Artifacts in the Electron Paramagnetic Resonance Spectra of C_{60} Fullerene Ions: Inevitable $C_{120}O$ Impurity

Parimal Paul,[†] Kee-Chan Kim,[‡] Dayong Sun,[‡] Peter D. W. Boyd,[§] and
Christopher A. Reed*,[‡]

*Contribution from the Departments of Chemistry, University of California, Riverside, California
92521-0403 and The University of Auckland, Private Bag 92019, Auckland, New Zealand*

Abstract: Aspects of the electron paramagnetic resonance (EPR) spectra of $C_{60}{}^{n-}$ fulleride ions ($n = 2, 3$) and the EPR signal observed in solid C_{60} are reinterpreted. Insufficient levels of reduction and the unrecognized presence of $C_{120}O$, a ubiquitous and unavoidable impurity in air-exposed C_{60}, have compromised most previously reported spectra of fullerides. Central narrow line width signals ("spikes") are ascribed to $C_{120}O^{n-}$ ($n =$ odd). Signals arising from axial triplets ($g \sim 2.0015$, $D = 26-29$ G) in the spectrum of $C_{60}{}^{2-}$ are ascribed to $C_{120}O^{n-}$ ($n = 2$ or 4). Their D values are more realistic for $C_{120}O$ than C_{60}. Less distinct signals from "powder" triplets ($D \sim 11$ G) are ascribed to aggregates of $C_{120}O^{n-}$ ($n =$ odd) arising from freezing nonglassing solvents. In highly purified samples of C_{60}, we find no evidence for a broad ~ 30 G signal previously assigned to a thermally accessible triplet of $C_{60}{}^{2-}$. The $C_{60}{}^{2-}$ ion is EPR-silent. Signals previously ascribed to a quartet state of the $C_{60}{}^{3-}$ ion are ascribed to $C_{120}O^{4-}$. Uncomplicated, authentic spectra of $C_{60}{}^{-}$ and $C_{60}{}^{3-}$ become available when fully reduced samples are prepared under strictly anaerobic conditions from freshly HPLC-purified C_{60}. Solid off-the-shelf C_{60} has an EPR signal ($g \sim 2.0025$, $\Delta H_{pp} \sim 1.5$ G) that is commonly ascribed to the radical cation $C_{60}{}^{\bullet+}$. This signal can be reproduced by exposing highly purified, EPR-silent C_{60} to oxygen in the dark. Doping C_{60} with an authentic $C_{60}{}^{\bullet+}$ salt gives a signal with much greater line width ($\Delta H_{pp} = 6-8$ G). It is suggested that the EPR signal in air-exposed samples of C_{60} arises from a peroxide-bridged diradical, $\bullet C_{60}-O-O-C_{60}\bullet$ or its decomposition products rather than from $C_{60}{}^{\bullet+}$. Solid-state C_{60} is more sensitive to oxygen than previously appreciated such that contamination with $C_{120}O$ is almost impossible to avoid.

The addition of electrons to C_{60} is its most characteristic chemical property. As a consequence, over the past decade, a great deal of effort has been put into characterizing the electronic structure of fulleride anions, $C_{60}{}^{n-}$.[1] In this paper, we show that the electron paramagnetic resonance (EPR) characterization of these ions has been significantly compromised by imprecise levels of reduction and by the presence of an unrecognized impurity in [60]-fullerene, namely, $C_{120}O$.
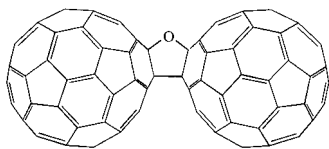
In addition, we question the widely held belief that the EPR signal commonly observed in solid "pristine" C_{60} is due to the radical cation $C_{60}{}^{\bullet+}$.[2-6] In contrast to the easy addition of electrons, the removal of electrons from C_{60} is extremely difficult.[7] Thus, the formation of air-stable $C_{60}{}^{\bullet+}$ radical cation centers is not easy to chemically rationalize. Now that a synthetic route to $C_{60}{}^{\bullet+}$ has become available,[8] a purposeful doping experiment into C_{60} can be performed.

The $C_{60}{}^{3-}$ ion is a particularly important fulleride ion to characterize well because it gives rise to superconductivity in A_3C_{60} fulleride phases (A = alkali metal). The triply degenerate nature of the t_{1u} lowest unoccupied molecular orbital (LUMO) of C_{60} led to the intuitive expectation of a spin-quartet $S = 3/2$ ground state for this ion. Similarly, the $C_{60}{}^{2-}$ ion was expected to have a $(t_{1u})^2$ spin-triplet $S = 1$ ground state. Neither expectation was borne out by experiment. Both ions disobey Hund's rule. The $C_{60}{}^{3-}$ ion has a doublet $S = 1/2$ ground state, and despite early assumptions of a triplet ground state,[9] a consensus has developed that the $C_{60}{}^{2-}$ ion has a singlet

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† Visiting Scientist at UC Riverside from the Central Salt and Marine Chemicals Research Institute, Bhavnagar, India.

‡ University of California, Riverside.

§ The University of Auckland, New Zealand.

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(diamagnetic) $S = 0$ ground state.[1,10] Nevertheless, there has always been a strong suspicion that the intuitively expected higher spin states must be low-lying in energy and thermally accessible.[11,12] This probably contributed to the ready acceptance of EPR evidence for their existence. In 1995, Eaton and co-workers[13] and Jones, Kadish, and co-workers[14] independently interpreted the variable-temperature EPR spectrum of C$_{60}^{2-}$ in terms of a thermally accessible triplet state with a singlet−triplet gap of ca. 600 cm^{-1}. More recently, Shohoji, Takui, and co-workers[15] interpreted a portion of the EPR spectrum attributed to the C$_{60}^{3-}$ ion in terms of a quartet state.

We have recently shown that the long-debated origin of the extraneous "spike" in the EPR spectrum of C$_{60}^{-}$ is due to the presence of C$_{120}$O^{-}.[16] This arises from C$_{120}$O impurity in air-exposed samples of C$_{60}$.[17] It behooved us therefore to investigate whether the features ascribed to thermally accessible excited states in the EPR spectra of the C$_{60}^{2-}$ and C$_{60}^{3-}$ ions might also be reinterpreted in terms of C$_{120}$O^{n-} impurities. The EPR signals in question are minor components of complex spectra and their line shapes are not typical of the assigned states. Specific dynamic effects had to be invoked to rationalize their shapes. The D values assigned to signals from the alleged quartet of C$_{60}^{3-}$ (0.0014 cm^{-1}) and triplet of C$_{60}^{2-}$ (∼30 G) are much smaller than that found in the triplet state of neutral C$_{60}$ (0.0114 cm^{-1}, 122 G).[18] These observations raise additional skepticism about their correct assignment and suggest that the signals might be arising from a larger molecule than C$_{60}$.

