High-Yield Synthesis, Separation, and Mass-Spectrometric Characterization of Fullerenes C_{60} to C_{266}

Deborah Holmes Parker,*,‡ Peter Wurz, Kuntal Chatterjee, Keith R. Lykke, Jerry E. Hunt, Michael J. Pellin, John C. Hemminger,‡ Dieter M. Gruen, and Leon M. Stock

Contribution from the Materials Science/Chemistry Divisions, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439. Received April 29, 1991. Revised Manuscript Received July 9, 1991

Abstract: The preparation of fullerenes C_{60} to C_{266} in very high yield (up to 44% extractable) by a plasma discharge is reported. Almost one-third of the extractable material is composed of giant fullerenes C_{84} to C_{200}. An extraction scheme for isolating selected molecular weight fractions of fullerenes is described. The extractions were characterized by time-of-flight mass spectrometry and Fourier transform mass spectrometry. We find that a Soxhlet extraction with benzene extracts 50% more soluble fullerenes than benzene reflux. Soxhlet extractions with 1,2,3,5-tetramethylbenzene preferentially extract higher molecular weight fullerenes. Hexane appears to limit the amount of higher fullerenes extracted, giving solutions containing C_{60} and C_{70} with only small traces of the higher molecular weight fullerenes. Heptane extraction following the hexane extraction appears to preferentially extract C_{60}, C_{70}, and C_{84}. This solvent scheme is useful in preparing selected molecular weight fractions for subsequent separation by column chromatography.

Introduction

In 1985, a stable carbon molecular ion consisting of 60 carbon atoms was observed in the mass spectrum of laser ablated graphite.[1] In early 1990, Krätschmer and co-workers reported evidence for the presence of C_{60} in a sample of carbon dust prepared from vaporized graphite[2] and were able to isolate macroscopic quantities of C_{60} and C_{70}.[3] Reports of the synthesis[3-7] of gram quantities of C_{60} and C_{70} have generated a flurry of interest in this new class of closed-caged carbon molecules, termed "fullerenes" after Buckminster Fuller, designer of the geodesic dome.[1] The methods used to synthesize fullerenes are of two types, either evaporation of carbon by using resistive heating or an arc discharge source both of which produce carbon soot. Fullerenes are extracted from the soot by using an appropriate solvent. Krätschmer et al.[3] reported the preparation of soot containing about 1% C_{60} from the evaporation of carbon (graphite) electrodes in a helium atmosphere. A paper by Taylor et al.[4] reports an 8% yield of benzene-soluble material obtained by resistive heating of graphite to form carbon smoke from which the soluble fullerenes were isolated. Aije et al.[5] reported a yield of 14% benzene-soluble material from soot collected from the evaporation of a graphite rod using resistive heating. The soluble material is mostly C_{60} and C_{70}, but also contains C_{84}. A slightly different method of fullerene synthesis was reported by Haufler et al.[6] In their method, a "contact arc" was used so that the power was dissipated in an arc rather than in resistive heating of the graphite rod. The power consumption in this method was reported to be up to 4 kW for "burning" a 6-mm ($\sim^1/_4$ in.) graphite rod. This procedure resulted in a yield of $10 \pm 2\%$ toluene-soluble material based on the weight of the soot collected. Hare et al.[7] have reported a very similar procedure and note that, if the rods touch, virtually no carbon vaporizes. They observe a yield of 5–10% trichloromethane-soluble extract depending on the type of graphite used. Wudl and co-workers[8] have developed a simple apparatus using ordinary laboratory glassware which uses a gravity-feed mechanism for contacting the electrodes. This method gives yields of about 4%.

In this paper we report improvements in the method of generation of fullerenes which gives much higher yield at lower power consumption than previously reported. This high yield at lower power may have significant economic implications for the bulk production of fullerenes should a practical use for these interesting molecules be realized. This possibility seems likely in view of the recent reports on the superconductivity of alkali metal-doped C_{60}[9]

and the synthesis of fullerene derivatives.[6,10] We also report the results from several extraction schemes that were designed to improve the separation of various molecular weight fractions which would then facilitate further chromatographic separations. We have characterized the various extraction fractions by using time-of-flight mass spectrometry (TOF-MS) and Fourier transform mass spectrometry (FTMS).

