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EPR Studies Associated with the Electrochemical Reduction of C_{60} and Supramolecular Complexes of C_{60} in Toluene−Acetonitrile Solvent Mixtures

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Electron paramagnetic resonance (EPR) studies at 295 K of the radical anion of buckminsterfullerene ($C_{60}^{\bullet -}$) generated electrochemically by bulk-controlled potential electrolysis of neutral C_{60} in mixed toluene−acetonitrile solvents (5−20% v/v acetonitrile with 0.1−0.2 M n-Hex$_4$NPF$_6$ or n-Bu$_4$NPF$_6$ as the supporting electrolyte) have shown that at least three different forms of $C_{60}^{\bullet -}$ exist in solution. The radical anions have different g values and can thus be detected by EPR spectroscopy in the form of single line signals with different line widths. The familiar species with the broad line width signal ($\Delta H_{pp} = 6$ mT) was present in a high percentage (ca. >95%) along with two species with narrow line width ($\Delta H_{pp} = 0.16$ and 0.07 mT) signals that were present between 1 and 5% of the total concentration of $C_{60}^{\bullet -}$. The concentrations of the species with narrow line width EPR signals increased with increasing time so that over a 20-h period their EPR signal intensity approximately doubled. The purity of the toluene was found to be very important in determining the number of species detected with sharp EPR signals. Although two species were always detected with sharp EPR signals, when lower purity toluene (<99%) was used, the number of species with narrow line width signals increased to >2. The increase in the sharp EPR signals with increasing time is not inconsistent with a slow reaction between $C_{60}^{\bullet -}$ and low levels of impurities in the solvent to form lower symmetry paramagnetic species, the narrow line width signals being very similar to those reported for substituted fullerene radicals. EPR and cyclic voltammetry experiments were conducted on C_{60} in the presence of several complexing agents, cyclotriveratrylene (CTV), the symmetrical tris-allyl substituted analogue of CTV [CTV(allyl)$_3$], and p-benzylcalix[5]arene. The intensity of the narrow and broad line width EPR signals decreased when $C_{60}^{\bullet -}$ was electrochemically generated in the presence of the complexing agents, indicating that the host−guest $\pi-\pi$ interactions were sufficiently strong to alter the EPR signals of $C_{60}^{\bullet -}$. Cyclic voltammetry experiments performed on C_{60} in the presence of the complexing agents showed that the first four reduction processes of C_{60} split into two new processes upon complexation, with the time allowed for the host−guest reaction being critical in determining the voltammetric behavior.

1. Introduction

There have been many studies describing the electron paramagnetic resonance (EPR) spectroscopy of $C_{60}^{\bullet -}$[1−9] and more negatively charged anions[3,5] of C_{60} in solution and frozen solution phases. However, despite the large amount of attention focused on these radical compounds, there is still a great deal of controversy in the literature as to the assignment of the signals detected by EPR spectroscopy, both in solution and frozen solution phases. One particularly interesting case is the mixture of EPR signals with broad and narrow line widths that have been obtained at room temperature during the reduction of C_{60} to $C_{60}^{\bullet -}$. Several groups[1−3,5] have reported obtaining a broad EPR spectrum for the solvated anion, $C_{60}^{\bullet -}{}_{(solv)}$, in solution at room temperature with a peak-to-peak line width of > 4.5 mT and a g value close to 2.0000. Also present along with the species with the broad EPR line width signal was reported[1−3,5] a variable percentage (<10%) of a species with a narrow peak-to-peak line width signal (<0.3 mT) and a g value also close to 2.0000. Several models have been proposed to explain the origin of the narrow line width EPR signal including, a strong ion-pairing between $C_{60}^{\bullet -}$ and the supporting electrolyte cation used during electrochemical reduction experiments,[1] presence of the C_{60}^{2-} paramagnetic species,[2b] impurities in the C_{60},[3b] a percentage of a thermally excited state of C_{60}^{-},[5a] and a reaction between $C_{60}^{\bullet -}$ and O_2 to form $C_{60}O_2^{\bullet -}$.[7]

Recently, and in contrast to the earlier findings, other workers have reported obtaining exclusively species with narrow line width EPR signals during the reduction of C_{60} to $C_{60}^{\bullet -}$.[8,9] These later reports also list evidence of two or more species with narrow EPR line width signals, which have been proposed as the monoanion and dianion dimer of $C_{60}^{\bullet -}$,[8] or as a mixture of $C_{60}^{\bullet -}$ and more negatively (> 1$^-$) charged anions of C_{60}.[9] One group has concluded that the narrow line width signal is due to $C_{60}^{\bullet -}{}_{(solv)}$ and the broad line width signal due to a $C_{60}^{\bullet -}$ precipitate or aggregate,[8d] which forms preferentially in the presence of bulky anions such as PF_6^- and $B(C_6H_5)_4^-$. However, it has also been noted[3d] that it is often difficult to detect the broad line width EPR signal even when the integrated

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[†] This paper is dedicated to the memory of Dr. Scott A. Olsen who died (aged 29) on 29 April 1996.

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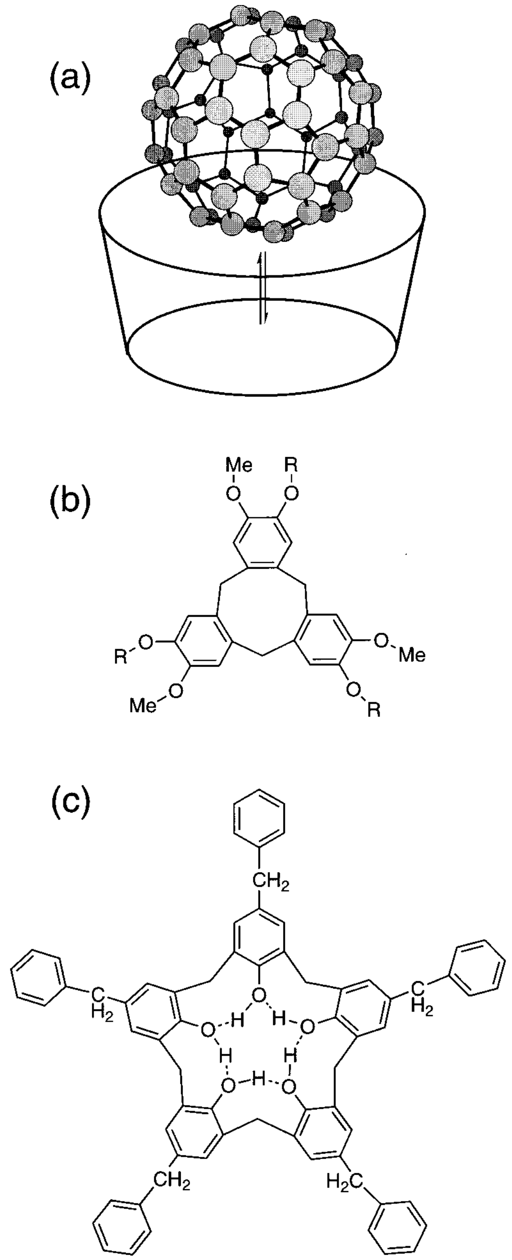

