J. Am. Chem. Soc. 1992, 114, 6446-6451

Electroreduction of Buckminsterfullerene, C_{60}, in Aprotic Solvents: Electron Spin Resonance Characterization[1] of Singly, Doubly, and Triply Reduced C_{60} in Frozen Solutions

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Abstract: The results of ESR studies on frozen solutions of buckminsterfullerene anion radicals, C_{60}^{n-} (n = 1, 2, and 3), in the solvents benzonitrile, dichloromethane, pyridine, and tetrahydrofuran are reported and discussed. The samples are prepared by electrochemical reduction techniques which allow the preparation of samples which contain, quantitatively and selectively, the desired anionic species. The ESR spectral features of the anions in frozen solutions were studied as a function of temperature. The ESR line shapes and linewidths are dependent upon the solvent and the temperature whereas the g values are independent of solvent and only weakly dependent upon temperature. The C_{60}^- ($S = 1/2$) g value averages 1.998 over the four investigated solvents and the temperature range of 77–210 K. The resonances of C_{60}^{2-} are centered at about $g = 2.00$ and indicate a triplet ground state with an average separation of 12.6 Å between the two unpaired electrons. The C_{60}^{3-} resonance has a g value of 2.001–2.002 which is closer to that of the free electron as compared to C_{60}^- and C_{60}^{2-}. It also exhibits features similar to the monoanion, suggesting a spin of 1/2.

Introduction

The recent discovery of the class of carbon containing molecules known as the fullerenes[2] has produced a series of materials with a wide range of chemical and physical properties including the observation of superconductivity.[3,4] Theoretical calculations of the electronic energy levels for C_{60}, under the assumptions of perfect truncated icosahedral symmetry and no static Jahn-Teller distortion, suggest that the LUMO of neutral C_{60} is triply degenerate.[5] Thus, anion radicals prepared from C_{60} are expected not only to be degenerate but also possibly triply degenerate.

Orbitally degenerate (i.e., doubly degenerate) organic free radicals are known to exhibit unique electron spin resonance phenomena.[6] For example, doubly orbitally degenerate organic free radicals display such phenomena as large ESR linewidths, short spin relaxation times, anomalous g values, etc. in comparison to nondegenerate organic free radicals.[6] In addition, only a few of the doubly degenerate organic free radicals are known to exist in multiple oxidation states relative to the neutral parent compound.[7] Therefore, because of the high degree of orbital degeneracy expected in the C_{60} LUMO,[5] it was of interest to study the ESR spectra of the series of anion radicals of C_{60}^{n-} (n = 1, 2, and 3) in order to learn the nature of their respective magnetic ground states. For example: Is the magnetic ground state of the dianion a singlet or a triplet and is the ground state of the trianion a doublet or a quartet magnetic state? Are the spin–lattice relaxation times of the various ions shorter than for other aromatic molecules whose ground state is also degenerate? Is there evidence for significant disproportionation among the various anionic species?

Recent reports have demonstrated that C_{60} could be stepwise reduced by up to five[8] or six[9] electrons. Spectroelectrochemical experiments have demonstrated the stability of the mono- and dianion of C_{60}[10] while coulometric experiments indicated that stable solutions of the C_{60}^{3-} ion could also be obtained by simple controlled potential electrogeneration.[8] The singly reduced species has one unpaired electron, and the ESR spectrum of the resulting anion radical has been reported for an isolated tetraphenylphosphonium salt,[11] in frozen solutions,[10,12] and in molecular sieves.[13] A brief report has also described the ESR spectrum of C_{60}^{2-} in frozen solution,[10] but virtually nothing else in known about ESR spectra for higher reduced forms of the fullerene such as C_{60}^{3-}. This is examined in the present study which also extends the earlier frozen solution data for C_{60}^- and C_{60}^{2-} over a wide temperature range in four different frozen solutions. The g values and the ESR line shape of the three anions are reported. The spectral linewidths of the mono- and trianion increase as a function

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(1) A preliminary account of portions of this work has been presented at the Fall 1991 Materials Research Society Meeting in Boston, MA, 2–6 Dec 1991 (Electrical, Optical and Magnetic Properties of Solid State Materials. In *Mat. Res. Soc. Proc.* Chiang, L. Y.; Garito, A. F.; Sandman, D. J. Eds.; 1992, Vol. 247, 345).

(2) (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354. (c) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213.

(3) (a) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600. (b) Stephens, P. W.; Mihaly, L.; Lee, P. L.; Whetten, R. L.; Huang, S.-M.; Kaner, R.; Deiderich, F.; Holczer, K. *Nature* **1991**, *351*, 632. (c) Holczer, K.; Klein, O.; Huang, S.-M.; Kaner, R. B.; Fu, K.-J.; Whetten, R. L.; Diederich, F. *Science* **1991**, *252*, 1154. (d) Kelty, S. P.; Chen, C.-C.; Lieber, C. M. *Nature* **1991**, *352*, 223. (e) Tanigaki, K.; Ebbesen, T. W.; Saito, S,; Mizuki, J.; Tsai, J. S.; Kubo, Y.; Kuroshima, S. *Nature* **1991**, *352*, 222. (f) McCauley, J. P., Jr.; Zhu, Q.; Coustel, N.; Zhou, O.; Vaughan, G.; Idziak, S. H. J.; Fischer, J. E.; Tozer, S. W.; Groski, D. M.; Bykovetz, N.; Lin, C. L.; McGhie, A. R.; Allen, B. H.; Romanow, W. J.; Denenstein, A. M.; Smith III, A. B. *J. Am. Chem. Soc.* **1991**, *113*, 8537. (g) Zhou, O.; Fischer, J. E.; Coustel, N.; Kycia, S.; Zhu, Q.; McGhie, A. R.; Romanow, W. J.; McCauley, Jr., J. P.; Smith III, A. B.; Cox, D. E. *Nature* **1991**, *351*, 462.