Experimental Section

The Fullerene Generator. Figure 1 presents a scale diagram of the fullerene generator used in this study. This apparatus is similar to those reported previously, but there are a few important improvements which warrant discussion here. The apparatus is contained in a standard 8-in. UHV four-way Conflat cross. The chamber is pumped by a mechanical pump to a base pressure of 10^{-2} Torr. For production of the fullerenes, the chamber is isolated from the pump and then backfilled with helium to a pressure of 200 Torr. The production of fullerenes is carried out within the water-cooled region. This region is lined with stainless steel shims which are cooled by contact with the water-cooled shield. At the end of a run, these shims can be easily removed and the soot scraped from them and collected for further purification. A large ($^1/_2$ in.) graphite rod ("Ultra Purity Spectroscopic Graphite Electrodes", United Carbon Products Co. Inc., Bay City, MI) is attached to a 2-in. linear feedthrough drive. The smaller carbon rod ($^1/_4$ in., National, "Special Spectroscopic Electrodes") is held in a stainless steel holder which can be fed into the chamber by means of a modified Ultra-Torr union. This holder design allows almost the entire length (12 in.) of the rod to be "burned" without breaking vacuum. The holder is attached to the positive lead of the power supply. A ceramic-to-metal insulator electrically isolates the smaller carbon rod from the chamber. The negative lead of the power supply is

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167.

(3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(4) Taylor, R.; Hare, J. P.; Abdul-Sada, A.; Kroto, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

(5) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, D.; Whetten R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

(6) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(7) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394.

(8) Koch, A.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.*, submitted for publication.

(9) Hebard, A. F.; Roseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* **1991**, *350*, 600.

(10) Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibato, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250.

‡ Department of Chemistry, University of California, Irvine, CA 92717.
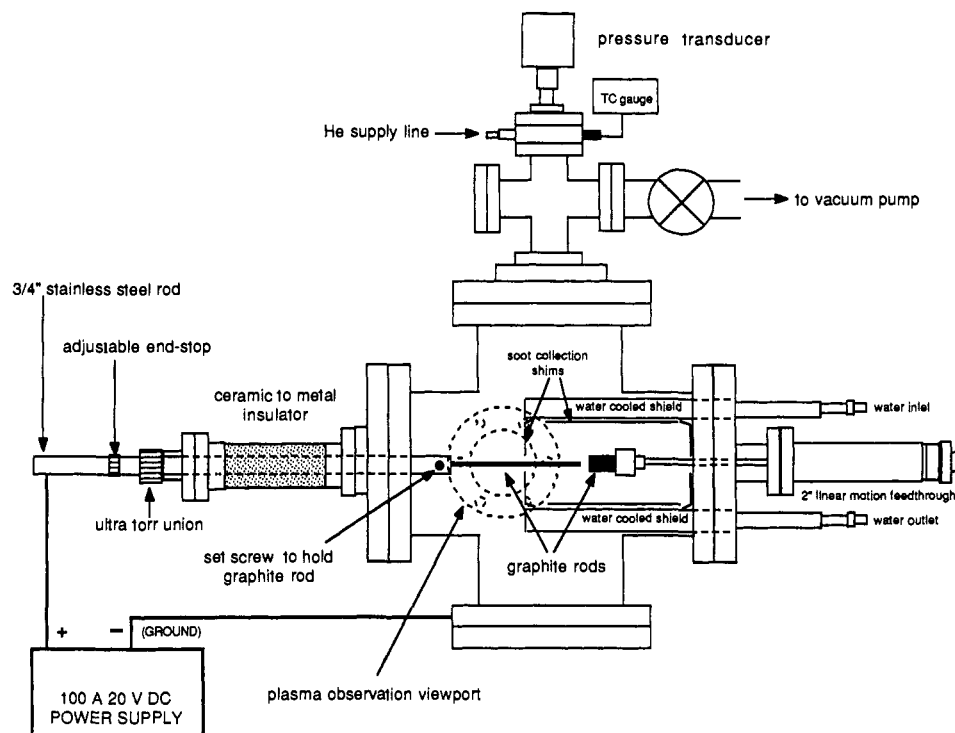
Figure 1. Scale diagram of the apparatus used to produce fullerenes from graphite rods.

attached to the grounded chamber. The power supply is a Hewlett Packard Model 6011A (0–20 V, 0–100 A, 1000 W) regulated DC power supply.