Experimental Section

C$_{60}$ was purchased from MER Corp. or BuckyUSA and purified by HPLC on a semipreparative Buckyprep Cosmosil column with toluene as eluent. C$_{120}$O was prepared and HPLC-purified by literature methods.[17,19,20] Peak separation of C$_{60}$ from C$_{120}$O was 12 min, monitored at 330 nm. Concentrations were chosen such that baseline separation was typically ca. 4 min. All reductive titrations and syntheses were carried out in a Vacuum Atmospheres Corp. inert atmosphere glovebox (O$_2$, H$_2$O < 0.5 ppm). C$_{60}^{n-}$ fulleride salts[12,21,22] and a C$_{60}^{\cdot+}$ fullerenium ion salt[8] were prepared by literature methods. Solvents were purified by standard methods[23] and vacuum-distilled inside the glovebox shortly before use. Tetrabutylammonium hexafluorophosphate electro-
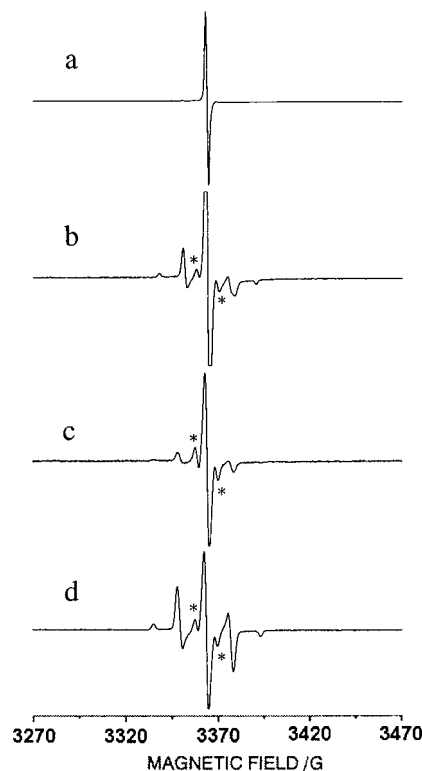
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Figure 1. X-band EPR spectra of frozen 5×10^{-4} M solutions of C$_{120}$O fullerides at 100 K in 1:2:4 *o*-dichlorobenzene/dimethylsulfoxide/tetrahydrofuran as a function of added equivalents of Co(Cp*)$_2$ reducing agent: (a) 0.8, (b) 2.0, (c) 3.0, and (d) 4.1. Asterisks mark the powder triplet (see text). Microwave power 5.7 mW, modulation 5 G.

lyte was recrystallized from dried tetrahydrofuran (THF)/hexane in the glovebox. Quartz EPR tubes were filled with samples inside the glovebox, attached to a vacuum line adapter via tightly fitting Tygon tubing, and torch-sealed under vacuum outside of the glovebox. States of reduction were monitored by near-IR spectroscopy[1] before and after EPR spectroscopy. Spectra were obtained on a Bruker ER200D spectrometer at UC Riverside or a Bruker EMX system at UCLA.

Results and Discussion

C$_{120}$O^{n-} Anions. To establish the EPR signatures of C$_{120}$O^{n-} anions, HPLC-pure C$_{120}$O was titrated with decamethylcobaltocene, Co(Cp*)$_2$. To optimize solubility, a solvent mixture of 1:2:4 *o*-dichlorobenzene/dimethyl sulfoxide/tetrahydrofuran was used. Dichloromethane and chemically related solvents with potentially extractable nucleophiles or acidic C−H bonds (e.g., acetonitrile) were avoided because highly charged fulleride anions are known to react with haloalkanes.[1] The sequential reduction potentials of C$_{120}$O (−836, −875, −1238, and −1299 mV vs Fc/Fc^{+})[20] are such that mixtures of both C$_{120}$O^{-} and C$_{120}$O^{2-} will be present when 1−2 equiv of reducing agent are added. Similarly, both C$_{120}$O^{3-} and C$_{120}$O^{4-} will be present when 3−4 equiv of reducing agent are added.

The EPR spectra with successive equivalents of Co(Cp*)$_2$ are shown in Figure 1. As established earlier,[16] the central narrow signal seen with 0.8 equiv ($g = 2.0012$, $\Delta H_{pp} = 2.0$ G) is assigned to an $S = 1/2$ (doublet) spin state of C$_{120}$O^{-}. The "wings" that grow in next with 2 equiv of reducing agent (Figure 1b) are typical of overlapping signals arising from $S = 1$ (triplet) spin states. The minor axial triplet-type signal, whose perpendicular (inner) portion is identified with asterisks, is discussed below. The major axial triplet-type signal ($g_{av} = 2.0007$, $D = $
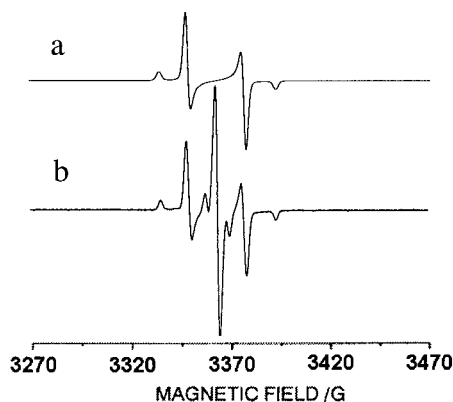
Figure 2. (a) Simulation of EPR spectrum of $C_{120}O^{4-}$ in terms of an axial triplet compared to (b) the measured spectrum of $C_{120}O^{3-/4-}$ from Figure 1d. Fitting parameters: $g_{||} = 2.0012$, $g_{\perp} = 2.0017$, $D = 29.0$ G. Remaining peaks in the central portion of the measured spectrum are assigned to the central spike of $C_{120}O^{3-}$ and its accompanying powder triplet from $C_{120}O^{3-}$ aggregates.