Figure 1. (a) Ball and socket model of C_{60} and complexing agents; (b) cyclotriveratrylene (CTV; R = Me) and CTV(allyl)$_3$ (R = allyl); (c) *p*-benzyl-calix[5]arene.

intensity of the broad signal is much greater than that of the sharp signal; thus, the reports of exclusively obtaining the narrow line width signal may be misleading. Therefore, to clarify the conflicting reports[1−9] on the broad and narrow EPR line width signals detected during the reduction of C_{60} to $C_{60}^{\bullet-}$, we (i) report new EPR data on the formation of $C_{60}^{\bullet-}$ in toluene−acetonitrile solution by electrochemical generation from C_{60}, and (ii) discuss EPR data obtained from $C_{60}^{\bullet-}$ in the presence of several supramolecular complexing agents.

An efficient purification of C_{60} involves the use of *p*-Bu^t calixarenes as selective complexing agents.[10] Calixarenes are bowl-shaped macrocyclic molecules containing hydrophobic cavities that bind C_{60} through an accumulation of weak van der Waals interactions (Figure 1a).[11,12] The size of the calixarene cavity determines in part the efficiency of the complexation of C_{60}, and inclusion complexes between calix[8]arenes,[10,12a,13] calix[6]arenes,[14] and more recently calix[5]arenes[11,12b] have been reported in organic solvents and as solid-state crystals with variable stoichiometry. Solution phase interactions have also been reported between a calix[4]arene and C_{60}[15] as well as the smaller cyclotriveratrylene (CTV) and CTV(allyl)$_3$.[16] For the complexing agents to function efficiently, the neutral host−fullerene complexes by necessity must be weak enough to enable reversible formation but strong enough to be selective for fullerenes. Therefore, to probe the nature of the host−guest interactions, studies utilizing electrochemical methods,[15] NMR spectroscopy,[12,13] and UV−vis absorption techniques[10a,12,16] have been performed.

Three complexing agents [CTV, CTV(allyl)$_3$[16] (Figure 1b), and *p*-benzyl-calix[5]arene[12b,17] (Figure 1c)] that differ in the size of their ring structure and the depth of their cavities were chosen to model complexation behavior. CTV is saucer shaped in solution, whereas the allyl groups on CTV(allyl)$_3$ provide a deeper cavity and hence allow stronger interactions with C_{60}. *p*-Benzyl-calix[5]arene has a deep bowl-shaped cavity due to the *p*-benzyl groups and, of the three molecules studied in this paper, has a structure in solution closest to the ball-and-socket model shown in Figure 1a. The host−guest interactions were studied by cyclic voltammetry and for the first time by EPR spectroscopy where $C_{60}^{\bullet-}$ was generated electrochemically in the presence of the complexing agents.

2. Experimental Section

Cyclic voltammetric experiments were conducted with Au, Pt, and glassy carbon (GC) working electrodes of macro (1 mm) and micro (10 μm) dimensions. An Ag/Ag$^+$ (0.05 M $AgNO_3$ and 0.1 M *n*-Bu_4NPF_6 in acetonitrile) reference electrode and a platinum basket auxiliary electrode were used. All test solutions were thoroughly deoxygenated with solvent-saturated argon prior to analysis. Solutions of C_{60} were prepared by dissolving C_{60} in pure toluene by sonication and then adding the appropriate amount of acetonitrile and supporting electrolyte. The potentiostats used were a BAS-100A, a Cypress System, and a Eco Chemie Autolab. For bulk controlled potential electrolysis experiments, a two-compartment electrolytic cell where the auxiliary and working electrodes were isolated by a salt bridge was used. This efficient electrolysis cell is of a design similar to that described previously[18] except that the working and auxiliary electrodes were both platinum mesh. The volume of the working electrode compartment was ~5 mL, and the electrolyte solution was deoxygenated with argon prior to and during electrolysis. In all the bulk electrolysis experiments, the reduction potential, which was determined by cyclic voltammetry experiments, was held between the first and second reduction processes of C_{60}. Synthetic preparations and coulometric analysis in the aforementioned electrolysis cell have been performed on a number of organic compounds,[18,19] which has led to the conclusion that the potential control of the working electrode is accurate to within ±10 mV. Hence, there is little likelihood that C_{60} anions of a charge higher than 1^- were generated under the employed reduction conditions. Typical electrolysis times in toluene with 10% acetonitrile (v/v; 0.1 M supporting electrolyte) for a one electron bulk reduction of 0.5 mM C_{60} to $C_{60}^{\bullet-}$ were 60 s for 33% bulk conversion, 150 s for 67% bulk conversion, and 600 s for >98% conversion. The data for the fraction of electrons transferred was calculated from

$$N = Q/n\mathrm{F} \tag{1}$$

where N is the number of moles, Q is the charge, n is the number of electrons, and F is the Faraday constant. Increasing the acetonitrile concentration and/or increasing the electrolyte concentration decreased the electrolysis times because of lowering of the solution resistance. The data were calibrated to take into account the effect of background processes on the overall measured charge.

Continuous wave X-band EPR spectra were recorded on either a Bruker ECS-106 spectrometer or on a Bruker ER200D spectrometer, both employing rectangular TE_{102} cavities. Solutions for EPR experiments were generated in the electrolysis cell already described and transferred under an argon atmosphere into a conventional silica flat cell. For some experiments, an in situ stationary solution electrochemical-EPR cell was used that has been described elsewhere.[20] All experiments were conducted at 295 ± 2 K, with the modulation frequency set at 50−100 kHz and the microwave power 2.0 mW. The magnetic field was calibrated with a pure crystal of DPPH ($g = 2.0037 \pm 0.0002$), and accurate frequency values were obtained with a Bruker frequency counter. The error in the reported g values is in the order of ±0.0002.