To generate the fullerenes, the two carbon rods are first positioned so that they are touching. The power supply is set for a current limit of 70 A. The voltage is then set to 20 V. Resistive heating occurs when the rods are touching. We then move the electrodes apart using the fine control provided by the linear motion feedthrough until the plasma is burning steadily. We observe the plasma through a view port and adjust the gap between the electrodes to attain maximum brightness of the plasma. We do not observe the plasma directly under normal operating conditions. Instead, we observe the light emitted from the end of the collection region which is aligned directly in front of the view port. On occasion we have moved the electrode gap region in front of the view port for observation. In this manner we are able to determine that the gap between the rods is about 4 mm during operation. The typical power requirement under these conditions is 18 V at 60 A (~1 kW). We consume the $^1/_4$-in. electrode at a rate of about 0.2 in./min. The larger electrode is not consumed at all. Occasional removal of light-colored "slag" from the larger electrode is necessary (after four or five rods have been consumed). We have not yet identified this species. Laser desorption mass spectrometry of the slag shows only carbon present in the spectrum. It is not necessary to sharpen the rods to a point to achieve good results with this procedure. We have performed this procedure using other sizes of electrodes. Smaller $^1/_8$-in. electrodes tend to break easily when using the full length, but require less power (18 V, 25 A). Two $^1/_2$-in. electrodes require more power than our power supply can provide. The $^1/_4$-in electrodes seem optimal for this experimental configuration. At the end of a run, the apparatus is filled to atmospheric pressure with He and allowed to cool. The chamber is then opened, the collection shims are removed, and the soot is scraped from the shims and collected for further purification.

Mass Spectrometry. Our time-of-flight (TOF) mass spectrometer has been described in more detail in a previous publication.[11] Briefly, the TOF mass spectrometer consists of an ion optics stack for ion acceleration, deflection plates, a field-free region, and a dual microchannel plate assembly for detection of ions. The experiment measures the mass spectrum of negative ions emitted directly from the sample in the desorption process. The mass resolution $(m/\Delta m)$ of the apparatus is 400 under these experimental conditions. The base pressure of the system is typically 2×10^{-9} Torr. Neutral and ionized fullerene clusters are desorbed from the stainless steel substrate by a XeCl excimer laser (308

nm). The fluence of the desorption laser is held constant at approximately 10–100 mJ/cm^2. The desorption laser is operated at 100 Hz repetition rate with a pulse width of approximately 20 ns. The laser desorption does not produce fragmentation of the desorbing fullerene molecules.[12]

The Fourier transform mass spectrometer (FTMS) consists of a three-region vacuum chamber with each region separated by gate valves. The first region is a rapid sample change region. A sample preparation stage is located in the second region and contains an evaporative fullerene doser (described below), argon ion sputter gun, and gas-dosing capability. The third region contains the optical path for an FTIR spectrometer, additional gas-dosing capability, and an extension arm containing the analyzer cell for FTMS. In this region, the typical base pressure is 1×10^{-10} Torr. The entire apparatus is on a cart which can be moved to place the analyzer cell in the bore of a 7-T superconducting magnet. The sample is transferred between the various regions of the apparatus by a transfer rod. The FTMS experiments are performed with an Ionspec Omega data acquisition system. Radio-frequency chirp excitation is used to accelerate the ions into cyclotron orbits inside the cell. The data were acquired with an analog to digital conversion rate of 4 MHz, and 64K data points were acquired for each transient. Twenty transients were acquired and averaged for each spectrum.