26 G) is assigned to an $S = 1$ state of $C_{120}O^{2-}$. With 3 equiv of reducing agent, subtle changes occur in both the triplet-state signal region and the central narrow-line region. The new central narrow signal ($g = 2.0013$, $\Delta H_{pp} = 2.6$ G) is assigned to $C_{120}O^{3-}$. Finally, with 4 equiv, a new, well-defined axial triplet-type signal reappears ($g_{av} = 2.0015$, $D = 29$ G). This is assigned to an $S = 1$ triplet state of the $C_{120}O^{4-}$ ion.

The line shapes of the axial triplet-type signals are entirely typical of those derived from molecules with $S = 1$ states[24] and are readily simulated (Figure 2a). Both the strong inner (perpendicular) pair of signals and the weaker outer (parallel) pair of signals are faithfully reproduced. Collectively, we refer to these signals as arising from a "proper triplet". By use of the usual simplified model ($D = 3g_e\beta/2r^3$) of localized electrons separated by distance r, the spectrum with $D = 29$ G gives $r = 9.9$ Å. This is a very reasonable approximation for one unpaired electron on each ball of the $C_{120}O^{4-}$ ion. Our D values are twice those reported in ref 20 due to an inadvertent error in the scale posted in Figures 6 and 7 of this reference. For 5 G, one should read 10 G.[25]

With three added electrons, the spin state of the $C_{120}O^{3-}$ ion could be an $S = 1/2$ doublet or an $S = 3/2$ quartet. An $S = 3/2$ simulation with $D = 14.5$ G gave a spectrum not unlike that of Figure 1c but the spectrum could just as easily arise from an overlay of a doublet-type narrow line signal from $C_{120}O^{3-}$ and axial triplet-type signals from $C_{120}O^{2-}$ and $C_{120}O^{4-}$. As the reduction proceeds, the central peak of the spectrum varies in intensity with respect to the outer pairs of lines in a very complex manner because of the unavoidable overlap of signals from $C_{120}O^{n-}$ ($n = 2-4$) and the potential coincidence of peaks from triplet states with those from a quartet. Thus, simulations cannot rigorously distinguish between these two possibilities. Nevertheless, we favor an $S = 1/2$ state for the $C_{120}O^{3-}$ ion because, when given a choice between high and low spin states, fullerides show a marked tendency to adopt the lower spin state, even if this disobeys Hund's rule.[1]

Also appearing in these spectra are a pair of less distinct features 5.5 G either side of the central narrow lines (marked
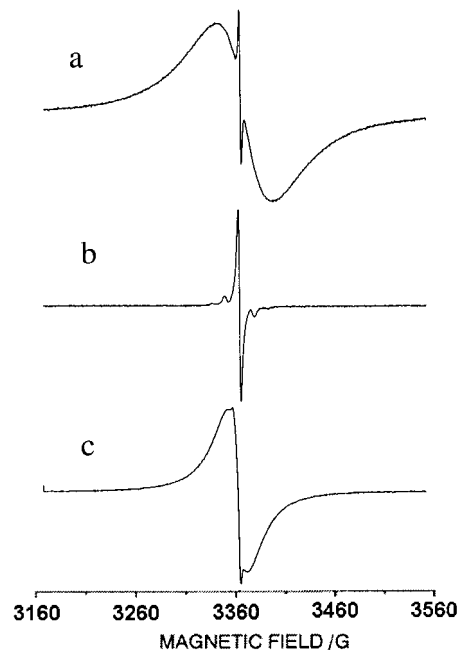
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Figure 3. EPR spectra of progressively reduced off-the-shelf C_{60}: (a) $[Co(Cp^*)_2^+][C_{60}^-]$, (b) $[Co(Cp^*)_2^+]_2[C_{60}^{2-}]$, and (c) $[Na(dibenzo-18-crown-6)^+]_3[C_{60}^{3-}]$. Conditions were the same as in Figure 1 except the temperature was 150 K.

with asterisks in Figure 1). These are assigned to perpendicular portions of powder spectrum triplets associated with aggregated $C_{120}O^-$ or $C_{120}O^{3-}$ radicals ($D = 11$ G). The *parallel* (outer) portions of these *powder* triplets coincide approximately with the *perpendicular* (inner) portions of the *proper* triplets arising from $C_{120}O^{2-}$ or $C_{120}O^{4-}$, sometimes distorting the line shape of the latter (e.g., see right-hand side of Figure 1b). For reasons of low solubility, we are unable to work in truly glassing solvents that suppress aggregation. It is a well-known phenomenon in EPR spectroscopy that freezing a crystalline solvent extrudes solutes, giving rise to aggregates of the EPR active species. The result is the appearance of so-called powder triplet signals. They are often seen as somewhat broadened "wings" either side of doublet-type narrow-line spectra. Their relative intensity varies with solvent, freezing rates, etc. They are common in fulleride spectra because of generally poor solubility. According to the simplified model of localized electrons, the radicals are separated by 13.6 Å, a reasonable approximation for associated $C_{120}O^{n-}$ ions.

At 225 K, which is the melting point of the solvent mixture used, all signals arising from triplet states in Figure 1d disappear, leaving only the central narrow line signal assigned to $C_{120}O^{3-}$. This is the expected behavior of proper triplets in fluid solution.[24] It is also the expected behavior of a powder triplet since fluid solution will redisperse solute aggregation brought about by freezing a nonglassing solvent. Thus, the loss of both triplet-type signals in fluid solution supports the assignment of the proper triplet to $C_{120}O^{4-}$ and the powder triplet to $C_{120}O^{n-}$ aggregates (n odd).

Off-the-Shelf C_{60}^{n-}. EPR spectra were obtained for off-the-shelf C_{60} reduced under the same conditions as the $C_{120}O^{n-}$ work. As $[Co(Cp^*)_2^+][C_{60}^-]$ is titrated with $Co(Cp^*)_2$ in 1:2:4 *o*-dichlorobenzene/dimethylsulfoxide/tetrahydrofuran, the broad signal of C_{60}^- (with its attendant narrow line "spike" due to $C_{120}O^-$)[16] gradually disappears (see Figure 3a,b). A slight excess

of Co(Cp*)$_2$ can be added to push the reduction of C$_{60}^{2-}$ to completion because, as judged by near-IR spectroscopy, Co-(Cp*)$_2$ is not a strong enough reducing agent to produce C$_{60}^{3-}$ in the present solvent system. [The EPR signal from the excess Co(Cp*)$_2$ is too broad to interfere.] All that remains in the EPR spectrum at the C$_{60}^{2-}$ level (Figure 3b) are superimposed narrow-line and triplet-type signals with parameters *identical* to those of C$_{120}$O^{3-} and C$_{120}$O^{4-}. We note that the powder triplet features appear to have almost disappeared in Figure 3b relative to Figure 1d (there is 0.5 horizontal scale change between these figures). They are barely perceptible shoulders on the central line. This is understandable in terms of less C$_{120}$O^{3-}/C$_{120}$O^{3-} aggregation in the presence of excess (diamagnetic) C$_{60}^{2-}$ ions. The identity of these signals with those from authentic C$_{120}$O anions is compelling evidence that the signals ascribed to the C$_{60}^{2-}$ ion in the early literature arise from C$_{120}$O impurity.[26]

