# Elevated Temperature Gel Permeation Chromatography and Electrochemical Behaviour of the $C_{84}$ Fullerene

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The $C_{84}$ fullerene was isolated by high temperature gel permeation chromatography; cyclic voltammetry reveals five reversible reduction waves but no oxidation waves.

Higher fullerenes, the large fullerenes which can be extracted from fullerite soot with toluene ($C_{76}$–$C_{90+}$),[1] have been studied in much less detail than the more plentiful $C_{60}$ and $C_{70}$ fullerenes, largely owing to the miniscule quantities present in fullerite soot and the difficulty in isolating and purifying these compounds. We are interested in the relationship between the rich structural chemistry of the fullerenes and the chemical properties of these materials. NMR evidence has shown that the higher fullerenes $C_{76}$,[2] $C_{78}$,[3,4] $C_{82}$[4] and $C_{84}$[4] exist in a number of isomeric forms. Six reversible reductions,[5,6] but no reversible oxidations[7] have been reported in the cyclic voltammetry of $C_{60}$ and $C_{70}$. Reversible oxidation waves have been observed in the cyclic voltammetry of only one of the fullerenes, $C_{76}$.[8] We report the isolation and the electrochemical behaviour of $C_{84}$.

Higher fullerenes have been isolated by HPLC,[1,2,9–11] usually requiring multiple (as many as 30) passes through the column.[11] We have successfully applied gel permeation chromatography[12] to the purification of $C_{60}$ and $C_{70}$, and we have noted partial resolution of the higher fullerenes on the same columns.[13] In contrast to the behaviour of fullerenes on π-acidic Pirkle columns,[14] we observe very little change in the retention times for the fullerenes between 25 and 95 °C.[13] However, the bands become substantially more narrow with increasing temperature, leading to a more useful separation. The high temperature also decreases the chance that injections of saturated solutions will precipitate in the column. We have taken advantage of these phenomena in the purification of $C_{84}$.

A mixture enriched in higher fullerenes, containing residual $C_{60}$ and $C_{70}$, was obtained by collection of the tail of the $C_{70}$ band from several $C_{60}$–$C_{70}$ purification runs as described earlier.[13] This material was concentrated to near saturation and passed through a heated bank (95 °C) of four Waters Ultrastyragel (500 Å) columns using 250–500 μl injections with toluene as mobile phase. Collection of the $C_{84}$ band at 57.1 min, which followed a $C_{76}$–$C_{78}$ band at 55.1 min, a $C_{70}$ band at 53.0 min and a $C_{60}$ band at 49.6 min (Fig. 1), produced a deep olive-green[1] solution of $C_{84}$. This sample was concentrated and further purified by two additional passes through the column bank. High-resolution reversed phase HPLC of this sample showed a single near-Gaussian band (Fig. 1, inset). The UV–VIS spectrum of this sample closely matched the UV–VIS spectral data reported previously.[11]

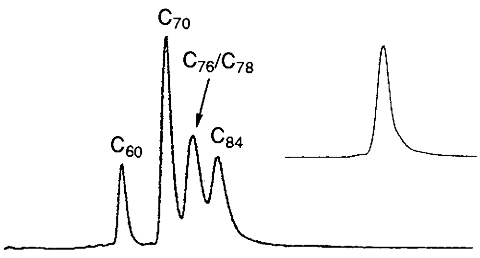

**Fig. 1** GPC of higher fullerene mixture. Conditions: four 7.8 mm × 30 cm Waters 500 Å Ultrastyragel GPC columns, toluene mobile phase (1 ml $min^{-1}$), 95 °C, UV detection at 500 nm. Inset: $C_{18}$ HPLC chromatogram of $C_{84}$, Waters Nova-pak $C_{18}$ 8 mm × 10 mm RCM column, 60% propan-2-ol, 40% toluene mobile phase (1 ml $min^{-1}$), UV–VIS detection at 330 nm.