The fullerene doser consists of a tantalum cup filled with a mixture of solid fullerenes. The doser was prepared by filling the cup with a benzene solution of fullerenes and allowing the solution to evaporate. After repeated evaporations, the filled cup was then covered with a tantalum foil lid in which a 500-μ hole was punched. This cup was attached to support rods which also supply the current for resistive heating. A thermocouple is attached to the cup to monitor the dosing temperature. The fullerenes were evaporated onto the surface of a palladium substrate foil which had been previously cleaned by Ar ion bombardment. The substrate was kept at room temperature, and the temperature of the doser was held constant at 425 °C. The dosed foil was moved in front of the FTMS cell. The desorption laser described above was used to desorb the fullerenes from the substrate. Desorbed positive ions were trapped in the analyzer cell and FTMS spectra were acquired.

Results

To determine if the fullerene synthesis was successful, we stirred a portion of the soot in warm benzene for 1 h. Filtration of this mixture yielded a dark reddish-brown solution indicating the

(11) Hunt, J. E.; Lykke, K. R.; Pellin, M. J. In *Methods and Mechanisms for Producing Ions from Large Molecules*; Plenum Press: Minaki, Canada, 1991.

(12) Lykke, K. R.; Pellin, M. J.; Wurz, P.; Gruen, D. M.; Hunt, J. E.; Wasielewski, M. R. In *Mater. Res. Soc. Symp. Proc.* **1991**, *206*, 679.
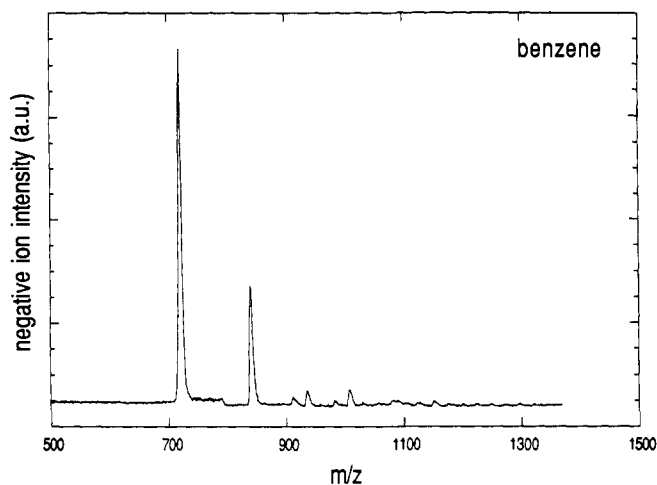
Figure 2. Time-of-flight mass spectrum of fullerenes extracted by washing in benzene, showing C_{60}, C_{70}, and small amounts of C_{78} and C_{84}.

presence of C_{60} and C_{70}.[5] We analyzed this solution by two procedures. First, a small amount of solution was evaporated onto a stainless steel sample holder, and laser desorption TOF mass spectrometric measurements were performed on the residue. The TOF mass spectrum of this sample (Figure 2) shows primarily C_{60} and C_{70} with small amounts of C_{78} and C_{84}. We also performed these initial extractions with toluene and carbon tetrachloride which gave identical results. In the second procedure, we evaporated the fullerenes obtained from the same solution onto the Pd substrate using the fullerene doser in the FTMS apparatus. FTMS is more sensitive at higher molecular weights than our TOF spectrometer owing to the velocity-dependent detection sensitivity of the microchannel plates. Figure 3 shows the FTMS spectrum indicating that small amounts of the higher fullerenes are indeed present in the benzene extract. A spectrum acquired with ejection of the ions below mass 850 is shown in the inset. This spectrum clearly shows that fullerenes up to cluster size C_{266} can be identified in the benzene extract prepared from soot formed in our fullerene generator.