The signals previously known as the "low-temperature triplet" and "high-temperature triplet" in the C$_{60}^{2-}$ spectrum[1,12] are now the "powder triplet" of aggregated C$_{120}$O^{3-} and the "proper triplet" of C$_{120}$O^{4-} respectively. An earlier calculation of an r = 12.6 Å separation for two electrons on the C$_{60}^{2-}$ ion[9] can be given a more realistic interpretation. Given that C$_{60}$ has a carbon-to-carbon atom diameter of only 7.1 Å (van der Waals diameter of 10 Å), its explanation in terms of a powder triplet from aggregates of C$_{120}$O^{3-} makes better chemical sense.

From all of these data, the C$_{60}^{2-}$ ion is clearly EPR-silent at 100 K, removing any lingering doubts about its diamagnetic ground state. This issue has seen considerable debate in the last six years.[1]

The EPR spectrum of C$_{60}^{3-}$, prepared from off-the-shelf C$_{60}$, is shown in Figure 3c. Sodium/crown ether was used to reduce C$_{60}$ to the (-3) level because in the solvent system used, Co-(Cp*)$_2$ is not a strong enough reducing agent. The reduction level was checked by near-IR spectroscopy (λ_{max} = 1370, 995, 865, 775 nm) before and after the EPR experiments were performed. Consistent with earlier studies,[1] the major, broad feature in Figure 3c (g = 2.0022, ΔH_{pp} = 21 G) is assigned to the doublet ground state of C$_{60}^{3-}$. The narrow line width "spike" has parameters similar to those of C$_{120}$O^{3-} and similar to those expected for C$_{120}$O.$^{5-}$ Accordingly, it is assigned to the doublet state of an n = odd C$_{120}$O^{n-} impurity. The value of n will depend on whether the sample is slightly under- or overreduced.

Purified C$_{60}^{n-}$. Confirmation that some of the EPR signals previously assigned to C$_{60}^{n-}$ arise instead from impurities would be to demonstrate their absence in fulleride samples prepared from highly purified C$_{60}$. Accordingly, we collected a middle cut of baseline-pure C$_{60}$ directly from the HPLC under an argon atmosphere and reduced it within minutes. The resulting EPR spectra for the C$_{60}^-$, C$_{60}^{2-}$, and C$_{60}^{3-}$ ions are shown in Figure 4.

Comparisons of Figures 3 and 4 show that the extraneous signals in the purified sample have been reduced to undetectable levels for C$_{60}^-$ and C$_{60}^{3-}$ ions and essentially undetectable levels for C$_{60}^{2-}$. However, EPR spectroscopy is a very sensitive technique, and for the EPR-silent C$_{60}^{2-}$ ion, we can usually optimize conditions (ca. 100–150 K) to detect a tiny spike with signal characteristics indistinguishable from those of C$_{120}$O^{3-}.
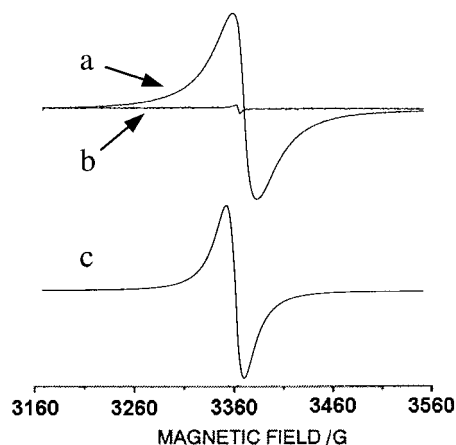
(26) This comment applies strictly to the fullerene triplet-type signals. We leave open the possibility that other $S = \frac{1}{2}$ impurities could contribute to the central narrow line.

Figure 4. EPR spectra of progressively reduced, freshly HPLC-purified C$_{60}$: (a) [Co(Cp*)$_2^+$][C$_{60}^-$], (b) [Co(Cp*)$_2^+$]$_2$[C$_{60}^{2-}$], and (c) [Na(dibenzo-18-crown-6)$^+$]$_3$[C$_{60}^{3-}$]. Spectra a and b were taken at identical concentration and instrument gain. Conditions were the same as in Figure 1.

It is difficult to determine whether the trace of C$_{120}$O in such C$_{60}$ samples arises from an imperfect HPLC separation or from subsequent reaction of C$_{60}$ with traces of oxygen on the glassware prior to reduction, but we suspect the latter. In concentrated form, C$_{60}$ is much more sensitive to oxygen than previously believed. Even with inert atmosphere glovebox handling and storage, C$_{120}$O contamination increases with time. Traces of oxygen on the surface of glassware are apparently all that is necessary to form some C$_{60}$O, which presumably reacts with C$_{60}$ to form C$_{120}$O during concentration and workup after HPLC. The spectra of Figure 4 can be taken as the most authentic spectra of C$_{60}^-$, C$_{60}^{2-}$, and C$_{60}^{3-}$ achieved to date. They confirm that the doublet states of C$_{60}^-$ and C$_{60}^{3-}$ give rise to broad EPR signals (with temperature-dependent line widths) and that C$_{60}^{2-}$ is EPR-silent. The temperature range in which the latter statement holds true is discussed next.

Does C$_{60}^{2-}$ Have a Thermally Accessible Triplet State? Eaton and co-workers[13] have proposed that C$_{60}^{2-}$ has a thermally accessible triplet state with a singlet–triplet gap of ca. 600 cm^{-1}. The data on which this proposal is based are reproduced in Figure 5. As the temperature is raised from 109 to 257 K, a broad signal grows in around the base of the sharp central line. Deconvolution leads to the dashed line signal, having a line width of ca. 30 G. Although this Lorentzian-shaped signal is not typical for a triplet, it was suggested that lifetime phenomena might lead to its broadened shape.