(4) (a) Wang, H. H.; Kini, A. M.; Savall, B. M.; Carlson, K. D.; Williams, J. M.; Lykke, K. R.; Wurz, P.; Parker, D. H.; Pellin, M. J.; Gruen, D. M.; Welp, U.; Kwok, W.-K.; Fleshler, S.; Crabtree, G. W. *Inorg. Chem.* **1991**, *30*, 2838. (b) Wang, H. H.; Kini, A. M.; Savall, B. M.; Carlson, K. D.; Williams, J. M.; Lathrop, M. W.; Lykke, K. R.; Parker, D. H.; Wurz, P.; Pellin, M. J.; Gruen, D. M.; Welp, U.; Kwok, W.-K.; Fleshler, S.; Crabtree, G. W.; Schirber, J. E.; Overmyer, D. L. *Inorg. Chem.* **1991**, *30*, 2962.

(5) (a) Haymet, A. D. *J. Chem. Phys. Lett.* **1985**, *122*, 421. (b) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459. (c) Satpathy, S. *Chem. Phys. Lett.* **1986**, *130*, 545. (d) Hale, P. D. *J. Am. Chem. Soc.* **1986**, *108*, 6087. (e) Larsson, S.; Volosov, A.; Rosen, A. *Chem. Phys. Lett.* **1987**, *137*, 501. (f) Rosen, A.; Wastberg, B. *J. Chem. Phys.* **1989**, *90*, 2525.

(6) (a) Jones, M. T. In *Radical Ions*, Kaiser, E., Kevan, L., Eds.; Interscience; New York, 1968; p 256. (b) Rataiczak, R. D.; Jones, M. T. *J. Chem. Phys.* **1972**, *56*, 3898. (c) Jones, M. T.; Kuechler, J. C.; Metz, S. *J. Magn. Reson.* **1973**, *10*, 149.

(7) (a) Jesse, R. E.; Biloen, P.; Prins, R.; van Voorst, J. D. W.; Hoijtink, G. J. *Mol. Phys.* **1963**, *6*, 633 (triphenylbenzene dianion). (b) Brassem, P.; Jesse, G. K.; Hoijtink, G. J. *Mol. Phys.* **1964**, *7*, 587 (decacyclene dianion). (c) Jansen, E. G.; Pacifici, J. G. *J. Am. Chem. Soc.* **1965**, *87*, 5504 (pentaphenylcyclopentadiene dianion). (d) Sommerdijk, J. L.; de Boer, E.; Pijpers, F. W.; van Willigen, H. Z. *Phys. Chem.* **1969**, *63*, 183 (trinaphthalene dianion).

(8) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773. (b) Dubois, D.; Moninot, G.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* In press. (c) Koh, W.; Dubois, D.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Phys. Chem.* **1992**, *96*, 4163.

(9) (a) Xie, Q.; Pérez-Cordero, E.; Echegoyen, L. *J. Am. Chem. Soc.* **1992**, *114*, 3978. (b) Ohsawa, Y.; Saji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 781.

0002-7863/92/1514-6446$03.00/0

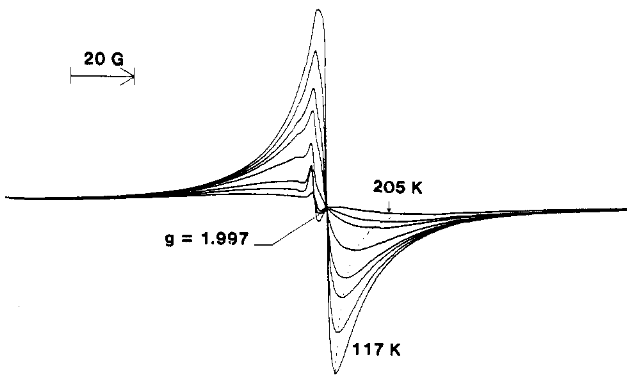

Figure 1. ESR spectra of C_{60}^- in frozen pyridine containing 0.1 M $TBAClO_4$ as a function of temperature.

of temperature, and this behavior is analyzed in terms of an activated process.

Experimental Section

Chemicals. The fullerene mixture was purchased from Research Materials, Inc. C_{60} was purified by gravity chromatography on an alumina column using hexane/benzene or hexane/toluene solvent mixtures as the eluent. Pyridine (py) was distilled from CaH_2 under a nitrogen atmosphere. Benzonitrile (PhCN) was distilled from P_2O_5 under vacuum. Dichloromethane (CH_2Cl_2) was purified according to published procedures.[14] Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Tetrabutylammonium perchlorate ($TBAClO_4$) was the supporting electrolyte (0.1 M) and was recrystallized twice from absolute ethanol and dried in vacuum at 40 °C prior to use.