Once we determined that our fullerene synthesis was successful, we designed an extraction scheme to attempt isolation of various molecular weight fractions. A summary of this separation scheme is shown in Figure 4. In the first step, we compared the efficiency of Soxhlet extraction with ordinary reflux technique with benzene as the extraction solvent. A small amount of the soot was placed in the thimble of a Soxhlet extractor and a similar sample was placed in the still-pot of a reflux apparatus. The extractions were

carried out for 24 h, yielding a strongly colored reddish-brown solution for both techniques. Small amounts of the extract were saved for later analysis by mass spectrometry. The remainder of the sample was stripped of solvent in a rotary evaporator in order to determine the yield relative to the initial amount of soot used in the extraction. In all of our extractions, we obtained a mass balance to within ~2% by measuring the weight loss of the soot. We found that the Soxhlet extraction worked much better, giving a 26% yield of soluble material. By contrast, the reflux extract gave a 14% yield of soluble material. Figure 5 shows the TOF mass spectrum of the material isolated from the benzene Soxhlet extractions showing that the benzene solvent dissolves primarily C_{60} and C_{70} in a ratio of approximately 3:1 with very small amounts of higher fullerenes up to mass 1200. The mass spectrum of the sample prepared by reflux was identical. Since Soxhlet extraction resulted in yields almost twice as high as with reflux, all subsequent extractions were performed by the Soxhlet method. All extractions were performed for 24 h with cycling times of 25 min per cycle.

Next, we attempted to isolate higher molecular weight fullerenes by extraction with a more polar solvent. The material remaining in the Soxhlet thimble was Soxhlet extracted with pyridine, yielding an additional 4% yield of soluble material. The TOF mass spectrum of this material, depicted in Figure 6, shows C_{60} and C_{70} in a ratio of 2:1 with small amounts of the higher fullerenes. This extraction gives results very similar to the benzene extraction. There appears to be no advantage to using pyridine over benzene. The material remaining in the thimble from the Soxhlet extraction was then extracted with 1,2,3,5-tetramethylbenzene. This extraction yielded a dark greenish-brown solution with an additional 14% soluble material. TOF mass spectrometry (Figure 7) shows that this solution contains significant concentrations of fullerenes up to mass 2400 (C_{200}). The solution may contain even higher molecular weight species which cannot be seen because of the decreasing sensitivity of our detection for higher mass species. From peak areas and abundance considerations, it appears that C_{60} and C_{70} are present in concentrations of less than 1%. Based on the yields from the successive extractions of the soot with benzene, pyridine, and 1,2,3,5-tetramethylbenzene, the total yield of soluble material consisting of fullerenes C_{60} to C_{200} is 44 ± 2%. As an interesting aside, we noted that it was very difficult to remove the high molecular weight fullerene residue from the sample holder after the TOF measurement.

A second extraction scheme was performed to isolate either pure C_{60} or C_{70}. A fresh portion of the soot was Soxhlet extracted with hexane for about 4 h. This extraction yielded 21 ± 1% soluble material. The mass spectrum shown in Figure 8 indicates that hexane extracts C_{60} and C_{70} with only trace amounts of C_{76}, C_{78},
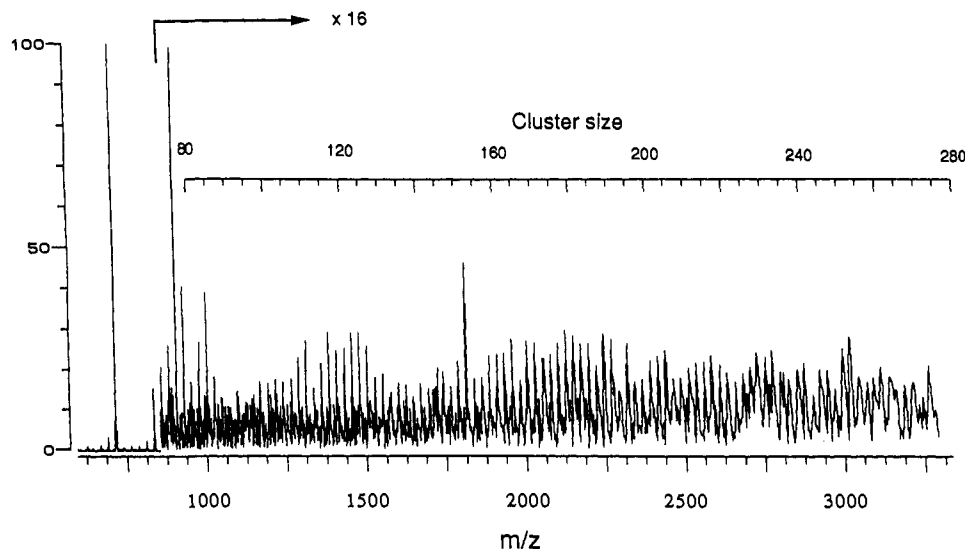