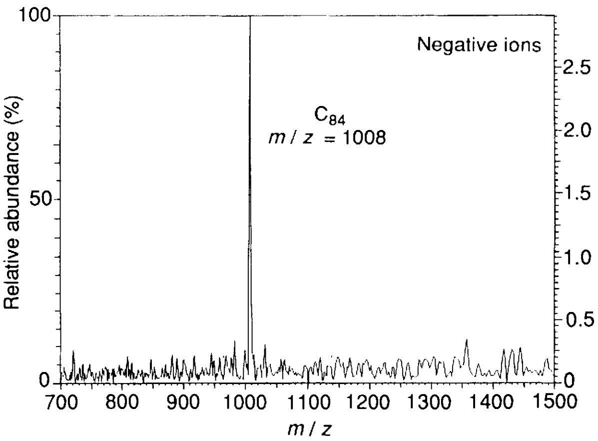

**Fig. 2** Negative ion laser desorption FT mass spectrum of $C_{84}$

**Table 1** Redox potentials[a] of $C_{84}$

| | $E$(PhCN)[b]/mV | $E$(ODCB)[c]/mV |
|---|---|---|
| Rest Potential | +122 | +92 |
| $C_{84}^{0,1-}$ | −157 | −309 |
| $C_{84}^{1-,2-}$ | −479 | −600 |
| $C_{84}^{2-,3-}$ | −809 | −910 |
| $C_{84}^{3-,4-}$ | −1110 | −1265 |
| | | −1520[d] |
| $Fc^{+/0}$[e] | +468 | +690[f] |

[a] All redox potentials are taken as the average of the anodic and cathodic peak potentials and are reported *vs.* Ag wire pseudoreference. $C_{84}$ concentrations were at or near saturation, estimated to be ≤0.5 mg $ml^{-1}$. [b] 0.1 mol $l^{-1}$ $Et_4NPF_6$ electrolyte; scan rate = 10 mV $s^{-1}$; 3 mm glassy carbon disk as the working electrode. [c] 0.1 mol $l^{-1}$ $Bu_4NPF_6$ electrolyte; scan rate = 20 mV $s^{-1}$, 1 mm Pt disk as the working electrode. [d] Nature of this process is unknown (see text). [e] Fc = ferrocene. [f] Measurement complicated by adsorption and uncompensated resistance effects in this electrolyte. Reported value is ±40 mV.

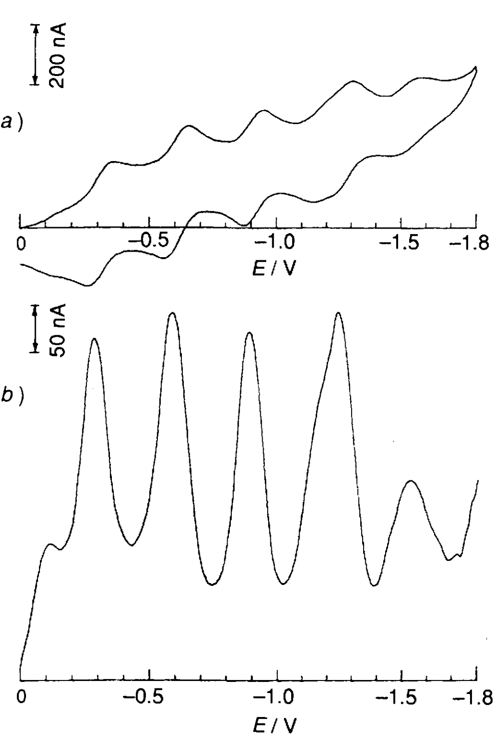

**Fig. 3** (*a*) Cyclic voltammogram of $C_{84}$ in ODCB with 0.1 mol $l^{-1}$ $Bu_4NPF_6$ as supporting electrolyte. The working electrode was a 1 mm diameter Pt disk and the counter electrode was a coiled Pt wire. An Ag wire functioned as a quasireference electrode. Scan rate 20 mV $s^{-1}$. (*b*) Differential pulse voltammogram: pulse amplitude = 50 mV; pulse width = 166 ms; period = 1 s; scan rate = 4 mV $s^{-1}$.

We have confirmed the identity and purity of the $C_{84}$ sample by Fourier transform mass spectrometry (FT–MS). The negative ion spectrum (Fig. 2) shows a single peak corresponding to $C_{84}$. The positive ion spectrum (not shown) displays a $C_{84}$ peak, accompanied by $C_{82}$ and $C_{80}$ fragments resulting from the loss of $C_2$ units, a pattern that is common to all fullerenes. Scans over wide mass ranges did not show significant quantities of any other species.

