

EVIDENCE FOR ENTRAPMENT OF C₆₀ AND C₇₀

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ABSTRACT

The carbon arc soot from coal produced in a fullerene generator has been exhaustively extracted with toluene and pyridine. Complete extraction of C₆₀ and C₇₀ was not fully achieved with toluene since the residue was shown to contain pockets of C₆₀ and C₇₀ some of which could subsequently be extracted by pyridine as demonstrated by negative ion laser desorption mass spectrometry, infra-red spectrometry and solid state nuclear magnetic resonance spectrometry. Threshold laser power experiments also indicated the presence of fullerenes to m/z 1800. These results clearly indicated the entrapment of C₆₀ by other fullerenes or fullertubes of higher molecular weight. When laser ablation techniques were used odd numbered cluster ions were observed indicating the presence of ruptured or chain substituted fullerenes.

INTRODUCTION

The isolation of stable carbon clusters including C₆₀ and C₇₀ fullerenes from carbon arc soot produced via the vaporisation of graphite in an inert gas atmosphere has recently been reported¹⁻⁶. For example, Diederich et al.⁴ and Ettl et al.⁵ have extracted arc soot with toluene and separated and identified C₇₆, C₇₈, C₈₄ and C₉₄ fullerenes. It is expected that a range of other fullerenes may be present in the soot and little is known about how C₆₀ and C₇₀ are formed and whether any are entrapped in the soot with other fullerenes. In this work we report the use of pyridine to extract the soot residue after toluene extraction. Both pyridine soluble and pyridine insoluble fractions have been characterised by FTICR mass spectrometry and FTIR spectrometry and in some cases also by solid state ¹³C NMR spectrometry.

EXPERIMENTAL

Preparation of fractions

The preparation of the fullerene soot from graphite and coal was carried out in a modified fullerene generator as reported elsewhere⁷.

The soot was generated from coal or graphitic rods using 25V and 100A d.c. We observed that holes drilled in the graphite rods increased the yield of soot for a given time and current.

Use of an inner water cooled chamber for the arcing process was designed to limit the penetration of the soot into the main chamber and thence its pumping system. The removal of the inner chamber also facilitated the easy recovery of the soot after each run for quantitative analysis and to limit the 'possible' health hazards that may arise handling this light fluffy material.

The resulting soot (3 g) was divided equally into two portions. One portion was Soxhlet extracted with toluene for 6 h. This yielded 85 mg of fullerene extract after solvent removal. After drying, the soot residue was Soxhlet extracted exhaustively with pyridine for 12 h (under nitrogen to prevent solvent decomposition). A clear brownish yellow solution was obtained. This yielded 65 mg of solid extract after solvent removal. This was dried in a vacuum oven at 80°C for 2 h to remove residual pyridine.

The second portion was Soxhlet extracted with pyridine for 11 h under nitrogen to yield a brownish yellow solution which gave 150 mg solid extract after solvent removal. After drying, the soot residue was Soxhlet extracted with toluene. A faint reddish solution was obtained which yielded a negligible amount (<5 mg) of solid fullerene residue.

Analysis

Details of the laser desorption FTICR mass spectrometry technique have been described previously⁸. Mass spectrometric studies were carried out using the fundamental frequency of a Nd YAG laser (1064 nm) and a Spectrospin CMS-47 Fourier transform ICR mass spectrometer. Careful variation of the laser power was carried out with neutral filters which allowed the determination of the threshold energies for laser desorption of the fullerenes. The laser power was determined using a Scientec power meter. Pressed samples of the soot were ablated in the ICR cell and the ions directly observed.

Fourier transform infra-red spectra (FTIR) were obtained on a Digilabs FTS 80 instrument. The soot was carefully pressed into KBr plates before observation. A sample of the material was mixed with KBr and then pressed in a 13 mm die at 9 t for 5 min.

Solid state nuclear magnetic resonance (n.m.r.) spectra were obtained on a Bruker CXP 100 instrument at 22.5 MHz for ¹³C. Spectra were obtained by single pulse (Bloch decay) techniques using a 4 μs pulse and 5 s recycle time⁹.

RESULTS AND DISCUSSION

The total amount of toluene extract and pyridine extract from the first portion of soot is identical to the total amount of pyridine extract and toluene extract from the second portion of soot. This shows that an equal amount of material can be extracted from the soot with these solvents irrespective of the sequence. Of this total, 57 wt. %

can be first extracted by toluene and a further 43 wt. % can be extracted by pyridine afterwards.

The soot and soot residue after solvent extraction have been examined by FTIR spectroscopy. Adsorptions from C_{60} can clearly be seen in the infra-red spectrum of the raw soot at 527 and 577 cm^{-1} . When the soot is extracted with toluene, the toluene extract contains C_{60} and C_{70} in the ratio of about 10:1 as reported previously by us and others^{1,3,7}. However when the extracted soot was examined by FTIR C_{60} resonances were still found to be present even though the soot had been exhaustively extracted with toluene. This result shows that much of the C_{60} is trapped in the soot in some way, so that it becomes unextractable. Pyridine extracts C_{60} . However after pyridine extraction the soot still contained C_{60} adsorptions showing that even pyridine cannot remove all C_{60} .