Figure 3. Fourier transform mass spectrum of fullerenes extracted by washing in benzene, showing C_{60} and C_{70}. The inset depicts a spectrum acquired by ejecting ions with m/e less than 850, showing that fullerenes up to cluster size C_{266} are produced in our apparatus.

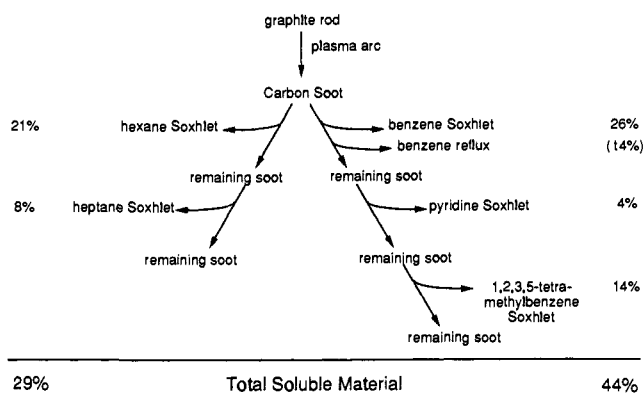## Fullerene Separation Scheme

Figure 4. Separation scheme showing the sequence of extractions used to separate various molecular weight ranges of fullerenes. The yields of the various steps are shown to the side.
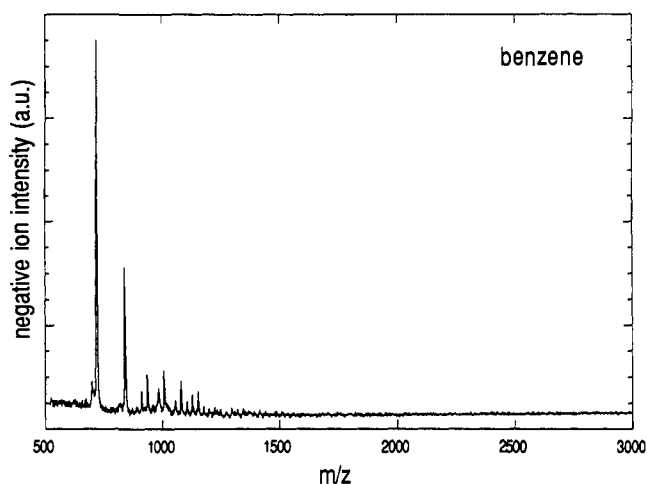

Figure 5. Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in benzene showing C_{60}, C_{70}, and small amounts of fullerenes up to cluster size C_{100}.
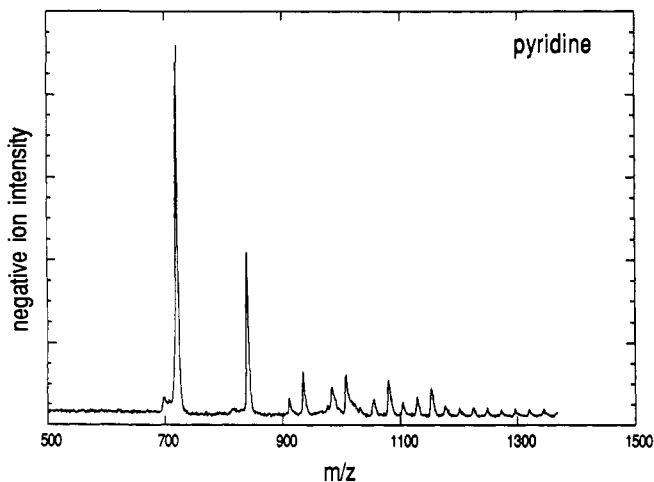