When we repeated this experiment with purified C$_{60}$ under strictly anaerobic conditions, *no new signal grew in with increasing temperature*. Only signals due to remnant C$_{120}$O were seen. Typical data for [PPN]$_2$[C$_{60}$] in DMSO are shown in Figure 6 but the same observation was made with high-purity [Co(Cp)$_2$]$_2$[C$_{60}$] in 1:2:4 *o*-dichlorobenzene/dimethyl sulfoxide/tetrahydrofuran up to 225 K. This suggests that the thermal in-growth observations of Eaton et al. arise neither from C$_{60}^{2-}$ nor from C$_{120}$O^{n-}. The unlikely possibility that the energy of the triplet state was critically sensitive to the presence of [Bu$_4$N]-[PF$_6$] electrolyte, present in Eaton's DMSO solution sample, was also investigated. At three different electrolyte concentrations of tetrabutylammonium hexafluorophosphate (between 10^{-3} and 1.0 M), we saw no in-growth of a 30 G signal with increasing temperature. The possibility that the absence of an in-growing signal in our samples was due to power setting
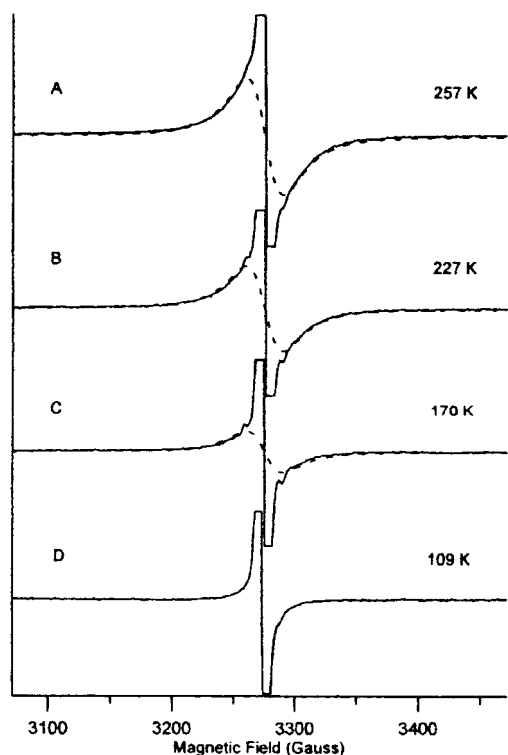
Figure 5. EPR spectra (9.17 GHz, 50 mW microwave power, 4 G modulation) ascribed to C_{60}^{2-} from Figure 5 of ref 13 (copyright American Chemical Society). The dashed line represents a deconvolution of the ~30 G broad signal believed to grow in with increasing temperature.

differences (the spectra of ref 13 were taken at 50 mW power whereas those in Figure 6 were run at 0.63 mW) was ruled out by the observation that the signals of Figure 6 are unchanged at power settings up to 63 mW.

We did, however, observe something like Eaton's results in one aged sample of C_{60}^{2-}. This is shown in Figure 7a. Comparing these data with those of Eaton in Figure 5 illustrates how a broad (ca. 30 G line width) signal can be more cleanly observed when the impurity level giving rise to the central spike is lowered.

What is the origin of the broad signal in Figure 7a? We assign it to C_{60}^- on the basis of the data in Figure 7b where the EPR signature of a purposefully prepared sample of C_{60}^- ion (from off-the-shelf C_{60} contaminated with $C_{120}O$) is reproduced under conditions of cation, solvent, electrolyte, and spectrometer settings similar to those in Figure 7a. The line width of C_{60}^- (the broad signal in Figure 7b) increases from 27 to 37 G between 125 and 280 K, consistent with previous observations.[27] The line width of the broad signal in Figure 7a is similar except for small differences in the peak-to-peak separations. These differences are ascribed to the familiar phenomenon of peak distortion from closely overlapping maxima, i.e., the peak positions of the broad signal in Figure 7 spectrum a versus spectrum b differ because of differing relative intensities of the adjacent central spike, arising from differing amounts of $C_{120}O$ impurity.

The assignment to C_{60}^- makes good chemical sense since slight underreduction can easily occur at the initial production stage of C_{60}^{2-} or arise subsequently via traces of air getting