Aldrich toluene (99.85%), BDH toluene (99%), and Fisher acetonitrile (high purity) were used directly from the bottle. n-Bu_4NPF_6 (puriss, electrochemical grade) was purchased from Fluka and n-Hex_4NPF_6 was prepared by a standard literature procedure.[21] C_{60} (99.95%) was purchased from MER Corporation, Tucson, AZ. Cyclotriveratrylene (CTV), CTV(allyl)$_3$, and p-benzyl-calix[5]arene were prepared according to literature procedures.[17,22] The complexing agents were of analytical purity (> 99%) as determined by elemental analysis.

3. Results and Discussion

3.1. EPR Spectroscopy of $C_{60}^{\bullet -}$. $C_{60}^{\bullet -}$ was generated by bulk-controlled potential electrolysis experiments in toluene−acetonitrile (5−20% v/v acetonitrile) with 0.1−0.2 M n-Bu_4NPF_6 or n-Hex_4NPF_6 as the supporting electrolyte (see *Experimental Section* for more details). The experiments were conducted to determine if it was possible to control the relative intensities of the broad and sharp signals seen in the EPR spectra of $C_{60}^{\bullet -}$ by varying the experimental conditions under which the anion radical was generated. This variation was achieved by controlling (i) the solvent and electrolyte composition, (ii) the time after which $C_{60}^{\bullet -}$ was first generated, and (iii) the purity of the solvents. Each of these factors are considered in the following discussion.

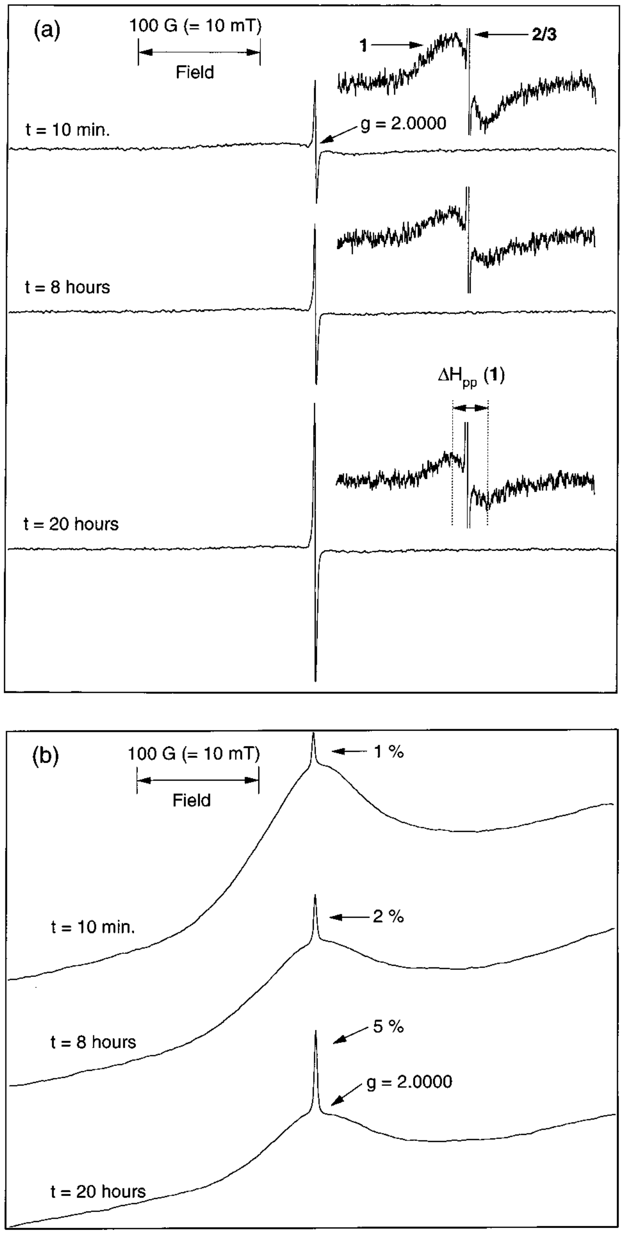

Figure 2. (a) First-derivative EPR spectra of $C_{60}^{\bullet -}$ in toluene−acetonitrile (90:10) with 0.1 M n-Bu_4NPF_6 obtained after >98% electrolysis of 0.5 mM C_{60}. The time refers to the time from when the electrolysis was first commenced. The inserts in the right-hand side of the spectra are the expanded vertical scale and reduced horizontal scale to highlight the broad line width signal (see text; **1** and **2/3** refer to the three different species). (b) The integrated spectra shown in (a). The listed percentages are the relative amounts of the species with the sharp signal compared with the species with the broad signal. The EPR modulation amplitude = 1.0 G, time constant = 1 s, sweep width = 500 G, and sweep time = 500 s. The ordinate axis are in constant but arbitrary units.

Figure 2a shows an EPR spectrum of >98% $C_{60}^{\bullet -}$ recorded over a 50 mT sweep width with a modulation amplitude of 0.1 mT. The times given in Figure 2a refer to the time after which the bulk electrolysis of C_{60} was first begun ($t = 0$) and include the delay in transferring the sample from the electrolysis cell into the EPR cell. With this modulation amplitude, the first-derivative EPR spectra clearly show the narrow line width signal with a g value very close to 2.0000 (the low g value is characteristic of $C_{60}^{\bullet -}$).[1−9] The inserts on the right-hand side in Figure 2a show an expanded vertical scale of each spectrum, and the integrated version of the spectra are shown in Figure 2b, illustrating that the species associated with the broad line width signal (**1**) is present in a high percentage, whereas the narrow line width species is present between 1 and 5% (of the species with the broad line width). At modulation amplitudes <0.02 mT, the narrow line width signal is resolved into two signals, which have subsequently been assigned as radicals **2** and **3** and whose assignments will be discussed in detail later. The data in Figures 2a and 2b show that with increasing time, the intensity of the narrow line width EPR signal increased, whereas concomitantly the broad line width signal decreased in intensity. The intensity of the narrow line width signal approximately doubled over a 20-h period. However, the integrated ratios of the broad and narrow signals did not simply correspond to the species with the broad signal undergoing transition into the species with the narrow line width signal (Figure 2b). It appears that the species with the broad line width signal decays on the time scale of the experiment (cf., Figure 2b, $t = 10$ min and $t = 20$ h). Moriyama *et al.*[6] performed a time-dependent EPR study over 0−45 days on a single-crystal salt of $C_{60}^{\bullet -}$ and noted the appearance of two sharp line width signals increasing over time concomitantly with the broad line width signal decreasing in intensity. Hwang *et al.*[7] detected sharp EPR signals associated with $C_{60}^{\bullet -}$ increasing in intensity