Figure 6. Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in pyridine showing C_{60}, C_{70}, and small amounts of fullerenes up to cluster size C_{100}.

and C_{84} (<1%). The soot remaining in the Soxhlet thimble was then extracted with heptane. This extraction yielded an additional 8% soluble material, bringing the total yield to 29 ± 1% by weight. The TOF mass spectrum of this extraction is shown in Figure 9. The heptane extract is enriched in C_{84} compared to other extracts and contains C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}. The ratio of fullerenes
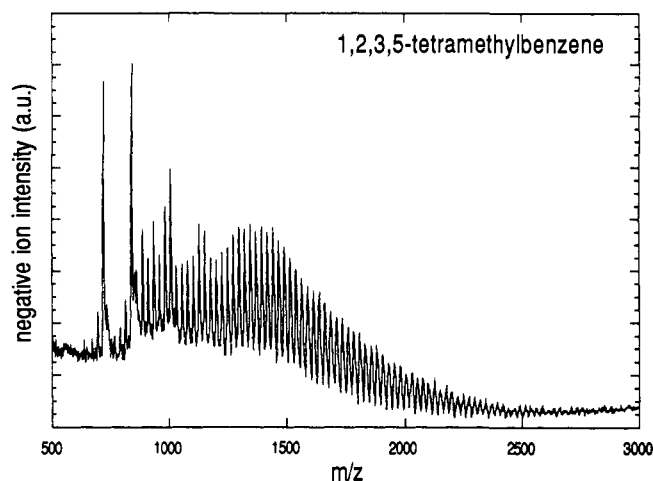

Figure 7. Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in 1,2,3,5-tetramethylbenzene showing C_{60}, C_{70}, and large amounts of higher molecular weight fullerenes up to cluster size C_{200}.
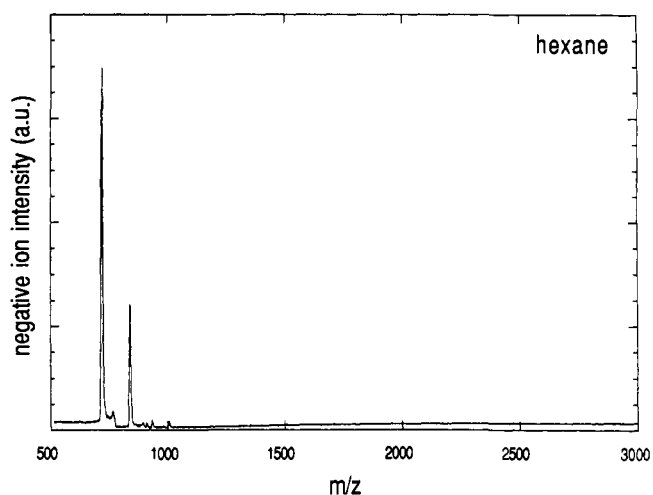

Figure 8. Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in hexane showing C_{60}, C_{70}, with trace amounts of fullerenes C_{78} and C_{84}.
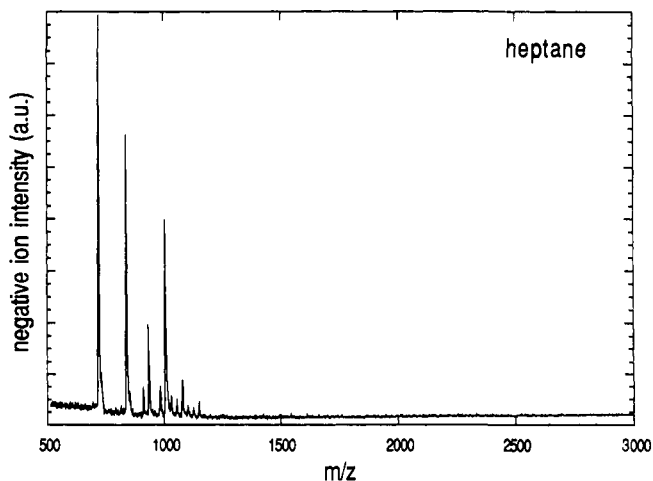

Figure 9. Time-of-flight mass spectrum of fullerenes prepared by Soxhlet extraction in heptane showing C_{60}, C_{70}, and C_{84} occurring a ratio of 2:1.4:1, respectively.

in this extract is 2 : 1.4 : 0.5 : 1 for C_{60}, C_{70}, C_{78}, and C_{84}, respectively.