(27) Schell-Sorokin, A. J.; Mehran, F.; Eaton, G. R.; Eaton, S. S.; Viehbeck, A.; O'Toole, T. R.; Brown, C. A. *Chem. Phys. Lett.* **1992**, *195*, 225−231.
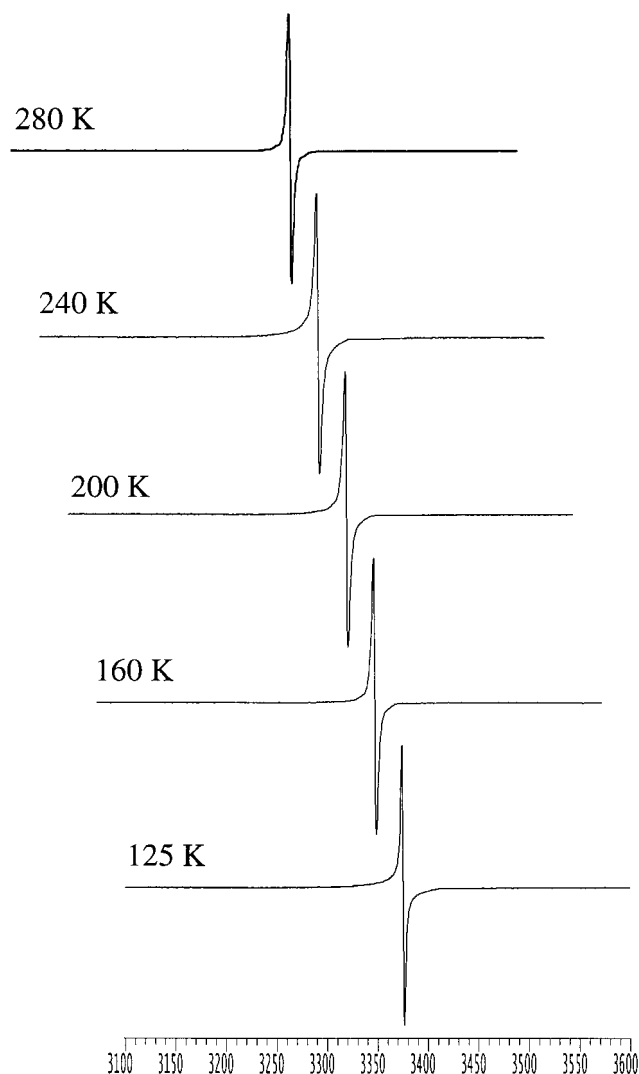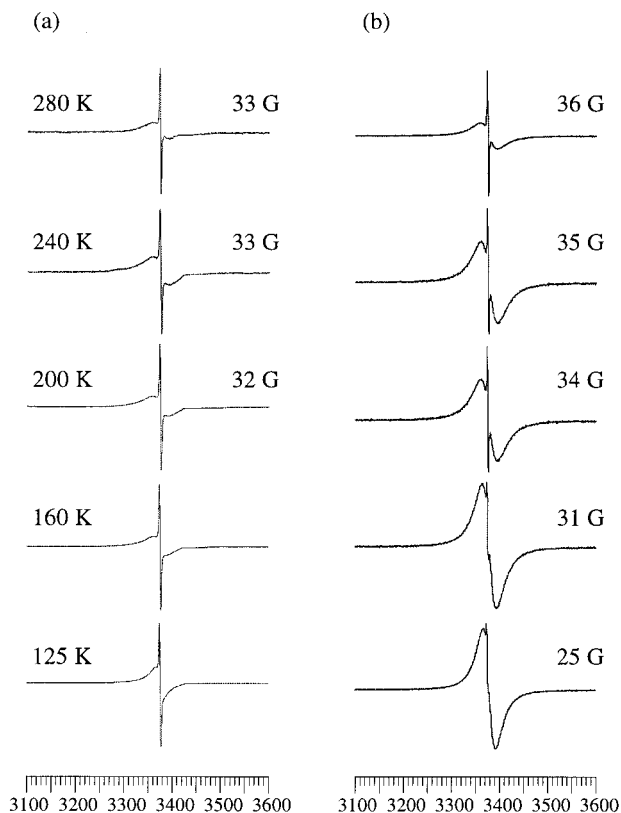
Figure 6. Offset stacked EPR spectra (9.45 GHz, 0.63 mW microwave power, 4 G modulation) of $[PPN^+]_2[C_{60}^{2-}]$ in DMSO. All signals are ascribed to anions of residual $C_{120}O$ impurity despite the use of HPLC-purified C_{60}. This particular sample contained more $C_{120}O$ than that used for Figure 4b.

into the sample. Unfortunately, other spectroscopies are not as sensitive as EPR and are not useful to probe small excursions either side of the precise level of reduction. From our experience, a few percent of one fulleride in the presence of another is impossible to detect by near-IR spectroscopy, for example. The samples used to collect the data for Figures 6 and 7a were indistinguishable by near-IR and had spectra identical to those published for C_{60}^{2-} in DMSO solution.[22]

Eaton et al. considered the possibility that the 30 G signal was due to C_{60}^- but ruled it out on the basis of line width considerations and the appearance of thermal activation. However, as indicated above, signal line widths are readily distorted by proximity to other peaks. Together with any imperfections in the deconvolution process represented by the dotted line in Figure 5, this may have led to the accidental appearance of an approximately constant 30 G line width signal. If C_{60}^- is the source of the signal, the illusion of thermal activation could have arisen from two factors. First, signal intensity would be coming out of the central narrow line and going into the broad signal as the temperature increases because the line width of the C_{60}^- is increasing from ca. 25 to 35 G during this

(a)   (b)

Figure 7. (a) EPR spectra of an aged sample of $[PPN^+]_2[C_{60}^{2-}]$ in DMSO made with low $C_{120}O$-containing C_{60}. Partial oxidation to C_{60}^- is presumed. Conditions were the same as in Figure 6. (b) EPR spectra of $[PPN^+][C_{60}^-]$ made with high $C_{120}O$-containing C_{60}. ΔH_{pp} line widths for the broad signals (± 1 G) are indicated for each spectrum where they are measurable without deconvolution (i.e., not overlapped with the narrow central signal).

temperature rise. Second, we have observed that, unlike normal EPR signals, the intensity of the signal from $C_{120}O^{3-}$ *increases* with increasing temperature. The instrument gain had to be *decreased* as the temperature was raised to keep the spike on scale. The explanation for this observation may lie in changing signal saturation and/or a Nernstian response of the $C_{120}O^{3-/4-}$ ratio to changing temperature. Whatever the explanation for Eaton's signal, the important observation is that we cannot observe it when highly purified C_{60} is fully reduced to C_{60}^{2-}.

The preliminary data of Jones, Kadish, and co-workers,[14] also interpreted in terms of a thermally accessible triplet state, were gathered at $167-295$ K in fluid rather than frozen solution. Given that triplets from $C_{120}O^{n-}$ anions disappear in fluid solution, it is difficult to know what species might have given rise to the appearance of thermal activation in this work. The observed signals are quite narrow ($\Delta H_{pp} = 2-4$ G) so they would seriously overlap with those of the central line(s) from $C_{120}O^{n-}$. The present work leaves little likelihood that they arose from C_{60}^{2-}. Impurities other than $C_{120}O$ are the likely sources. Possibly these arose from reaction of C_{60}^{2-} with the solvent or impurities in the solvent. The use of impure solvents has been reported to give greater concentrations of spurious signals in fulleride EPR studies,[28] and commercial sources of C_{60} are known to contain a variety of impurities.[29]

Does C_{60}^{3-} Have an Observable Quartet State? The EPR spectrum of C_{60}^{3-} published by Shohoji, Takui, and co-

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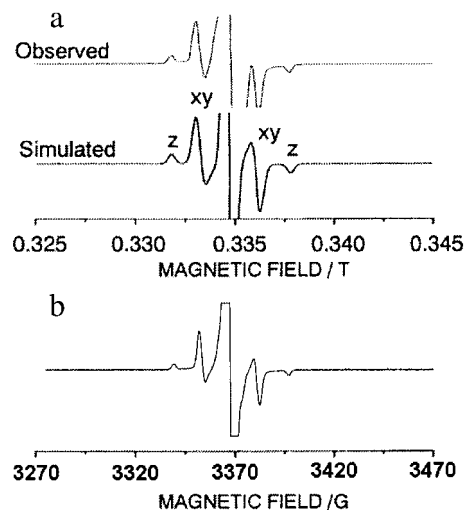(29) Rausch, H.; Braun, T. *Anal. Chem.* **1997**, *69*, 2312–2316.