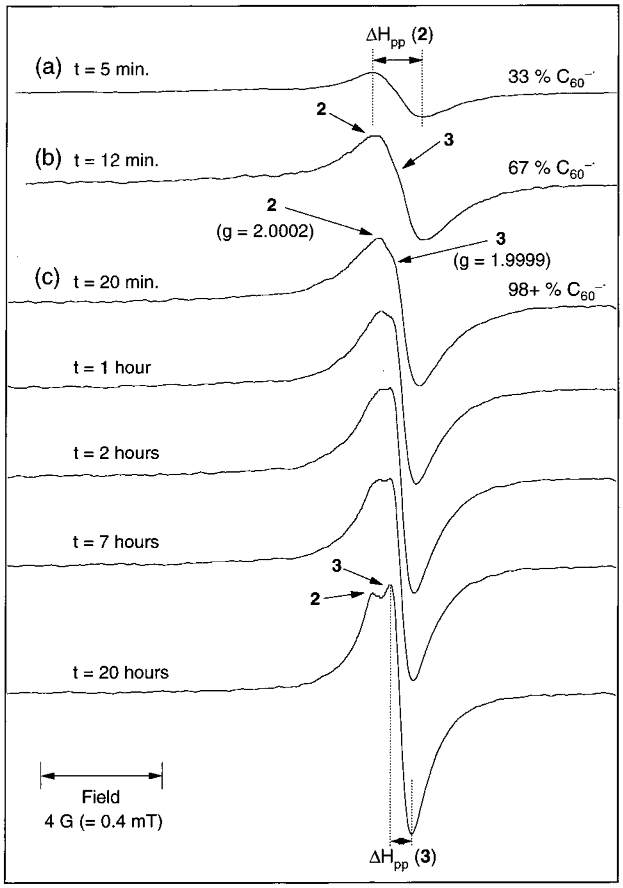

Figure 3. First-derivative EPR spectra of $C_{60}^{\bullet-}$ in toluene−acetonitrile (90:10) with 0.1 M *n*-Bu_4NPF_6 obtained after electrolysis of 0.5 mM C_{60}. The time refers to the time from when the electrolysis was first commenced (see text): (a) after 33% conversion of C_{60} to $C_{60}^{\bullet-}$; (b) after 67% conversion of C_{60} to $C_{60}^{\bullet-}$; (c) after >98% conversion of C_{60} to $C_{60}^{\bullet-}$. The EPR modulation amplitude = 0.2 G, time constant = 1 s, sweep width = 20 G, and sweep time = 100 s. The ordinate axis is in constant but arbitrary units.

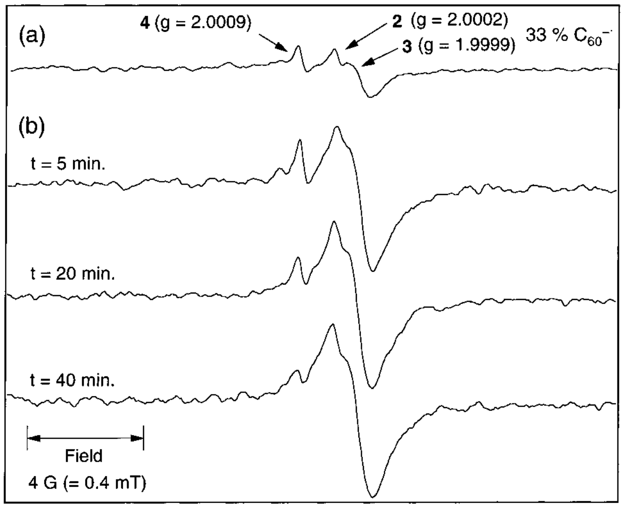

Figure 4. First-derivative EPR spectra of $C_{60}^{\bullet-}$ in toluene−acetonitrile (90:10) with 0.1 M *n*-Bu_4NPF_6 obtained after 33% electrolysis of C_{60}. The time refers to the time from when the electrolysis was first commenced (see text): (a) 0.2 mM and (b) 1.0 mM. The EPR modulation amplitude = 0.2 G, time constant = 1 s, sweep width = 20 G, and sweep time = 100 s. The ordinate axis is in constant but arbitrary units.

over a 14-h period if the toluene−methanol solution was exposed to the atmosphere, and concluded that the sharp signals were due to $C_{60}O_2^{\bullet-}$ species. However, the *g* values of the sharp line width signals were 2.0008 and 2.0023,[7] which are considerably greater than the *g* values of the sharp signals reported in this paper. We observed that the sharp and broad line width signals at $g \approx 2.0000$ disappeared almost immediately after the solution was exposed to the atmosphere. This result suggests that the source of the narrow line width signals reported by Hwang *et al.*[7] is different than that of the signals reported in this paper.

A detailed EPR study was also conducted on the narrow line width signals by employing a lower modulation amplitude (0.01−0.02 mT). Figure 3 illustrates the appearance of the narrow line width EPR signals as a function of the ratio $C_{60}^{\bullet-}$: C_{60} and as a function of time for a sample of $C_{60}^{\bullet-}$ in toluene with 10% acetonitrile (v/v). At 33% $C_{60}^{\bullet-}$, there exists two species with EPR signals **2** and **3** (Figure 3a and 3b) and *g* values of 2.0002 and 1.9999, respectively. The percentage of $C_{60}^{\bullet-}$ was determined by coulometry (eq 1). The peak-to-peak line widths (ΔH_{pp}) of signals **2** and **3** were estimated to be 0.16 and 0.07 mT, respectively. The line widths of **2** and **3** were estimated at $C_{60}^{\bullet-}$ concentrations and times where there was the maximum of each species present (Figure 3). However, because we were not able to exclusively generate each radical species, the line widths should be treated as approximate. Stasko et al.,[8] who also detected two narrow line width species with very similar *g* values have reported the ΔH_{pp} of both species to be <0.1 mT. As the percentage of $C_{60}^{\bullet-}$ was increased from 67% (Figure 3b) to >98% (Figure 3c), signal **3** increased in intensity relative to signal **2**. However, it was observed at the 33% conversion stage that with increasing time, signal **3** increased in intensity relative to signal **2** (the sample was left unstirred in the EPR cell). Therefore, the time after generation of $C_{60}^{\bullet-}$ appears to be the most important factor in determining the relative amounts of **2** and **3**. Figure 3c shows the increase in signal intensity of **2** and **3** as a function of time after >98% conversion of C_{60} to $C_{60}^{\bullet-}$. It is uncertain whether the increase in signal intensity of **3** relative to **2** is due to **2** converting into **3**, or due to **2** being less stable and decaying faster than the species responsible for signal **3**. Nevertheless, the signal intensity of *both* species increased as a function of time, most likely at least partly at the expense of the broad line width signal (**1**) decreasing in intensity.