Discussion

Our high yield (44 ± 2%) of soluble fullerenes can be attributed to optimizing conditions for the generation of the soot and proper

selection of extraction solvents. We achieve higher yield than previously reported even after the first extraction with benzene (26 ± 2% compared to 1–14%[4-7]). There are several improved design factors in our apparatus which contribute to the higher yield. First, we use a plasma to generate the soot rather than a contact arc or resistive heating. We have very fine control over the gap distance, and we continually adjust the distance to obtain the brightest plasma. In doing so, most of the electric energy is dissipated into the plasma rather than into resistive heating of the carbon rods. Only the end portion of the rod which confines the plasma becomes hot enough to glow. This is significantly different from the resistive heating method where the entire rod is heated to glowing. Another reason for our high yield is that we use a static He pressure rather than flowing He[6,7] which could pump away fullerenes not immediately condensed onto the collection shims. Additional experiments are being performed to try to optimize the He pressure to increase the yield even further. Also, it is possible that the presence of the end shims, by controlling convective flow, contribute to fullerene nucleation and growth.

The second reason we attain high yield is the procedure we use for the extractions. Soxhlet extraction gives higher yield than reflux since the soot is continuously washed with fresh hot solvent. Use of a high-boiling solvent such as 1,2,3,5-tetramethylbenzene isolates higher molecular weight fullerenes. These giant fullerenes may constitute up to one-third of the soluble material extracted from the soot. We cannot rule out the possibility that part of the yield from the 1,2,3,5-tetramethylbenzene extraction may be due to reaction of species present in the soot with the solvent, or polymerization of the solvent itself. We do not, however, find any evidence for such reaction products with mass spectrometric analysis. The heptane/hexane branch of the extraction scheme has a lower total yield than the benzene/pyridine/1,2,3,5-tetramethylbenzene branch. This is because the higher fullerenes are not extracted with heptane and hexane and remain in the soot.

The extraction scheme provides information that will be useful in designing separation schemes to separate other fullerenes besides the "commonly" used C_{60} and C_{70}. For example, if pure C_{84} were desired, one could select the hexane/heptane extraction combination which is enriched in C_{84} and then separate the mixture by column chromatography. We are in the process of doing this separation and other separations to isolate the higher molecular weight fullerenes in order to characterize these species spectroscopically. We are also in the process of performing extractions with other solvents which may result in even greater specificity. The high molecular weight fullerenes may be even more soluble

in solvents which have higher boiling points than 1,2,3,5-tetramethylbenzene. Because of the similar chemical characteristics of the fullerenes, complete separation of the fullerenes by solvent extraction alone was not possible with this extraction scheme, and column chromatography is still necessary to obtain pure samples of single fullerenes.

Conclusion

We have shown that it is possible to synthesize fullerenes in very high yield (44% extractable material) from a plasma discharge by optimizing the electrode gap to obtain the brightest plasma. Up to one-third of this yield may be composed of giant fullerenes. We have described an extraction scheme for isolating selected molecular weight fractions of fullerenes (from C_{60} to C_{266}). The extractions were characterized by TOF-MS and FTMS. Soxhlet extraction in benzene is twice as efficient as benzene reflux in dissolving fullerenes. With Soxhlet extractions in 1,2,3,5-tetramethylbenzene, it is possible to extract higher molecular weight fullerenes up to C_{200} which are not readily dissolved by benzene or pyridine and have been left in the soot. Extraction in hexane appears to limit the amount of higher fullerenes extracted, giving solutions containing primarily C_{60} and C_{70}. Heptane extraction following the hexane extraction appears to isolate C_{60}, C_{70}, and C_{84}. This solvent scheme will be useful in preparing selected molecular weight containing fractions for subsequent separation by column chromatography.

(13) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548.