Figure 8. (a) Purported observed and simulated EPR spectra of C_{60}^{3-} reproduced from ref 15 (copyright American Chemical Society). (b) EPR spectrum of $C_{120}O^{3-/4-}$. Conditions were the same as in Figure 1.

workers[15] is reproduced in Figure 8a. Comparison to Figure 3b,c suggests that their sample was reduced only to about the C_{60}^{2-} level. At the temperature of their experiment (90 K), the presence of C_{60}^{3-} should have given rise to an intense, broad signal of line width ca. 15 G.[9,22,30] The signals assigned to an $S = 3/2$ quartet state (labeled z and xy) are indistinguishable from the triplet features of $C_{120}O^{4-}$ when it is a contaminant in C_{60}^{2-} (Figure 3b) or in bulk form (Figure 1d). This is illustrated in Figure 8 where the data of Takui et al. are compared directly with those from a $C_{120}O$ sample reduced to the (-4) level in DMSO. We have verified that the signal parameters of $C_{120}O^{4-}$ are not condition-dependent. In 2-MeTHF/diglyme, the solvent mixture used by Takui et al., the parameters differ insignificantly (<2 G) from those in DMSO. Only the relative prominence of the powder triplet peaks varies with conditions. This is an expected result since different degrees of aggregation from solute extrusion will occur upon freezing of different solvents.

The implications for the proposed quartet state of C_{60}^{3-} are clear. The EPR peaks used to identify it arise not from C_{60} but from $C_{120}O$ impurity. Two-dimensional electron spin transient nutation (2D-ESTN) spectroscopic investigation and theoretical analysis were used to corroborate the existence of a quartet state for C_{60}^{3-}, but alternative interpretations must now be considered. One possibility for the observation of a quartet spin state system in their sample via 2D-ESTN spectroscopy is an $S = 3/2$ spin state for the $C_{120}O^{3-}$ ion. However, as indicated earlier, fullerides do not favor high-spin states.

Does the EPR Signal in C_{60} Arise from $C_{60}^{\bullet+}$? Solid samples of C_{60} are widely reported to show a low-abundance EPR signal.[2,31,32] The spectrum shown in Figure 9a for a commercially acquired sample is typical. It has spin-doublet form with $g = 2.0027 \pm 0.0003$ and a line width of 1.5 ± 0.3 G, which varies little with temperature. These parameters are qualitatively similar to those of mono- or difunctionalized fullerene radicals such as $RC_{60}^{\bullet}$ or $R_2C_{60}^{\bullet-}$.[1,33] The signal is

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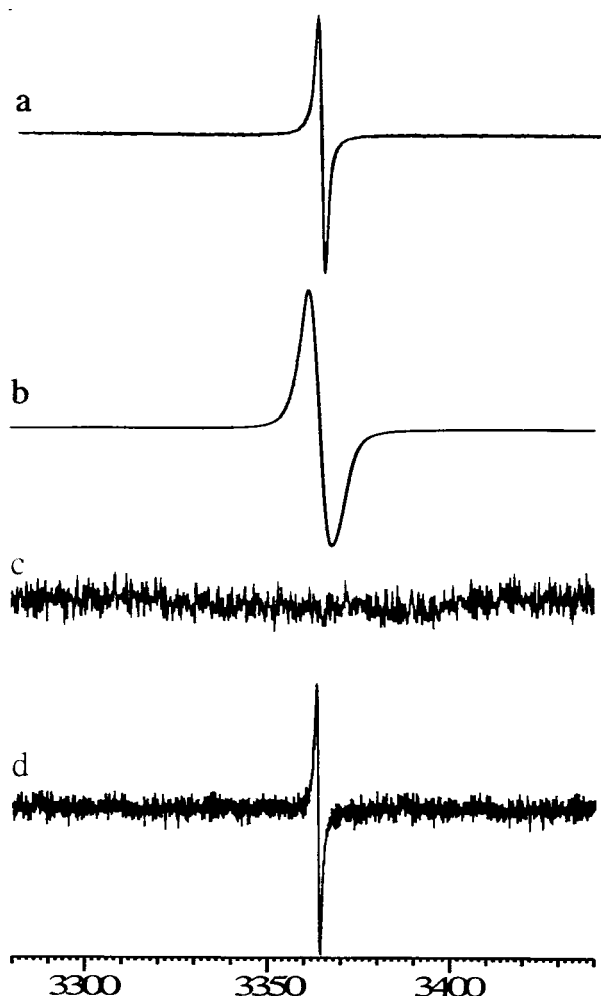
Figure 9. EPR spectra of (a) off-the-shelf C_{60} solid, (b) $[C_{60}^+][CB_{11}H_6Cl_6^-]$ as a solid, (c) purified C_{60} solid, and (d) purified C_{60} solid after exposure to O_2 in the dark for 25 days. All spectra were taken at 100 K at 6.3 mW power with 2 G modulation [except for spectrum b, at 5 G modulation].

not typical of the radical states of unfunctionalized fulleride anions, C_{60}^{n-}, where g values are lower and line widths are much larger, varying significantly with temperature. In addition to this signal from a spin doublet, weak signals due to a spin triplet have also been reported.[2,32]

Many researchers have assigned the major, spin-doublet signal to $C_{60}^{\bullet+}$.[5,6,34] This hypothesis has remained plausible as long as $C_{60}^{\bullet+}$ has remained poorly characterized. Over the years, EPR signals have been ascribed to $C_{60}^{\bullet+}$ under a variety of conditions with g values in the range 2.0016−2.0033 and line widths in the range 0.75−12 G.[1] Now that a method has been worked out for synthesizing bulk samples of $C_{60}^{\bullet+}$ as a carborane salt,[8] definitive EPR spectra can be obtained and intentional doping into purified C_{60} can be performed to test the validity of the hypothesis.