The pyridine extracted toluene insoluble material was studied in more detail. Its solid state n.m.r. spectrum showed a large resonance at 143 ppm and smaller resonances between 147 and 133 ppm with a small shoulder at 128 ppm. C_{60} resonates at 143 ppm in the solid state¹⁰ and hence this resonance can be ascribed to C_{60} . The other resonances although not fully resolved may be ascribed to C_{70} ¹⁻³.

Laser desorption studies at low laser powers (2 kW cm^{-1}) were in full agreement with the FTIR and N.M.R. results. Initial FTICR spectra of the residue from toluene extraction indicated the presence of C_{60} and C_{70} and smaller amounts of higher fullerenes on laser desorption. However when the experiment was repeated continually, the amount of C_{60} and C_{70} observed was found to be quite variable. This suggests successive desorption through the surface of the extract indicating that C_{60} and C_{70} were entrapped in various layers.

At higher laser powers (>100 kW cm^{-2}) ablation occurs. Positive ion spectra of the toluene residues indicated the presence of higher fullerenes (Figure 1). The most interesting observation from these experiments was the observation of odd numbered carbon clusters (see Figure 1). Thus some open ruptured fullerenes or fullerenes with odd chain length appendages must be formed. As far as we are aware this is the first reported observation of higher molecular weight odd numbered clusters.

As predicted from the infra-red data, the pyridine extracts were shown to contain both C_{60} and C_{70} by laser ablation. Negative ions were observed at threshold values of 2 kW cm^{-2} indicating the presence of fullerenes up to $m/z \sim 1800$ daltons (C_{150}). Increasing the laser power resulted in the appearance of fullerenes of m/z up to 2400 daltons (C_{200}), but further increase in power caused a loss of intensity in negative ions as reported previously for C_{60}/C_{70} mixtures⁸.

In summary, these results clearly show that during the formation of fullerenes by arcing techniques C_{60} and C_{70} fullerenes are often formed entrapped within other molecules, possibly other fullerenes. On laser ablation these other molecules can react either alone or possibly with C_{60} and C_{70} to form species that have odd numbered molecular weights. These species must be ruptured fullerenes or species containing

odd-numbered side chain lengths. These results are consistent with the hyperfullerene or Russian egg structure recently proposed by Curl and Smalley¹¹ for fullerene soot or an encapsulating tube model. In these structures C_{60} is encapsulated by fullerenes of higher carbon number.

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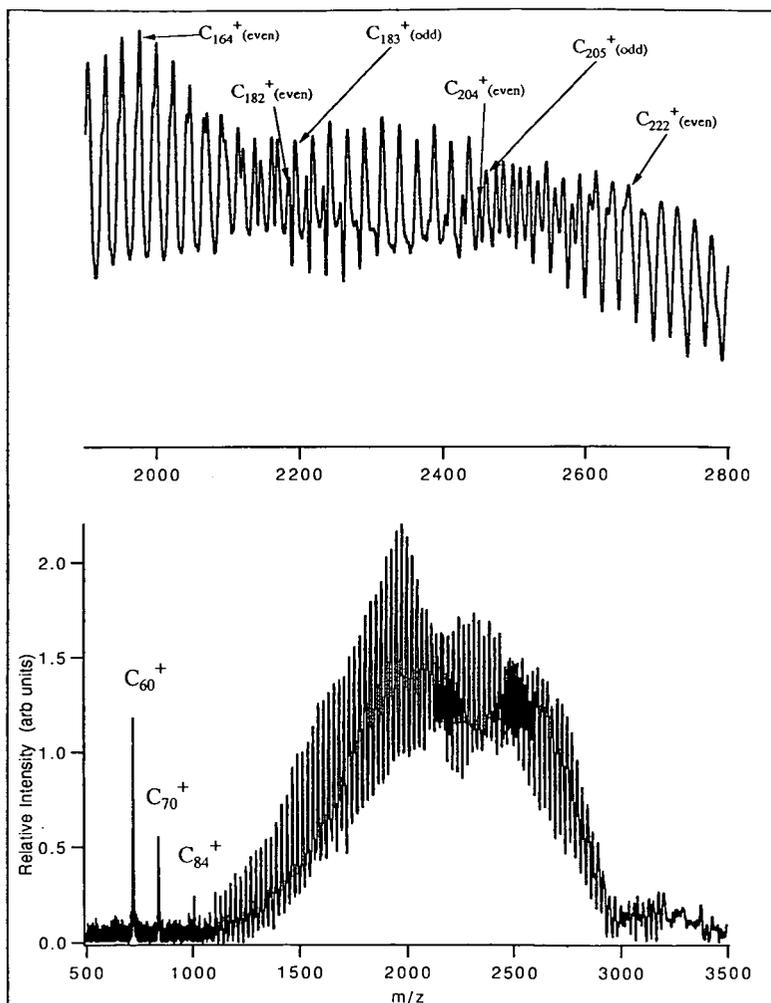


Fig. 1 Mass spectrum of the laser desorption ($\sim 4 \text{ k W cm}^{-2}$) of an insoluble residue