Instrumentation. Controlled potential electrolyses of C_{60} were performed in a Vacuum Atmospheres Co. glovebox filled with oxygen free nitrogen using an "H" type cell. Both working and counter electrodes were made of platinum gauze, and the working and auxiliary compartments were separated by a sintered glass frit. Solutions containing $1-5 \times 10^{-4}$ M of the desired C_{60} anionic species were obtained by setting the working potential at values 150–250 mV more negative than the half-wave potential of the desired $C_{60}^{n-}/C_{60}^{(n+1)-}$ redox couple in a particular solvent/supporting electrolyte system.[8] This allowed a 99.7–99.99% electrolysis completion in terms of the conversion of neutral C_{60} to the desired C_{60}^{n-} anion. The reference electrode was a home-made saturated calomel electrode (SCE) which was separated from the bulk of the solution by a bridge with a fritted glass. In most cases, the electrolysis was performed even if C_{60} was apparently not or only partially dissolved. As the electron transfer proceeded, all the substrate eventually dissolved, and no solid was left in the solution which then had the expected color of the generated anion (C_{60}^-, dark red-purple; C_{60}^{2-}, clear red-orange; C_{60}^{3-}, dark red-brown).

Controlled potential electrolyses were carried out using an EG&G Model 173 potentiostat equipped with an EG&G Model 179 digital coulometer to record the current/time curves and the charge transferred. A BAS 100 Electrochemical Analyzer was used to record cyclic voltammograms at a stationary platinum disk electrode in order to check the integrity of the solution at any given time (for $E_{1/2}$ values, see ref 8b). Electrogenerated solutions of singly, doubly, and triply reduced C_{60} were stable in an inert atmosphere for at least several hours (and very often for several days). However, upon exposure to atmospheric oxygen and water vapor, all of the anions were found to react irreversibly to eventually give light brown solutions of unknown composition. All electrochemical experiments were carried out at ambient temperature (22 ± 1 °C).

Samples for the ESR studies were taken from the freshly electrolyzed solutions and transferred into ESR tubes which were capped and sealed using Teflon tape and regular tube caps. They were subsequently taken out of the glovebox, promptly frozen, and stored in liquid nitrogen. ESR studies were performed at X-band on a Bruker ER 100D spectrometer equipped with a variable temperature apparatus. The maximum microwave available power output was 260 mW. g Values were measured versus DPPH ($g = 2.0037$) which was used as the external reference.

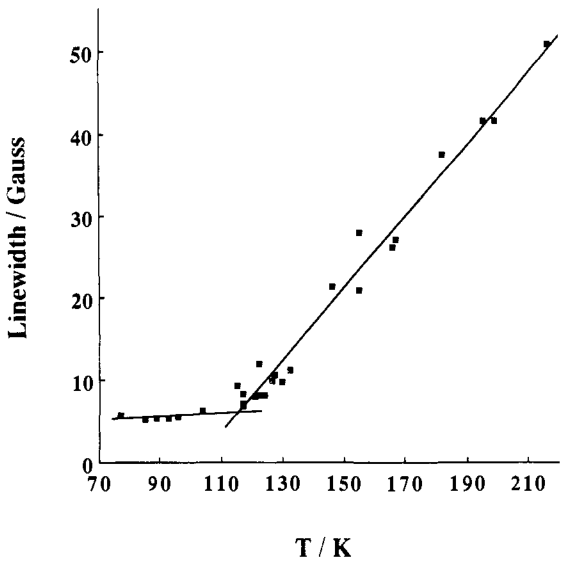

Figure 2. Plot of ESR spectral linewidth as a function of temperature for C_{60}^- in frozen pyridine containing 0.1 M $TBAClO_4$.

Table I. g Values for the Various C_{60} Anions Radicals in Different Solvents

solvent	anion charge	g value	temp (K)
pyridine	−1	1.997	77
	−1	1.998	117–155
	−1	1.999	199
	−2[a]	2.001	117
	−2[b]	2.000	117
	−3	2.002	117
	−3	2.001	203
benzonitrile	−1	1.998	77
	−1	1.998	209
	−2[a]	2.001	117
	−2[b]	[c]	
	−3	2.002	117
tetrahydrofuran	−1	1.997	77
	−2[a]	2.001	117
	−2[b]	2.000	117
	−3	2.002	85
	−3	2.001	117
dichloromethane	−1	1.998[d]	77
	−2[a]	2.001[d]	89
	−2[b]	2.000[d]	89

[a] Center of the triplet spectrum. [b] Narrow line spectrum. [c] Nonsymmetrical center spectrum apparently due to the presence of some C_{60}^- with $g = 1.998$. [d] Values reported in ref 10 could not be reproduced. All g values of the monoanion solutions at 77 K have been independently double-checked in another laboratory and found to be identical to those reported in this table.

Results

The Monoanion. Figure 1 shows a series of ESR spectra of the C_{60}^- monoanion as a function of temperature in pyridine. Generally, the ESR observations on frozen solutions of the monoanion of C_{60} are similar in pyridine, dichloromethane, tetrahydrofuran, and benzonitrile, and they can be summarized as follows. At temperatures in the range of 77 to ca. 100–110 K, a single rather sharp line (≈5 G) is observed. In this range of temperature, the linewidth of this signal shows very small variations. However, as the temperature of the frozen solution is increased above 110 K, the ESR linewidth significantly increases and broadens linearly with the temperature up to the melting point of the solution.[15] Figure 2 shows a typical plot of the ESR spectral

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(10) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(11) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2780.

(12) Kato, T.; Kodama, T.; Oyama, M.; Okasaki, S.; Shida, T.; Nakagawa, T.; Matsui, Y.; Susuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *186*, 35.

