The origin of the ‘spike’ in the EPR spectrum of C_{60}^{-}

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The long-debated origin of the narrow line-width signal in the EPR spectrum of C_{60}^{-} is shown to be $C_{120}O^{-}$, arising from unavoidable $C_{120}O$ impurity in air-exposed samples of C_{60}.

A vexing problem in C_{60} chemistry has been the origin of a narrow line-width signal or “spike” superimposed on the broad EPR spectrum of C_{60}^{-} (Fig. 1). In the nine years since it was first observed, no fewer than six different hypotheses have been forwarded to explain its existence, but none has been confirmed. In a recent comprehensive review of the literature on this subject,[1] we concluded that the most likely explanation lies in $C_{120}O$, a recently discovered, inevitable impurity in air-exposed samples of C_{60}.[2] In this communication, we provide data that confirm this hypothesis.

If $C_{120}O$ impurity is the source of the sharp signal, three experiments of proof suggest themselves. (a) The EPR characteristics of pure $C_{120}O^{-}$ should match those reported for the narrow line-width signal. (b) Addition of an authentic sample of $C_{120}O$ to a standard sample of C_{60}^{-} should enhance the sharp signal at precisely the same g value and line width. (c) The preparation of high purity C_{60}, free of detectable $C_{120}O$, should allow a spike-free EPR spectrum of C_{60}^{-} to be obtained.

A sample of $C_{120}O$ was prepared by literature methods[3] and purified by standard HPLC methods.[2] One-electron reduction to $C_{120}O^{-}$ was achieved with <1 equiv. of cobaltocene in *o*-dichlorobenzene. As shown in Fig. 2, the EPR spectrum at 100 K is characterized by a sharp signal at $g = 2.0013$ and $\Delta H_{pp} = 1.42$ G (calibrated against DPPH). These parameters closely match those of the major signal observed when a two-electron electrochemical reduction of $C_{120}O$ is carried out in *o*-dichlorobenzene ($g = 2.0016$, $\Delta H_{pp} = 1.1$ G at 77 K).[4] This suggests that $C_{120}O^{2-}$ may be EPR silent (or weak) under these conditions and that the observed sharp signal results from $C_{120}O^{-}$, present because of the difficulty of carrying out a precise, quantitative two-electron reduction. The temperature dependence of the line width of the $C_{120}O^{-}$ signal is minimal, decreasing to 1.33 G at 225 K. The variation of signal parameters with solvent is also small. For example, in 2-methyltetrahydrofuran at 100 K, $g = 2.0005$ and $\Delta H_{pp} = 2.0$ G. In tetrahydrofuran at 100 K, the values are $g = 1.9988$ and $\Delta H_{pp} = 2.6$ G. The signal characteristics of $C_{120}O^{-}$ are clearly compatible with the ‘spike’ in C_{60}^{-} where, depending on conditions, g values are reported in the range 1.9995–2.0012 and $\Delta H_{pp} = 0.1$–3.5 G.[5]

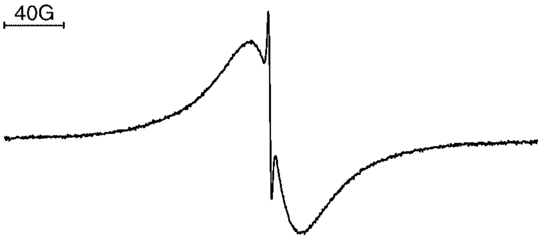

Fig. 1 Typical EPR spectrum of C_{60}^{-} prepared from off-the-shelf C_{60} showing the broad signal (major) and the sharp signal or ‘spike’ (minor). Conditions: $[Co(Cp)_2][C_{60}]$ in tetrahydrofuran at 140 K, microwave power 5.7 mW, modulation 5 G.

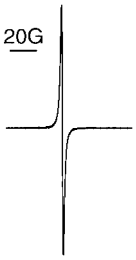

Fig. 2 EPR spectrum of $[Co(Cp)_2][C_{120}O]$ in *o*-dichlorobenzene at 100 K (microwave power 5.7 mW, modulation 1.25 G).

To explore whether this compatibility means identity, small additions of $[Co(Cp)_2^{+}][C_{120}O^{-}]$ were made to solutions of $[Co(Cp)_2^{+}][C_{60}^{-}]$ to ascertain whether the sharp signal increased relative to the broad signal. As shown in Fig. 3, this is exactly what happens. Moreover, the peak positions are *precisely* those of the spike. Experimental error and reproducibility variances are <0.08 G. The data in Fig. 3 provide