Changing the supporting electrolyte (from *n*-Bu_4NPF_6 to *n*-Hex_4NPF_6) or altering the toluene−acetonitrile ratio (between 5 and 20%) did not appreciable alter the ratio of the signals corresponding to **1** and **2**/**3**. Also, altering the supporting electrolyte (0.1−0.2 M) and C_{60} (0.2−1 mM) concentration had no appreciable effect on the ratio of the broad and narrow line width signals, indicating that the relative concentrations of the radicals were not sensitive to those variables. However, additional narrow line width EPR signals were detected when grades of solvents other than the highest purity were used. For example, Figure 4 shows the EPR spectrum obtained when 99% pure toluene was used (rather than the usual 99.85% pure) and demonstrates the appearance of an additional signal at g = 2.0009 for two concentrations of C_{60}. The intensity of the sharp signals varied depending on the C_{60} concentration (Figures 4a and b), and the low *g* values of the signals suggest that they are associated with $C_{60}^{\bullet-}$ and not solely from some other paramagnetic impurities. A control experiment, where the lower grade toluene and electrolyte were electrolyzed without any C_{60} present, did not lead to the detection of any EPR signals with *g* values close to 2.000. Other workers have reported the appearance of more than one narrow line width EPR signal during the reduction of C_{60} to $C_{60}^{\bullet -}$.[7–9] It has been suggested that the narrow line width signals are due to higher (> 1^-) charged anion radicals of C_{60},[2b,9] but this explanation is unlikely in this case because the electrolysis conditions were carefully controlled so that >1^- charged anions were not generated in any significant quantity (see *Experimental Section*). Also, because C_{60} is electrochemically reversibly reduced to $C_{60}^{\bullet -}$, only very small quantities of anions with >1^- charge are thermodynamically possible (according to the Nernst equation) until after 100% of the 1^- anion has been produced,[5b] and in the experiments illustrated in Figure 4 there is only 33% conversion of C_{60} to the monoanion. Figure 4 also illustrates that signal **4** appears to decrease in intensity as signals **2** and **3** grow. However, care must be taken in this assignment because it was observed from the experiments represented in Figure 3 that species **2** and **3** also increase in intensity concomitantly with signal **1** decreasing in intensity.

Having described the appearance and relative intensities of the broad and narrow EPR line width signals, explanations can be proposed as to the origins of the signals in relation to the models that have been previously proposed.[1–9] It has been generally concluded that the species with the broad EPR signal is the solvated radical anion, $C_{60}^{\bullet -}{}_{(solv)}$, mainly because of the high percentage obtained of this species compared with the species with the narrow line width signals. Because purely organic radicals nearly always show narrow EPR line width signals (providing the EPR instrumental parameters are conducive to this), the explanation put forward to explain why the signal is broad is due to the high symmetry of $C_{60}^{\bullet -}$ enabling rapid spin relaxation, whereas the sharp line signals have been attributed to forms of $C_{60}^{\bullet -}$ where the symmetry has been lowered.[3b,3d,5d]

The observation that the number of narrow line width signals increased when low purity solvents were used is consistent with the species with the sharp signals being due to complexes between $C_{60}^{\bullet -}$ and low levels of impurities in the toluene, which is also consistent with the sharp line signals being due to lower symmetry forms of $C_{60}^{\bullet -}$. The major impurities in toluene are aromatic and sulfur compounds, and C_{60} is known to form weak π-complexes with both.[10–16,23,24] Because the species with the sharp signals were present in <5% of the concentration of $C_{60}^{\bullet -}$, and the experiments were conducted with between 0.2 and 1.0 mM of C_{60}, the reaction of $C_{60}^{\bullet -}$ with micromolar levels of impurities would be sufficient to account for the species with the sharp lines. Furthermore, it has been observed that functionalized C_{60} radicals characteristically display EPR signals with narrow line widths,[3d,5d] hence σ-bonded $(C_{60}\text{-impurity})^{\bullet -}$ radicals could account for the narrow line width signals. A radical anion dimer or trimer type arrangement of C_{60}, $(C_{60})_n^{\bullet -}$ (where $n > 2$), cannot be ruled out as one source of the sharp signals. However, a σ-bonded dimer of C_{60} (C_{120}) has recently been synthesized and reported to be unstable, even under short voltammetric time scales, when electrochemically reduced.[25] The narrow line width (~0.1 mT) of species **2** and **3** would suggest that $S > {}^1/_2$ species are unlikely for the organic radicals. Therefore, a dimer dianion, $(C_{60})_2{}^{2-}$, which has been proposed for one species,[8c] would have to be a biradical because the spin–spin interactions of a triplet produce substantially faster relaxation than for isolated spins and it is questionable whether the spectrum could be detected at room temperature.[26]

An alternative assignment of the narrow line width signal can be made on the basis of aggregation of $C_{60}^{\bullet -}$.[8d] C_{60} exists as a solvated monomer in pure toluene[27] but as aggregates or clusters in mixed polar and nonpolar solvents,[23,27,28] in phosphatidylcholine liposome colloidal solutions,[29] and in the presence of CTV[16] and *p*-Bu^t-calix[8]arene.[12a,30] It has been suggested[23] that in mixed toluene–acetonitrile solvents, at high percentages of acetonitrile (> 70%) where fullerenes are less soluble, π-bonding interactions between the fullerenes and toluene assist in the cluster formation. However, most cluster studies[23,28] have been performed at a 50–500 times lower concentration (~1–10 μM) of C_{60} than what was used in this work (~500 μM) and it is likely that at higher concentrations of C_{60}, such as in this work, less acetonitrile is necessary for aggregate formation. The EPR spectroscopy of matrix isolated clusters[31] and colloids[32] and of clusters in biological systems[33] have been well documented in the literature, and clusters of $C_{60}^{\bullet -}$ are known in the solid state[34] as well as clusters of $C_{60}^{\bullet -}$ with other organic radical anions in the gas phase.[35] However, the major experimental observation that suggests that the narrow line width signals are not due to clustered forms of $C_{60}^{\bullet -}$, was the insensitivity of the ratio of broad-to-narrow line width signals as the concentration of acetonitrile was varied. A 0.5 mM solution of C_{60} in toluene with 20% acetonitrile is slightly cloudy, indicating the presence of particulate material. Thus, if one or more of the sharp signals were due to an aggregate radical, the relative intensity should have increased with increasing acetonitrile concentration, where C_{60} is less soluble. However, no difference was detected in the relative intensities of the broad and narrow line width signals (at equal times after the generation of $C_{60}^{\bullet -}$) when the concentration of acetonitrile was varied between 5 and 20% (v/v).