(13) Keizer, P. N.; Morton, J. R.; Preston, K. F.; Sugden, A. K. *J. Phys. Chem.* **1991**, *95*, 7117.

(14) Kadish, K. M.; Anderson, J. E. *Pure Appl. Chem.* **1987**, *59*, 707.

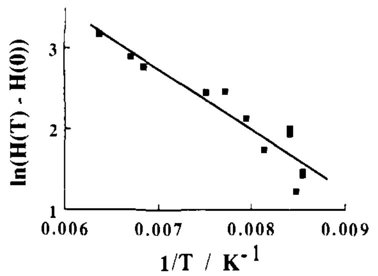

Figure 3. Plot of the natural log of the increase of ESR spectral linewidth vs $1/T$ for C_{60}^- in frozen dichloromethane containing 0.1 M $TBAClO_4$.

Table II. Comparison of Correlation Parameters for C_{60}^- and C_{60}^{3-} [a]

anion charge	solvent	activation energy (eV)	intercept, A	temp range (K)	intrinsic linewidth[b] (G)
−1	THF	0.036	7.0	118–148	≈4.0[e]
−1	CH_2Cl_2	0.065	8.0	117–157	3.1
−1	pyridine	0.053	7.1	115–216	3.8
−1	benzonitrile	0.050	7.0	107–188	3.2
−3	THF	*c*	*c*	*c*	*c*
−3	CH_2Cl_2	*d*	*d*	*d*	*d*
−3	pyridine	0.047	6.4	117–203	7.7
−3	benzonitrile	0.053	5.7	109–191	12.8

[a] Data fit the equation: $\ln (H(T) - H(0)) = A - E/kT$. [b] Extrapolated linewidth at 0 K from linewidth versus temperature plot. [c] A large hysteresis is observed upon temperature change, and thus results in a large scatter of data. [d] The trianion is not stable in dichloromethane. [e] Estimation.

Table III. Comparison of Triplet State Parameters Observed for $^3C_{60}$, $^3C_{70}$, and $^3C_{60}^{2-}$

triplet state identity	D (cm^{-1})	E (cm^{-1})	R (Å)
$^3C_{60}$	0.0114[a]	0.00069[a]	6.1[a]
$^3C_{70}$	0.0052[a]	0.00069[a]	7.9[a]
$^3C_{60}^{2-}$	0.00131	0.00000	12.6

[a] Taken from ref 20.

linewidth as a function of temperature for a frozen pyridine solution of the C_{60} monoanion. At a given temperature, the extent of the line broadening in a particular frozen solution depends on the solvent, but it is generally independent of whether the temperature of the measurement was approached from higher or lower values. Also, as the temperature is increased, a narrow line resonance signal appears, and this signal is superimposed upon the broad signal. The linewidth of this narrow line is of the order of 1-2 G depending on temperature. The intensity ratio of the two signals (narrow/broad) is below 1%. The average g value of the broad resonance line is 1.998 (see Table I for exact values), whereas that of the narrow line is close to 2.00. Analysis of the temperature dependent portion of the spectral linewidth indicates that the increase in linewidth is thermally activated. This is shown in Figure 3 which plots the natural log of the increase in linewidth versus the inverse of the temperature (in K) for the monoanion in frozen dichloromethane. The activation energies, intercepts, solvents, and the temperature range over which they have been studied are shown in Table II.

The g values of C_{60}^- in frozen solutions are shown as a function of temperature and solvent in Table I. Note that the values are all less than 2.000, and these data should correct an earlier erroneous report.[10] As seen from Table I, the g value of C_{60}^- seems to increase with temperature in pyridine. Similar increases with temperature may also occur in the other solvents but, if present, are beyond our experimental precision to be observed. In the range of 120–150 K, the ESR spectral amplitude of the main resonance increased continuously with increase of the incident power. No saturation of the signal (i.e., diminution in signal amplitude) was observed in any of the solvents within the maximum available incident power. In contrast, the secondary sharp line was easily saturated.

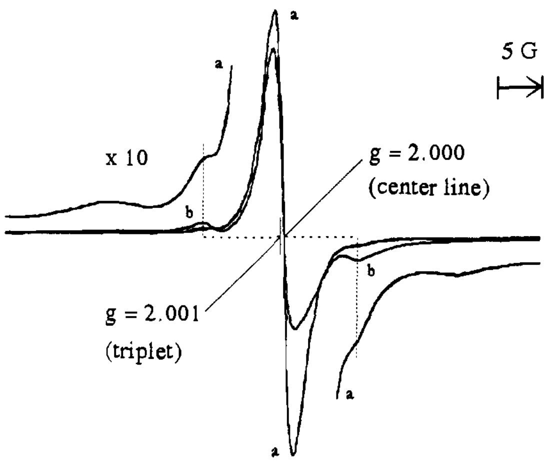

Figure 4. ESR spectrum of C_{60}^{2-} in frozen benzonitrile containing 0.1 M $TBAClO_4$ at (a) 226 K and (b) 123 K.