The electrochemistry of $C_{84}$ was successfully examined in both benzonitrile and *o*-dichlorobenzene (ODCB); results in the two solvents are summarized in Table 1. Although the solubility of $C_{84}$ in PhCN and ODCB is quite low, five couples can be clearly observed at potentials more negative than the rest potential. The first three of these are particularly well behaved, exhibiting differences in peak potentials $(E_{pa} - E_{pc})$ of 60–80 mV and ratios of anodic to cathodic peak current $(i_{pa}/i_{pc})$ approaching unity. Hence, these couples most likely represent chemically and electrochemically reversible one-electron processes that can be attributed to the formation of $C_{84}^{-}$, $C_{84}^{2-}$ and $C_{84}^{3-}$, respectively, by analogy with the well established electrochemistry of other fullerenes.[5,7]

The fourth cathodic wave, as well as its anodic partner, is substantially broadened and may contain two components. Interestingly, similar behaviour is seen in the published voltammogram of $C_{76}$.[8] In the present case, the existence of two overlapping processes is confirmed by differential pulse voltammetry [DPV, Fig. 3(*b*)], which clearly reveals a shoulder preceding the major peak. The DPV peak current is virtually identical to that of the first three reductions, suggesting the formation of $C_{84}^{4-}$. Subsequent voltammetric experiments have shown that the magnitude of the smaller couple varies from sample to sample and is somewhat dependent on the working electrode material. NMR results from Kikuchi[4] and Diederich[1,9] indicate the presence of several components, presumably isomers, in samples of chromatographically purified $C_{84}$. It is possible that the overlapping waves are caused by slightly different electrochemistry of two $C_{84}$ isomers. Our manually collected chromatographic fractions may contain slightly different isomeric distributions in different batches.

The fifth reduction is characterized by significantly smaller peak currents (in both CV and DPV modes) and a slightly larger (90 mV) peak-to-peak separation in the CV. The nature of this process is currently under investigation.

In view of the recently reported one-electron oxidation of $C_{76}$ at very low potential, the oxidative electrochemistry of $C_{84}$ is also of interest. Theoretical calculations suggest that the two isomers of $C_{84}$ found in fullerite soot[15,16] possess $D_2$ and $D_{2d}$ symmetries.[15–18] Both isomers have 28 hexagons each with four adjacent hexagons (neighbour index[15] of four), and four hexagons with five adjacent hexagons (neighbour index of five). The hexagons in $C_{60}$ have neighbour indices of three.

Since chiral $C_{76}$ has no structural subunits beyond those present in $C_{84}$ or $C_{60}$, it is surprising that $C_{76}$ displays oxidation waves below +1.0 V (*vs.* Ag/AgCl) while $C_{84}$ does not. No $C_{84}$ oxidation processes are observable within the accessible potential window for either PhCN or ODCB.† The differences between such closely related compounds highlight the complexity and subtleties of fullerene electrochemistry.

We thank the National Science Foundation (EPSCoR grant EHR-91-08764), the US Department of Energy (DE-FG05-85ER13432), the Center for Applied Energy Research, and the University of Kentucky (Research and Graduate Studies) for financial assistance; the University of Kentucky Research Instrumentation Bond Program (P-053-8E030) for equipment; Mr Kenneth Langley (Waters Chromatography Division of Millipore Corp.) for assistance in configuration of the chromatographic equipment; Drs Robert Hettich, Robert Compton and Changming Jin (Oak Ridge National Laboratory) for FT mass spectra; and Dr James Wakefield, Mr John Davis and Mr Andre Golden for the extraction of fullerite soot and the initial separation of higher fullerenes.

*Received, 10th July 1992; Com. 2/03669J*

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† A small anodic wave was observed at *ca.* +1.4 V *vs.* Ag in PhCN, only slightly less positive than the value[19] reported for $C_{60}$. However, we were unable conclusively to assign this peak to $C_{84}$ oxidation. In the event that this process should prove attributable to $C_{84}{}^{+/0}$, the striking difference in the oxidation potentials of $C_{76}$ and $C_{84}$ would still require explanation.