Accordingly, EPR spectra of the $C_{60}^{\bullet+}$ ion were acquired in both solution and solid state under a variety of conditions. The spectrum of solid $[C_{60}][CB_{11}H_6Cl_6]$ shown in Figure 9b is typical. At 100 K, the g value is 2.0026 ± 0.0002 and the peak-to-peak line width is 6.8 ± 0.2 G. The line width decreases slightly to 6.1 G when the temperature is increased to 300 K. A doped solid sample of 1% $[C_{60}][CB_{11}H_6Cl_6]$ in purified C_{60}
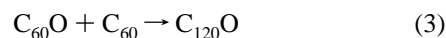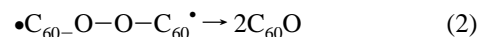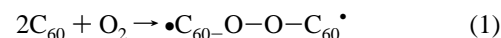
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behaves in a very similar manner except that the line widths are ca. 15% larger. In frozen *o*-dichlorobenzene solution at 100 K, the g value is 2.0027 ± 0.0002 and the peak-to-peak line width is 6.5 ± 0.2 G. The line width in frozen solution increases to 8.0 G as the temperature is lowered to 4 K. The small temperature dependence of the line width for $C_{60}^{\bullet+}$ contrasts markedly with the large dependence seen with the $C_{60}^{\bullet-}$ ion. The effects of the $(h_u)^{hole}$ configuration are obviously quite different from those of the $(t_{1u})^1$ configuration.

These measurements suggest that the line width of the $C_{60}^{\bullet+}$ signal is too large for legitimate assignment to the signal in solid C_{60}. The signal in bulk C_{60} consistently shows a line width of 1.2−1.5 G, whereas we have been unable to find conditions where the signal from $C_{60}^{\bullet+}$ becomes this narrow. We conclude that the signal in solid C_{60} does *not* arise from $C_{60}^{\bullet+}$.

To understand its origin better, we isolated an HPLC-pure sample of C_{60} under strictly anaerobic conditions. As shown in Figure 9c, it was completely EPR-silent. This is the expected and long-desired result for a diamagnetic closed-shell molecule. If kept in a flame-sealed glass tube under vacuum, no EPR signal develops even when the tube is exposed to laboratory light for weeks.

We then exposed the sample to dry oxygen at 1 atm pressure in the dark. Within 2 days, the familiar signal had appeared ($g = 2.0026$, $\Delta H_{pp} = 1.3 \pm 0.2$ G at 100 K) and it continued to accumulate over several weeks (see Figure 9d). It has previously been shown that the signal in bulk C_{60} increases quickly upon exposure of samples to air and light.[2] What is new in the present work is that the signal appears apparently without the assistance of light. It shows that C_{60} is much more sensitive to oxygen than previously appreciated. Triplet C_{60} is known to react with singlet oxygen.[35,36] It now appears that, in the solid state, triplet oxygen reacts with singlet C_{60}. This is quite unexpected.

A working hypothesis for this sensitivity begins with the reaction of oxygen with C_{60} to form a dimeric peroxide of formula $C_{60}-O-O-C_{60}$ (eq 1).

$$2C_{60} + O_2 \rightarrow ^{\bullet}C_{60}-O-O-C_{60}^{\bullet} \tag{1}$$

$$^{\bullet}C_{60}-O-O-C_{60}^{\bullet} \rightarrow 2C_{60}O \tag{2}$$

$$C_{60}O + C_{60} \rightarrow C_{120}O \tag{3}$$

Solid-state C_{60} would be particularly prone to this sequence of dimerization reactions because the lattice holds the C_{60} moieties in close proximity. The dimeric peroxide could decay by breaking apart homolytically, producing the well-known $C_{60}O$ epoxide (eq 2). The formation of $C_{120}O$ via reaction of the epoxide with free C_{60} is a well-known reaction.[19] After the exposure of HPLC-purified C_{60} to O_2 was terminated by placing the sample under vacuum, the EPR intensity continuously decreased to near baseline over 5 months. An HPLC analysis of the sample revealed $C_{120}O$ as a single major impurity in the C_{60} sample. By contrast, a continuously air-exposed C_{60} sample also showed the presence of $C_{60}O$. This observation supports the intermediacy of $C_{60}O$ in eqs 2 and 3.

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This mechanism readily rationalizes the facile formation of C$_{120}$O as well as the formation of an EPR-active species. The proposed peroxide intermediate is a diradical. It is reasonable to expect that spin coupling through the peroxide bridge will be very weak because, based on the nature of RC$_{60}$• radicals,[33] the spins are not localized at the C−O bonds. Thus, the EPR signal of the peroxide might be very similar to those from monomeric RC$_{60}$• radicals. As mentioned earlier, the g value and line width of the signal in C$_{60}$ is indeed very similar to these types of species. Alternatively, the EPR signal may arise from radical decomposition products of the peroxide. Of possible significance to this mechanism are weak signals of triplet character that have been observed in some samples of air-exposed C$_{60}$.[2,32] Further studies are needed to validate the mechanism, but it fits the data much better than the prevailing C$_{60}$•+ proposal.

Conclusions

After a decade of healthy questioning, the spectra of Figure 4 can now be taken as the true EPR signatures of the C$_{60}$−, C$_{60}^{2-}$, and C$_{60}^{3-}$ ions. With C$_{120}$O removed, their relatively uncomplicated form is now revealed. We find no EPR evidence for a triplet state of the C$_{60}^{2-}$ ion or a quartet state of the C$_{60}^{3-}$ ion. The C$_{60}^{2-}$ ion is EPR-silent. Given this result, the conclusion that the "hole-equivalent" C$_{60}^{4-}$ ion is also EPR-silent is probably correct.[37] Low-abundance peaks observed in its spectrum probably arise from C$_{120}$O^{n-} ions, their decomposition products, or reaction with solvent (or solvent impurities).

The photochemically enhanced degradation of C$_{60}$ at room temperature[31,38] and thermal oxidative degradation at elevated temperatures[39,40] has been known for a long time, but the present work shows that C$_{60}$ is even more aerobically unstable than previously believed. Even in the dark at room temperature, detectable reaction of solid C$_{60}$ with oxygen seems to occur. The formation of C$_{120}$O is the inevitable result of storing samples of C$_{60}$[17] because, in concentrated form, C$_{60}$ appears to react with oxygen with surprising efficiency. Previously gathered data on the properties of C$_{60}$ in the presence of oxygen, interpreted in terms of simple intercalation,[41,42] may need to be reassessed in terms of chemical reactivity.

Indeed, a sobering conclusion from this work is that, with the exception of C$_{60}$ samples freshly prepared by vacuum sublimation, C$_{120}$O has been an unrecognized small but ubiquitous impurity in nearly every physical measurements ever made on C$_{60}$. Interpretations of data involving minor spectroscopic peaks are now suspect and may need checking against data from C$_{120}$O. Theory, ^{13}C NMR spectroscopy, magnetic susceptibility, and near-IR studies still lend some credence to the concept of low-lying excited states in discrete fulleride ions,[1] but we find no EPR evidence to support their existence.

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