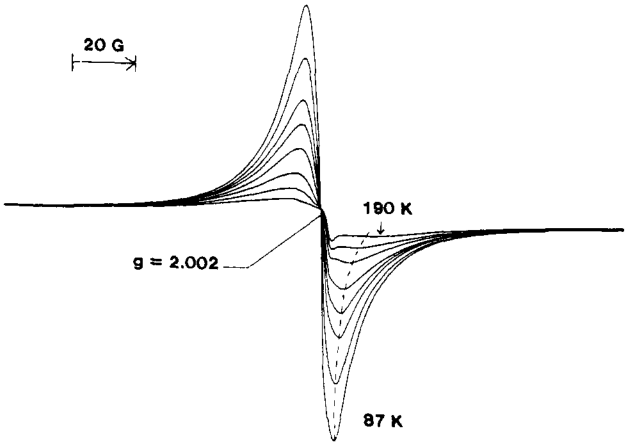

Figure 5. ESR spectra of C_{60}^{3-} in frozen benzonitrile containing 0.1 M $TBAClO_4$ as a function of temperature.

The Dianion. The ESR spectral envelope for frozen solutions of the C_{60}^{2-} dianion consists of two sets of superimposed resonances. One is due to a narrow line, and the other is similar to the two pairs of spectral lines which are expected for a randomly oriented solid solution of a triplet state radical for which $E = 0$.[16a] Such a spectrum is shown at two temperatures in Figure 4 for the case of C_{60}^{2-} in benzonitrile. The g values for the two resonances are summarized in Table II. The narrow line has a g value which is smaller than that of the triplet spectrum (i.e., it is shifted upfield). The position of the narrow ESR resonance relative to the triplet spectral envelope does not vary with solvent. However, with increase in temperature, the linewidth of this narrow resonance (≈2 G at 100 K) decreases as its amplitude increases. The separation of the triplet features did not seem to change with temperature, but the amplitude decreased at higher temperatures. The triplet lines were no longer detected at room temperature in liquid dichloromethane, but the center line remained and was strong. Attempts to completely deconvolute the two superimposed spectra have not been successful. However, it appears that the relative intensities of the two different spectra are of similar magnitude in frozen solutions when the temperature is around 100 K. As the microwave power is increased, the "triplet" spectral lines do not saturate as readily as the single resonance line.

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[15] Room temperature ESR studies of liquid solutions containing concentrated C_{60}^- also show an ESR spectrum which has features similar to those obtained in frozen solutions.

[16] (a) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill Book Company: New York, 1972; p 238. (b) Wertz and Bolton, *Electron Spin Resonance*, p 192.

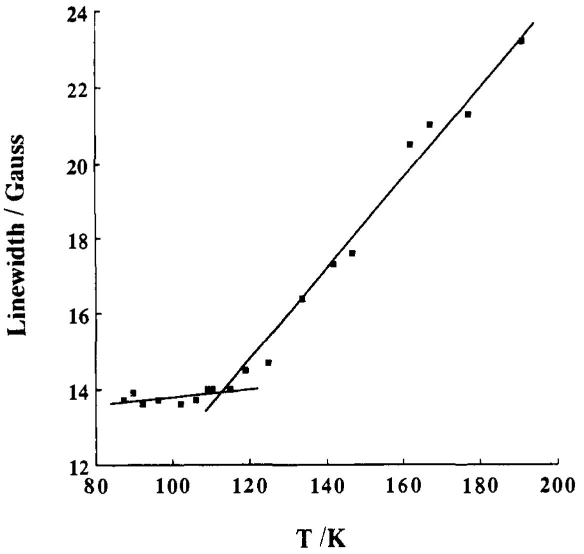

Figure 6. Plot of ESR spectral linewidth as a function of temperature for C_{60}^{3-} in frozen benzonitrile containing 0.1 M TBAClO$_4$.

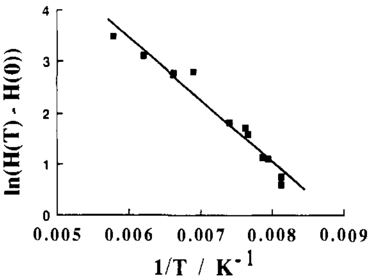

Figure 7. Plot of the natural log of the increase of ESR spectral linewidth versus $1/T$ for C_{60}^{3-} in frozen pyridine containing 0.1 M TBAClO$_4$.

Attempts to observe a half-field resonance have not been successful in the 77–200 K temperature range.

The Trianion. The spectral envelope of the C_{60}^{3-} trianion in frozen solutions behaves in a fashion similar to the monoanion, that is, the linewidth of the ESR spectrum increases with temperature. This is shown in Figure 5 for the case of C_{60}^{3-} in benzonitrile. As seen in this figure, a narrow line is superimposed upon the broad line of the C_{60}^{3-} spectrum which is easily saturated upon increase in incident power. The narrow line is estimated to make up only about 5–15% of the overall intensity of the spectrum. It is easier to observe as the linewidth of C_{60}^{3-} is increased at higher temperatures and may have the same origins as the sharp secondary line present in the C_{60}^- spectra. The narrow line was easily saturated, but the main line of the C_{60}^{3-} spectrum did not saturate within the available incident power range. The g values of the main line are summarized in Table I. Figure 6 shows a typical plot of the ESR spectral linewidth as a function of temperature for a frozen solution of the C_{60}^{3-} trianion in pyridine. As shown in Figure 7, the temperature dependent portion of the ESR linewidth can be treated as an activated process in exactly the same manner as was done for the case of the monoanion. The results are summarized in Table II.

Discussion

The Monoanion. Two observations warrant discussion because they differ rather significantly from those expected for a typical hydrocarbon free radical system. These are the ESR spectral linewidth which increases with temperature in frozen solutions and the g value which is some 0.004 units lower than the free electron g value of 2.002319. In addition, there is the question of whether the spin–lattice relaxation time (T_1) is shorter for C_{60}^- than for other orbitally degenerate systems (e.g., the benzene anion radical).