3.2. EPR Spectroscopy of $C_{60}^{\bullet -}$ in the Presence of Complexing Agents. Experiments were conducted on $C_{60}^{\bullet -}$ in toluene–acetonitrile (90:10) to determine if EPR spectroscopy could be used to detect π–π interactions between the fulleride and a supramolecular complexing agent. Solutions of C_{60} containing a twofold excess of the complexing agent were left for a sufficiently long period of time so that the characteristic magenta color of solvated C_{60} changed to brown color distinctive of supramolecular complexed C_{60}.[10,16] For CTV, where the host–guest interactions are known to be quite weak,[16b] the complete complexation reaction took 3–4 weeks; for CTV-(allyl)$_3$, the complexation reaction took ~2–3 days, and for *p*-benzyl-calix[5]arene, the solution turned brown almost immediately when the C_{60} and calixarene were mixed. The 10% acetonitrile used in these complexation studies has two important effects. First, in pure toluene, the CTV–C_{60} and *p*-benzyl-calix[5]arene–C_{60} complexes precipitate out, but the complexes remain soluble with 10% acetonitrile. Second, the acetonitrile slows down the complexation reaction considerably (in pure toluene, the complexation reaction between C_{60} and CTV takes several hours). Heating up the solutions to ~60 °C in all cases resulted in the magenta color of C_{60} returning, which confirms the complexation reaction is reversible. When the brown solutions containing the host–guest complexes were electrolyzed under controlled potential conditions and transferred to the silica cell for EPR measurements, the broad line width signal (**1**) could not be detected and only an exceptionally weak narrow line width signal at $g = 2.0000$ was observed. The intensity of the narrow line width signal was estimated at <5% of the intensity that was observed for the sharp signals of $C_{60}^{\bullet -}$ in the absence of the complexing agents. Leaving the electrolyzed solution for up to 48 h did not lead to any noticeable increase in signal intensity of the broad or narrow signals. It appears that the complexed form of $C_{60}^{\bullet -}$ is EPR silent, perhaps due to the aggregated host–guest complexes having a slow tumbling rate and/or faster relaxation time resulting in extensive line broadening. The T_1 relaxation time obtained from NMR experiments of C_{60} complexed with a calix[8]arene was drastically shortened compared with uncomplexed C_{60}.[13] The small amount of the sharp signal that was detected is most likely a residual amount of the uncomplexed $C_{60}^{\bullet-}$. Therefore, these results suggest that the sharp EPR signals that are often detected during the reduction of C_{60} are not due to $\pi-\pi$ bonded complexes of $C_{60}^{\bullet-}$ (as opposed to σ-bonded radical complexes) because a strong EPR signal was not detected for the $\pi-\pi$ bonded $(C_{60}\text{-host})^{\bullet-}$ radical [this is assuming that the $(C_{60}-\text{host})^{\bullet-}$ complex is stable for at least the time taken to perform the EPR experiments].

In addition to the controlled potential electrolysis cell that was used to generate $C_{60}^{\bullet-}$ outside of the EPR cavity, an in situ controlled potential electrolysis cell[20] was used that has been used successfully in the past to study a number of organic radicals.[18,19a,36] The advantage of this cell is that only very small quantities of solution are necessary (0.1−0.2 mL) and, because it is used in situ, there is a greater likelihood of detecting unstable radicals.[20] C_{60} (0.5 mM) plus a twofold excess of the complexing agent were dissolved in 5 mL of toluene−acetonitrile (90:10). At various time intervals from when the C_{60} and the complexing agent were first mixed, a 0.2-mL aliquot of the solution was taken and an in situ electrochemical-EPR experiment was performed. $C_{60}^{\bullet-}$ (or more accurately, complexed $C_{60}^{\bullet-}$) was generated by holding the reduction potential between the first and second redox processes. The potential control of the in situ electrochemical-EPR cell is not as accurate as with the 5-mL controlled-potential electrolysis cell (*Experimental Section*), but the conditions were controlled so that only a small amount of the C_{60} was reduced (using Faraday's law), which ensured that higher anions ($>1^-$) were not produced by exhaustive one-electron electrolysis of C_{60}.

Figure 5 shows the EPR spectra of the sharp signals obtained by reductive electrolysis of C_{60} in the in situ electrochemical-EPR cell at certain intervals after CTV (1.29 mM) and C_{60} (0.58 mM) were mixed together. Soon after the C_{60} and CTV were dissolved, the EPR spectrum (after electrolysis of C_{60}−CTV) was observed to change from that of pure $C_{60}^{\bullet-}$, indicating that a host−guest interaction was occurring (Figure 6, $t = 6$ h), and with increasing time the signal intensity of the sharp signals decreased. In the in situ electrochemical-EPR cell, the EPR spectra were recorded simultaneously when the potential was applied; hence, there was no 10-min waiting period to transfer the sample into the EPR cavity as with the conventional bulk electrolysis cell. Furthermore, the electrolysis time and conditions were controlled to be as close as possible to equal between the different experiments so that the data at different times could be compared directly. The decrease in the signal intensity of the sharp signals observed from the time of first mixing can most easily be explained by a slow reaction between C_{60} and the complexing reagent reducing the amount of free $C_{60}^{\bullet-}$ being able to be detected by EPR. A similar effect was observed for the broad signal, although for the longer time experiments ($t >$ 48 h), the broad signal became very difficult to detect, most likely because of the signal-to-noise ratio of the broad signal being much less than the signal-to-noise ratio of the sharp signals. Similar effects were observed when $CTV(allyl)_3$ and *p*-benzyl-calix[5]arene were mixed with a solution of C_{60} and the solutions electrolyzed in the in situ electrochemical-EPR cell. However, in these cases the complexation reactions with C_{60} were much faster, particularly for the calixarene, so the slow decrease in signal intensity over time were not as pronounced.