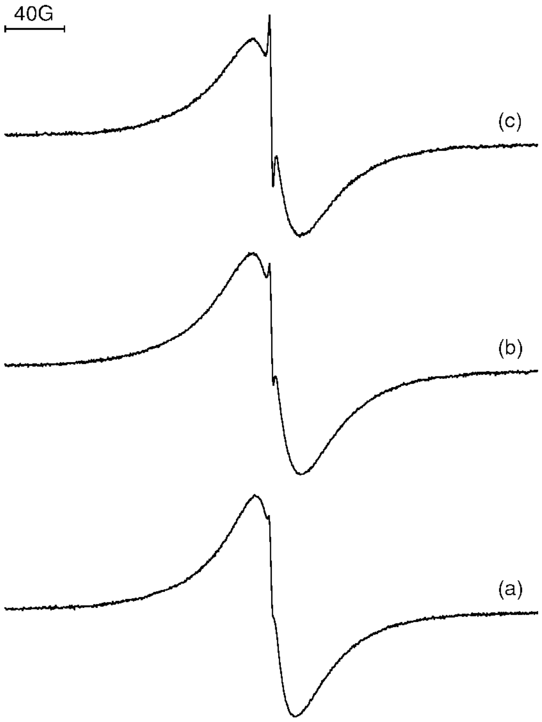

Fig. 3 EPR spectrum of C_{60}^{-}, prepared by cobaltocene reduction of freshly purified C_{60}, (a) and as a function of increasing increments of added $C_{120}O^{-}$ (b and c) (conditions same as Fig. 1).

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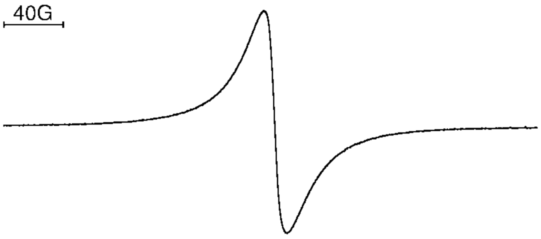

Fig. 4 EPR spectrum of C_{60}^- prepared from twice HPLC-purified C_{60} (conditions same as Fig. 1).

compelling evidence that the spike in C_{60}^- is due to $C_{120}O$ impurity.

Finally, we purified C_{60} by HPLC to try to obtain a spike-free EPR spectrum of C_{60}^-. Purification of C_{60} was carried out using a Cosmosil Buckyprep column with toluene as eluent. Double passage gave C_{60} with essentially undetectable quantities of $C_{120}O$ (monitoring at 330 nm) and a middle cut was collected anaerobically with exclusion of light. As shown in Fig. 4, the EPR spectrum of a cobaltocene-reduced sample of this material gave a spike-free spectrum at 100 K (g = 1.9963, ΔH_{pp} = 16.4 G). Interestingly, however, when we chose measurement conditions which optimized the observation of the sharp signal relative to the broad signal (higher temperatures where the broad signal becomes even broader and the use of the lowest possible microwave powers because the spike saturates more easily than the broad signal), traces of the $C_{120}O^-$ signal could still be detected as shoulders in the inflection region. This is partly a reflection of the extraordinary sensitivity of the EPR technique but it also shows how difficult it is to rid C_{60} entirely of $C_{120}O$. Traces of O_2 convert C_{60} to $C_{120}O$ with extraordinary ease.[2]

In summary, it now appears certain that all air-exposed samples of C_{60} contain $C_{120}O$ and that all EPR work using such samples has been compromised by its presence. It is likely that most (if not all) of the sharp signals observed in the EPR spectra of discrete C_{60}^{n-} fulleride ions (n = 1–4) arise from $C_{120}O^{n-}$ species (n = odd) or decomposition products therefrom. Further studies are in progress to investigate the full extent of the $C_{120}O$ influence in spectra of the more highly charged fulleride anions. There have been a number of reports of sharp signals increasing significantly at the expense of broad signals upon aging of C_{60}^- salts.[1] We do not find this to be the case with the present samples. The solution of $[Co(Cp)_2][C_{60}]$ that gave rise to Fig. 1 was kept in a torch-sealed quartz EPR tube for several weeks. Its spectrum has remained essentially unchanged, even with exposure to laboratory light. It is likely that release of oxygen from the walls of containers or aerobic leakage are responsible for reports to the contrary. C_{60}^- would be preferentially oxidized (to EPR silent C_{60}) giving the *appearance* of an increase in $C_{120}O^-$ concentration. (The overlay of the two signals, and their very different line-widths, has typically precluded reliable measurements of absolute intensities). In the extreme (*i.e.* room temperature, low reduction levels, low signal-to-noise ratios) the observation of *only* a sharp signal[6,7] can be explained. Even the metal-intercalated fulleride materials such as A_3C_{60} (A = Na, K, *etc.*) are reported to have the sharp signal of an 'impurity phase' superimposed on the broad signal arising from conduction electrons.[8] Perhaps it also arises from $C_{120}O^{n-}$ defects (n = 5 or 7). Indeed, a number of complex explanations for multiple signals in fullerides[9] may have more straightforward interpretations.

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