The Spectral Linewidth. Analysis of the temperature dependent portion of the spectral linewidth indicates that the increase in linewidth is thermally activated. This is shown in Figure 3 which plots the natural log of the increase in linewidth versus the inverse of the temperature (in K) for C_{60}^- in frozen dichloromethane. Similar plots were obtained for C_{60}^- in the other three solvents. The activation energies, intercepts, solvents, and the temperature range over which they have been studied are shown in Table II. One point which must be addressed is the mechanism by which the ESR spectral line is broadened as a function of temperature. Spin–spin exchange and electron transfer mechanisms are ruled out because the C_{60} monoanion concentration, which is low, is independent of temperature and because there can be no radical–radical collisions, since the solution is frozen.[16b] Another possible mechanism is that of molecular rotation. The observed correlation time for the ESR spectral line broadening of the C_{60} monoanion in pyridine solutions is $\approx 10^{-9}$ s at 233 K. This is exactly the value reported by Yannoni et al.[17] who used ^{13}C NMR techniques to study the rotation of C_{60} in the pure solid. Because there are no magnetic hyperfine interactions to be averaged or otherwise modulated by the rotation, it is concluded that this mechanism can also be ruled out.

Finally, one can ask the question if there is some means by which a given electronic ground state might be converted into another electronic state such that the conversion is a lifetime termination step for the initial electronic ground state? For example, one could assume that there are two electronic states available to the monoanion of C_{60}, one higher in energy than the other by an amount which would allow thermal averaging over the two states to occur. The relative populations of the two levels would then be varied by changing the temperature. It is not necessary that the cause of the level splitting be internal such as that due to a Jahn–Teller distortion as was considered by Kato et al. to explain the low g value.[12] In fact, external causes such as crystal field splittings due to the counterions and/or solvent molecules which surround or, perhaps, even form complexes with the C_{60} monoanion in the frozen solution are also likely possibilities. Examples of crystal field splittings and of thermal averaging over different electronic states are given by the case of the cyclooctatetraene anion radical trapped in the crystal field created by single crystals of the dianion of cyclooctatetraene[18] or by the well-known triplet exciton which exists in many TCNQ ion radical salts.[19] Thermal averaging over such states would provide a lifetime termination step and hence the ESR spectral broadening observed in the monoanion of C_{60}.

The most important experimental observation which is consistent with this model is the observed increase in ESR spectral linewidth as a function of temperature. As the temperature is increased above 0 K, the molecules in the ground electronic state would be thermally excited into the upper, but closely lying, electronic state. As the temperature is increased further, the population of the higher energy state would continue to increase relative to that of the lower energy state. However, more importantly, the rate at which such interconversions take place would increase with increasing temperature. This increasing rate of thermal averaging over these two electronic states, as the temperature is increased, would provide the ESR lifetime termination step and lead to broader ESR linewidths at higher temperatures. The ESR observations of Keizer et al.[13] of the monoanion of C_{60} trapped in a molecular sieve (13X Linde) are consistent with the above model. The major spectral component in the ESR spectrum is a single line with a width of 3.5 G over the temperature range 4–220 K. As the temperature is increased from 220 to 290 K, the ESR linewidth increases to 7 G. This is roughly the behavior one would expect if the crystal field is reduced or, perhaps, becomes nonexistent as the monoanions of C_{60} are moved from a frozen solution to the molecular sieve. In other words, if one assumes that the spectrum observed in the molecular sieve is equivalent to a "gas phase" spectrum, then the differences between the spectra observed in molecular sieves and in frozen solutions must arise

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(17) Yannoni, C. S.; Johnson, R. D.; Meijer, G.; Bethune, D. S.; Salem, J. R. *J. Phys. Chem.* **1991**, *95*, 9.

(18) Jones, M. T.; de Boer, E. *Mol. Phys.* **1982**, *47*, 487.

from crystal fields created by the presence of counterions in the frozen solution. One should also note that the low temperature linewidth of C_{60}^- in molecular sieves is similar to the intrinsic linewidth which is extrapolated in the present study from plots of the type given in Figure 2 (see Table II).

Of particular interest is a comparison of our results with that for the solid state ESR spectrum of C_{60}^- which was crystallized as a tetraphenylphosphonium salt from *o*-dichlorobenzene solutions.[11] In this case, the linewidth of the C_{60}^- resonance was observed to increase linearly with temperature in a manner similar to that observed in frozen solution.

The *g* Value. The origin of the low *g* value observed for the monoanion has already been discussed in the literature.[12] In agreement with the arguments given above to rationalize the line broadening as a function of temperature, the lifting of the orbital degeneracy, by whatever mechanism it may occur, partially quenches the orbital angular momentum and gives a *g* value much nearer to the free electron as compared to the value predicted if no splitting of the T_{1u} orbital occurs. However, this value is still less than the normally expected *g* value.