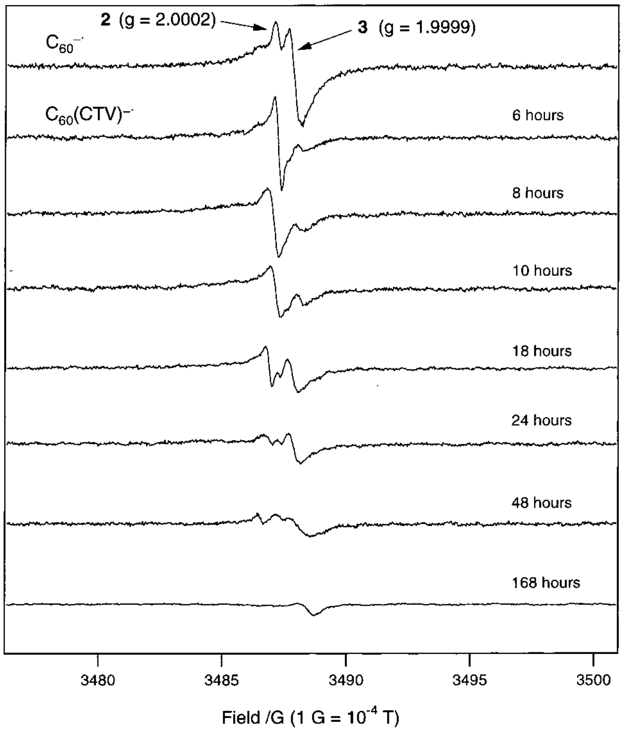

Figure 5. First-derivative EPR spectra obtained via reductive electrolysis of a solution of C_{60} (0.58 mM) and CTV (1.29 mM) in an in situ electrolysis cell (see *Experimental Section* for full details). The time refers to the time after which the compounds were first mixed in toluene−acetonitrile (90:10) with 0.1 M $n\text{-Hex}_4NPF_6$. The EPR modulation amplitude = 0.1 G, time constant = 10 ms, sweep width = 20 G, and sweep time = 10 s. The ordinate axis is in constant but arbitrary units. The spectrum at 168 h is the average of several accumulations.

3.3. Cyclic Voltammetry of C_{60}. C_{60} exhibits up to six one-electron reduction processes in organic solvents,[37] which corresponds to filling of the triply degenerate LUMO.[38] Several studies[39] have investigated the influence of the solvent and supporting electrolyte on the voltammetric behavior of C_{60}, which have showed that the $E_{1/2}$ values are dependent on the solvent and strong ion-pairing occurs between anions of C_{60} and *n*-tetraalkylammonium cations. However, these studies[39] were conducted in pure solvents, whereas all the EPR experiments reported in this paper were performed in mixed toluene−acetonitrile. Therefore, cyclic voltammetry experiments were conducted under similar conditions to those under which the EPR spectra of $C_{60}^{\bullet-}$ were obtained by varying the ratio of toluene−acetonitrile (95:5−80:20), the concentration of C_{60} (0.2−1.0 mM), the supporting electrolyte cation ($n\text{-Bu}_4N^+$ and $n\text{-Hex}_4N^+$) and the electrode surface (Au, Pt and GC).

Figure 6a shows a cyclic voltammogram of C_{60} in toluene at a GC electrode with 10% acetonitrile and 0.1 M $n\text{-Hex}_4NPF_6$ as the supporting electrolyte. The first three reduction processes appear chemically reversible, whereas the fourth process appears to be chemically irreversible, in the sense that no well-defined reverse peak is evident on the cyclic voltammogram for process 4. When the electrolyte is changed to $n\text{-Bu}_4NPF_6$ the fourth reduction process appears chemically reversible (Figure 6b). The apparent chemically irreversibility observed in some of the voltammograms (Figure 6a) for the fourth process is likely to be due to complex electrode/electrolyte/solute interactions because C_{60}^{4-} can be synthesized as a salt, albeit being highly oxygen and moisture sensitive.[5c] In addition, with $n\text{-Bu}_4NPF_6$ as the supporting electrolyte, the $E_{1/2}$ values for C_{60}^{n-} obtained by cyclic voltammetry shift to slightly more positive values for

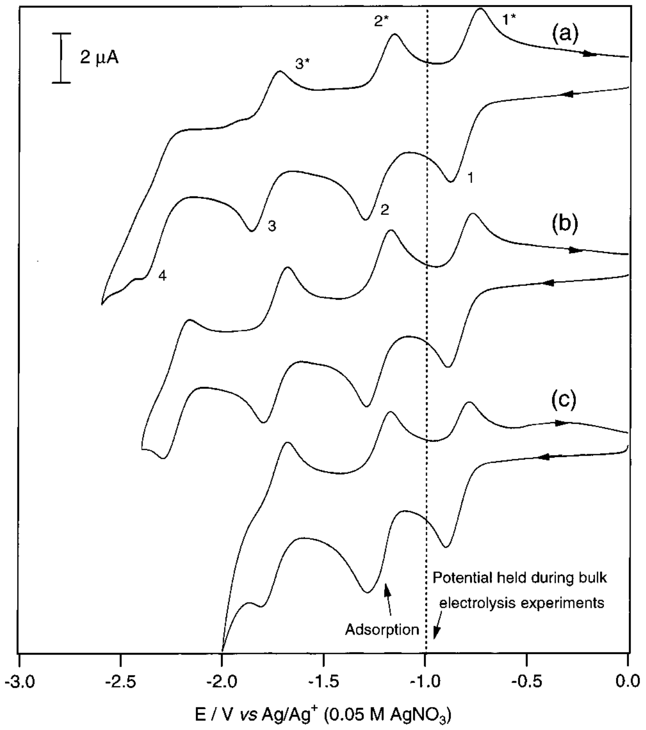

Figure 6. Cyclic voltammograms of 0.5 mM C_{60} in toluene−acetonitrile (90:10) recorded at a scan rate of 100 mVs^{-1} [the starting and finishing potentials were 0 V versus Ag/Ag^+ (0.05 M $AgNO_3$)]. (a) 1-mm diameter glassy carbon working electrode and 0.1 M *n*-Hex_4NPF_6; (b) 1-mm diameter glassy carbon working electrode and 0.1 M *n*-Bu_4NPF_6; and (c) 1-mm diameter Pt working electrode and 0.1 M *n*-Bu_4NPF_6.

the third and fourth processes and to more negative values for the first and second processes, which is in good agreement with the data of Dubois *et al.*[39a] obtained in several pure solvents. Increasing the acetonitrile concentration to 20% (v/v) shifted the $E_{1/2}$ values for the four reduction processes by ∼5 mV to more positive values. Solvent−fulleride interactions are generally much more important in shifting the $E^r_{1/2}$ values of $C_{60}{}^{n-/(n+1)-}$ couples than ion-pair formation between the solvent and electrolyte.[39] When the electrode surface was changed to platinum (Figure 6c), pronounced absorption features became evident in the form of pre-peaks before the main diffusion-controlled peaks, especially for process 2. The effects were most notable on Au > Pt > GC electrodes, when the acetonitrile concentration was <10%, when *n*-Hex_4NPF_6 was used as the supporting electrolyte, and when the concentration of C_{60} was >0.5 mM.

