhenius plot of $\log(\chi T)$ vs $1/T$.

Finally, Figure 2c shows the ESR spectrum obtained after bulk electrolysis in DMF/toluene at 5-C_{84}^{3-}. The ESR line shape and microwave power dependence of the resulting spectrum strongly suggest the presence of two distinct paramagnetic species, neither of which is the magnetic triplet state observed after reduction at 4–C_{84}^{2-}.

A tabulation of the ESR parameters for each electrogenerated C_{84}^{n-} anion is given in Table 1. 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-degenerate LUMO for the D_2 one. With this in mind, one would expect a broader ESR signal shifted toward higher magnetic fields for the D_{2d} C_{84}^- isomer as compared to the D_2 C_{84}^- one. Furthermore, the D_2 C_{84}^{2-} isomer is anticipated to be diamagnetic, while the D_{2d} C_{84}^{2-} isomer is expected to display a triplet ESR spectrum, in agreement with our observations.

In summary, we have confirmed the presence of two distinct isomers of C_{84}^{n-}, each of which forms three anions ($n = 1, 2, 3$) that are characterized by ESR spectroscopy in frozen solution. Further electrochemical and spectroelectrochemical characterization of each C_{84}^{n-} in different solvent systems is now in progress.

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