Is the Spin Lattice Relaxation Rate Enhanced? On the basis of the observed ESR linewidth, one can calculate an upper limit on the spin-lattice relaxation rate of 10^8–10^9 Hz. As noted in the Experimental Section, variable temperature measurements indicate that the C_{60} monoanion does not saturate at the highest power level available on the ESR spectrometer (260 mW). However, the ESR signal amplitude appears to approach a maximum at maximum power levels (i.e., it is close to saturation: it ceases to increase linearly with an increase in incident power). This behavior can be compared to that observed for a series of TCNQ ion radical salts[19] and the benzene anion radical,[6b] both of which have spin-lattice relaxation rates in the range of 10^6–10^7 Hz. In both cases, the ESR signal saturates at approximately 200 mW. Thus, in answer to the question posed, it appears that the spin-lattice relaxation rates in the monoanion of C_{60} are enhanced relative to typical (i.e., nondegenerate) hydrocarbon free radicals and comparable to, or somewhat greater than, that of the benzene anion radical. The definitive answer to this question awaits specific measurements of the spin relaxation times of the monoanion of C_{60}.

It appears that the spin-lattice relaxation in our studies is intrinsic to C_{60}^- and is not yet enhanced by the thermal averaging observed above because the averaging frequency is less than that of the spectrometer.[19]

The Dianion. ESR of the Triplet Magnetic State. We are cautious in our conclusion that the triplet magnetic state spectrum is due to a system for which $E = 0$. In such a case, the separation of the inner pair of lines should be exactly one half the separation of the outer pair of lines. Whereas in the case of $E \neq 0$, the distance between the inner pair should be less than one-half of the distance between the second pair of spectral lines and one would also expect to find a third pair of lines whose separations were equal to 2D. Our observation is the following: We see two pairs of lines. The inner pair is separated by a distance (11–13 G) which appears to be less than one-half the separation of the outer pair (26–30 G). However, we have not been able to observe a third set after repeated attempts to do so. Thus, we conclude that there are only two pairs of lines ($E = 0$) and that the reason that the separation of the inner pair is less than one-half the separation of the outer pair is because the two inner peaks lie on the shoulder of the center resonance line which causes an apparent shift toward the center of the spectrum. The data for the triplet magnetic state spectrum and an analysis of these data are summarized in Table III which also contains data obtained for the optically excited triplet magnetic states of C_{60} and C_{70} by Wasielewski et al.[20] We note that the mean separation of the two electrons in the triplet excited state of neutral C_{60} (6.1 Å) is smaller than that observed for the dianion (12.6 Å). It is also smaller than the mean atom-to-atom diameter of the C_{60} molecule (7.065 Å).[21] This trend is consistent with what one would expect since there is greater electron–electron repulsion between the two electrons of the triplet of the dianion than there is for the neutral molecule and one would therefore expect that, on average, the two electrons of the dianion would spend most of their time on the outside of the C_{60} cage. Initially, the mean electron separation of 12.6 Å for the dianion seemed somewhat larger than one might have expected. However, if one notes that the C_{60} molecule crystallizes with four molecules in space group T_h^6–$Pa\bar{3}$ of the cubic system, with lattice constant a = 14.052 Å,[21] and that the powder diffraction measurements on $Rb_{2.9}C_{60}$ indicate that it is face-centered cubic with an average lattice constant of 14.28 Å,[22] then the calculated mean electron–electron separation of 12.6 Å centered on a single C_{60}^{2-} ion appears to be quite reasonable. The model which is proposed to explain the linewidth behavior of frozen monoanion solutions is consistent with the observation of a triplet magnetic state (i.e., $S = 1$) for the dianion if the splitting of the initial T_{1u} level occurs such that the lowest state is doubly degenerate. On the other hand, whatever the origin of the center line may be, the fact that the intensity of this line decreases with lower temperature while the other resonances increase, clearly indicates that the ground state of the dianion is a triplet. Continued studies of the narrow line spectrum are in progress to both better characterize the spectrum and to aid in a determination of its origin.

While the observation of a half-field ESR resonance is conclusive evidence of the existence of a triplet state (i.e., $S = 1$), many known triplet state radical systems do not exhibit such a half-field resonance. For example, polycrystalline tetrabutylammonium cobalt bis(benzene-1,2-dithiolate), which is known by static magnetic susceptibility measurements to be a ground state triplet ($S = 1$) and displays an ESR spectrum at normal field, does not display a half-field ESR resonance.[23] On the other hand, the selenium analog displays both full-field and half-field resonances. The significant observation is that not all magnetic triplet systems display a half-field ESR resonance.

The Trianion. As described above, the C_{60}^{3-} spectral features are very similar to those of C_{60}^-. The extrapolated intrinsic linewidth of the C_{60}^{3-} resonance is larger than that of C_{60}^-, but, as seen in Table II, their respective correlation parameters are actually quite similar. This would imply that the broadening mechanism for the C_{60}^{3-} ESR spectrum is identical to what has been proposed for the monoanion. That is, there exists an electronic level which is thermally accessible to an unpaired electron of the ground state of C_{60}^{3-}. The fact that the ESR spectra of the trianion look and behave so similar to those of the monoanion suggests that the magnetic ground state of the trianion is a doublet (i.e., $S = 1/2$). Our studies have shown no evidence for a quartet state ($S = 3/2$). These observations are consistent with the model proposed to explain the spectral linewidth behavior in frozen solutions of the monoanion as well as for the trianion.