At high concentrations of acetonitrile, the aggregate form of C_{60} is favored.[23,28] However, cyclic voltammetry experiments at a 1-mm diameter working electrode or steady-state voltammetric experiments at a 10-μm microelectrode did not show appreciable changes in peak current or diffusion-controlled current as the concentration of acetonitrile was increased between 5 and 20% (v/v). Above 20% (v/v) acetonitrile in toluene, 0.5 mM C_{60} is not fully soluble, a precipitate forms immediately, and a decrease in the diffusion-controlled current was observed. This result is in good agreement with the EPR data, which showed no change in the EPR signal intensities between 5 and 20% acetonitrile (with 0.5 mM $C_{60}{}^{\bullet-}$).

3.4. Cyclic Voltammetry of C_{60} in the Presence of Complexing Agents. Figure 7 illustrates the change in the cyclic voltammetry when C_{60} was mixed with an excess of the complexing agents CTV, CTV(allyl)$_3$, and *p*-benzyl-calix[5]arene. (The complexation agents themselves are electro-inactive within the potential window studied.) In the experiments represented in Figure 7, the solutions were left for a long enough time and there was sufficient complexing agent added to ensure complete complexation, as indicated by the brown color of the solution. The cyclic voltammograms of C_{60} in the presence of the three complexing agents all show that the first four reduction processes of C_{60} are split into two processes, so that there are a total of eight processes for each complex labeled 1a − 4b* in Figure 7a (* refers to the reverse scan oxidation wave corresponding to a reduction wave). The cyclic voltammetric waves were all shifted to different potentials from that of pure C_{60}, indicating that no uncomplexed C_{60} was present. Also, the peak-to-peak separation of the processes were considerably greater than the theoretical separation of ∼60 mV for a one-electron electrochemically reversible wave.

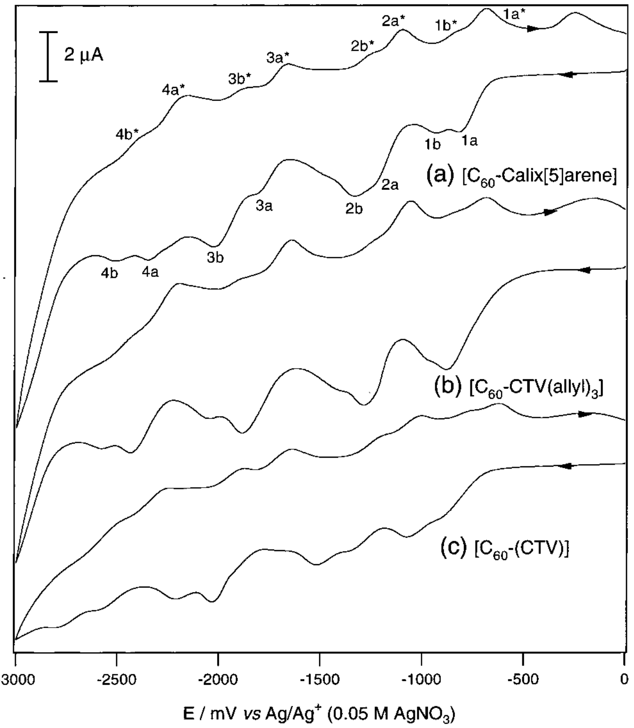

Figure 7. Cyclic voltammograms at a 1-mm diameter glassy carbon electrode of C_{60} and complexing agents in toluene−acetonitrile (90:10) with 0.1 M *n*-Hex_4NPF_6 and recorded at a scan rate of 100 mV s^{-1} [the starting and finishing potentials were 0 V vs Ag/Ag^+ (0.05 M $AgNO_3$)]: (a) 0.51 mM C_{60} and 1.1 mM calix[5]arene after the compounds were mixed in solution for 3 days; (b) 0.69 mM C_{60} and 1.74 mM CTV(allyl)$_3$ after the compounds were mixed in solution for 2 weeks; and (c) 0.53 mM C_{60} and 1.78 mM CTV after the compounds were mixed in solution for 2 weeks. For a−c, the solutions were a brown color, indicating that a complex between C_{60} and the ligand had been formed.

The observation that the reverse redox couple of each process (Figure 7) is evident on the reverse cyclic voltammogram even when the scan is extended to very negative potentials (0 − −3.0 V) suggest that the $(C_{60}{-}host)^{n-/(n+1)-}$ complexes are stable on the time scale of the voltammetric experiments (several seconds). Also, in Figure 7 there is no evidence for voltammetric waves associated with the reduction of pure C_{60} (cf. Figure 6), indicating that $C_{60}{}^{\bullet-}$ is not immediately ejected from the host upon reduction of the host−guest complex. However, there are still some uncertainties as to the absolute stability of the host−guest radical complexes because the voltammetric data were recorded over a shorter time scale (seconds) than the EPR experiments (minutes).

Chen et al.,[15] who used cyclic and square wave voltammetry to study the complexation of C_{60} by titrating increasing amounts of several *p-tert*-butylcalixarenes into a solution of C_{60} (and immediately recording the voltammograms), also observed each reduction process of C_{60} split into two processes, although they had to add large quantities (14-fold excess) of the complexing agent to observe any change in the first reduction process of C_{60}. The difference between the experiments of Chen et al.[15] and the data in this paper is the time allowed for the host−guest reaction. The data in Figure 7 show that only a small excess of complexing agent is needed to split each voltammetric wave of C_{60} into two waves providing there is sufficient time for the host−guest interaction to occur.

4. Conclusions

At least two narrow (1−5%) and one broad (> 95%) line width signals, all with g values close to 2.0000, were detected by EPR spectroscopy during the electrochemical reduction of C_{60} to $C_{60}{}^{\bullet-}$ in toluene−acetonitrile. The observation that the number of sharp signals increased when low purity toluene was used is suggestive that the sharp EPR signals are due to complexes between $C_{60}{}^{\bullet-}$ and impurities in the toluene, with σ-bonded (C_{60}-impurity)$^{\bullet-}$ radicals not being inconsistent with reports of narrow line width signals of substituted fullerenes. The relative intensities of the broad and narrow line width signals were not sensitive to changing the acetonitrile concentration (between 5 and 20%), suggesting that the narrow line width signals are not due to aggregate forms of $C_{60}{}^{\bullet-}$. The intensity of both the narrow and sharp signals of $C_{60}{}^{\bullet-}$ deceased substantially when host−guest complexes of C_{60} were reduced electrochemically, with the decrease in signal intensity being proportional to the time allowed for the host−guest interactions. Cyclic voltammetry experiments on C_{60} in the presence of several complexing agents consistently showed each reduction wave of C_{60} splitting into two processes, providing the host−guest complex is left for sufficiently long periods of time to react.

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