Is There Evidence for Significant Levels of Disproportionation among the Various Anionic Species? The differences between half-wave potentials for generation of the various anionic species are given elsewhere[8b] and enable calculation of the disproportionation constants for the reactions:

$$2C_{60}^{n-} \rightleftarrows C_{60}^{(n-1)-} + C_{60}^{(n+1)-} \qquad (1)$$

A value of $\Delta E_{1/2}$ of 400 mV (as observed between the first and second reduction) leads to a disproportionation constant of the order of 5×10^{-7} in the four utilized solvents. For example, the expected concentration of $C_{60}^{(n-1)-}$ and $C_{60}^{(n+1)-}$ at equilibrium (after complete electrolysis) would be of the order of 5×10^{-8} M for a 10^{-4} M concentration of C_{60}^{n-}. In the case of bulk C_{60}^- one expects to see about 0.5% of C_{60}^{2-} in solution. This amount

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[19] Jones, M. T. *J. Chem. Phys.* **1964**, *40*, 1837.

[20] Wasielewski, M. R.; O'Neil, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774.

[21] Liu, S.; Lu, Y.-J.; Kappes, M. M.; Ibers, J. A. *Science* **1991**, *254*, 408.

[22] Zhu, Q.; Zhou, O.; Coustel, N.; Vaughan, G. B. M.; McCauley, J. P., Jr.; Romanow, W. J.; Fischer, J. E.; Smith III, A. B. *Science* **1991**, *254*, 545.

[23] Sandman, D. J.; Allen, G. W.; Acampora, L. A.; Stark, J. C.; Jansen, S.; Jones, M. T.; Ashwell, G. J.; Foxman, B. M. *Inorg. Chem.* **1987**, *26*, 1664.

of dianion cannot be considered to be significant (there is no *quantitative* disproportionation), but the ESR technique is sufficiently sensitive to detect these quantities. For example, the data suggest that the sharp secondary line present in spectra of both the mono- and trianion actually arises from a small amount of the dianion. The characteristics of this line (*g* value, linewidth, saturation properties, and temperature behavior) are all similar to that of the center line seen in the spectrum of the dianion. Furthermore, when electrolysis to generate the monoanion was only partially carried out, the intensity of this sharp line decreased significantly as compared to its intensity for a fully electrolyzed solution of the same overall C_{60} concentration. This behavior is predicted by a disproportionation equilibrium of the type given in eq 1. On the other hand, when the electrolysis is carried out to give a coulometric value of slightly more than one electron per C_{60} molecule, the sharp line intensity was much larger as C_{60}^{2-} was generated in larger quantities. A signal for the monoanion was not clearly detected in spectra of the dianion, due perhaps to its broad linewidth, but this species may be responsible for truncation of the high field side of the dianion spectrum at low temperature.

Relative Order of the T_{1u} Orbitals in the Anions. The temperature dependence of the C_{60}^- ESR spectral linewidth suggests that a splitting of the initially triply degenerate T_{1u} orbitals occurs upon addition of an electron to the neutral C_{60} molecule in frozen solutions. On the other hand, the *g* value indicates that some degeneracy must remain. Two electronic configurations would fit this data. One can have two orbitals with the same energy below the third one or the reverse. In the first instance (i.e., two degenerate orbitals lying below the third), the expected *g* value would be less than that for the free electron. As the temperature is increased, averaging over the third orbital would lead to an increase in the *g* value toward the free electron *g* value. In the second ordering, the expected *g* value would be that of the free electron, and an increase in temperature should lead to a smaller *g* value.

On the basis of our experimental observations that the *g* value for the monoanion is less than that for the free electron and increases with temperature in pyridine, we conclude that the electronic ground state of the monoanion is doubly degenerate. This relative arrangement of the orbitals is consistent with the observation of an $S = 1$ ground state for the dianion as well as the observation that the magnetic ground state of the trianion is $S = 1/2$.

Conclusions

The ESR resonances of the C_{60}^{n-} anions ($n = 1, 2, 3$) have characteristics (*g* values and linewidths) that will allow unambiguous recognition of the first three reduced states of C_{60} in frozen solutions. In fact, we have already taken advantage of this to elucidate homogeneous redox reactions of C_{60} with organometallic derivatives.[24] The proposed model for the electronic structure of the C_{60} anions implies a lifting of the initial orbital degeneracy. Additional and more accurate studies of the temperature dependence of the *g* values are needed, and continued studies are now in progress to better characterize the dianion ESR resonances. Attempts are also being made to obtain stable solutions of higher reduced states of C_{60} in order to similarly characterize them.

Acknowledgment. Support of this work by the Texas Center for Superconductivity, the Robert A. Welch Foundation (Grants E-1208 (M.T.J.) and E-680 (K.M.K.)), the National Science Foundation (CHE-8822881 (K.M.K.)) is gratefully acknowledged. P. J. Bratt from Larry Kevan's group is acknowledged for double checking our C_{60}^- *g* values with independent measurements at 77 K.

Note Added in Proof. Professor S. I. Weissman (Washington University, St. Louis) has pointed out to us that there are difficulties in the use of the analysis, as used by Wasielewski et al. (ref 20) and by us, to estimate the mean electron–electron separation of the two electrons which comprise a triplet magnetic state when the two electrons are located on the same molecule. This suggests that the mean separation as calculated by us and as shown in Table III should be viewed as the mean separation that the two electrons in the triplet state would have if they were located on two different molecules such as in a dimer (ref 25).

Registry No. THF, 109-99-9; py, 110-86-1; C_{60}^-, 111138-12-6; C_{60}^{2-}, 120329-58-0; C_{60}^{3-}, 133318-63-5; PhCN, 100-47-0; CH_2Cl_2, 75-09-2.

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(24) Dubois, D.; Kadish, K. M. Manuscript in preparation.

(25) Lazarev, G. G. *Zeit. Phys.* **1991**, *173*, 143.