Synthesis of Gram Quantities of C_{60} by Plasma Discharge in a Modified Round-Bottomed Flask. Key Parameters for Yield Optimization and Purification

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Described is the fabrication of a plasma discharge reactor constructed from a 1-L round-bottomed flask that allows for the preparation of gram quantities of C_{60} in an 8-h period. The modified reactor design (1) is inexpensive, (2) requires almost no machining, (3) has high thru-put, (4) affords high yields of fullerenes, (5) allows one to have near-continuous feed of graphite rods, and (6) permits control over four major reaction parameters important for the clean formation of fullerenes. The four major reaction parameters necessary to control for the high yield of fullerenes are the absolute pressure, the rate of helium gas flow through the reactor, the current level of the arc as determined by the setting on the arc welding unit, and the arc gap maintained by monitoring the current on a clip-on digital AC current meter. Since the apparatus described can allow for easy adjustment of all four major reaction parameters, this design could also be used to study the changes in fulleroid content based on parameter modification. Also detailed is the efficacy of a procedure for the purification of the crude fullerene mixtures using activated charcoal as a chromatographic stationary phase.

Since the initial discovery of buckminsterfullerene (C_{60}) in 1985[1] and the subsequent development of the carbon arc method for producing macroscopic quantities of this material,[2] a large amount of effort has been directed toward the understanding and utilization of this new allotrope of carbon.[3] We describe here the fabrication of a plasma discharge reactor constructed from a 1-L round-bottomed flask that allows for the preparation of gram quantities of C_{60} in an 8-h period. The reactor design (1) is inexpensive, (2) requires almost no machining, (3) allows high thru-put, (4) affords high yields of fullerenes, (5) allows one to have near continuous feed of graphite rods, and (6) permits control over four major reaction parameters important to the clean formation of fullerenes. Since the apparatus described can allow for easy adjustment of all four major reaction parameters, this design could also be used to study the changes in fulleroid content based on parameter modification. We also detail the efficacy of a procedure for the purification of the crude fullerene mixtures using activated charcoal as a charomatographic stationary phase.

The most common method of producing C_{60} utilizes the Huffman–Krätschmer carbon arc method in which graphite electrodes are vaporized in a low pressure helium atmosphere by passing an electrical current through the electrodes, thus generating an arc. The soot produced by this carbon arc contains C_{60} as well as some other higher molecular weight fullerenes. A number of reports on this method have appeared that provide details of the apparati used.[4,5] There are two major variants of the carbon arc

method, namely, contact arc and plasma discharge. In the contact arc method, the graphite electrodes are kept in constant contact through either a gravity feed mechanism[4b] or through the use of a feed spring.[4c,e] To date, the most easily accessible apparatus for the contact arc method is the gravity feed apparatus developed by Wudl.[4b] This is a relatively inexpensive and simple device which uses an arc welder as the power source. However, like all other contact arc apparati, it suffers from overheating problems due to resistive heating of the graphite electrodes and the apparatus must be disassembled for the insertion of new graphite rods. The plasma discharge method[4a,d] maintains a constant arc gap between the electrodes, thus avoiding much of the resistive heating problems found in the contact arc methods. This method can potentially produce crude fullerenes more efficiently by providing more control over the conditions which form the fullerenes in the reactor. The drawback to the plasma discharge method is that it requires a fairly complex apparatus with special feed mechanisms to align the electrodes and maintain a constant arc gap. And, like most other methods, the apparatus must be disassembled for the insertion of new graphite rods.

Here we describe the simple fabrication and use of a low cost fullerene generator of the plasma discharge type (Figure 1). The reaction vessel is simply a 1-L Pyrex round-bottomed flask that has had an additional 24/40 female joint affixed opposite to the first joint. The Pyrex guide arms (12 mm o.d.) extend from outside the water cooling bucket and are fitted with vacuum take off adapters and tipped with 24/40 male joints that insert into the reactor vessel (the total length of the guide arm including the male joint is 25 cm). The guide arms help to align the 1-cm-diameter copper mounting rods (each copper mounting rod is 35 cm long). One end of the copper mounting rods has a 3/16 in. diameter hole drilled to a 1-cm depth for mounting the graphite electrodes and on the other end has a screw hole tapped so that the rods can be attached to the arc welder with brass screws. The copper mounting rods extend out through the end of the guide arms and through standard 19/22 septa which have

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

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

(3) For recent reviews on C_{60}, see: (a) McLafferty, F. W., Ed. *Acc. Chem. Res.* **1992**, *25*, 97. (b) Kroto, H. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 111. (c) Diederich, F.; Whetten, R. L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 678. (d) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213. (e) Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 70. Also see: (f) *Fullerenes*; Hammond, G. S.; Kuck, V. J.; Eds.; ACS Symp. Ser., 481; American Chemical Society: Washington, DC, 1992.

(4) (a) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499. (b) Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991**, *56*, 4543. (c) Pradeep, T.; Rao, C. N. R. *Mat. Res. Bull.* **1991**, *26*, 1101. (d) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett.* **1991**, *177*, 394. (e) 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.

(5) There are other methods of producing C_{60}, most notably from hydrocarbon flames and by the thermal evaporation of carbon, see: (a) Howard, J. B.; McKinnon, J. T.; Makarovsky, Y.; Lafleur, A. L.; Johnson, M. E. *Nature* **1991**, *352*, 139. (b) Peters, G.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 223.
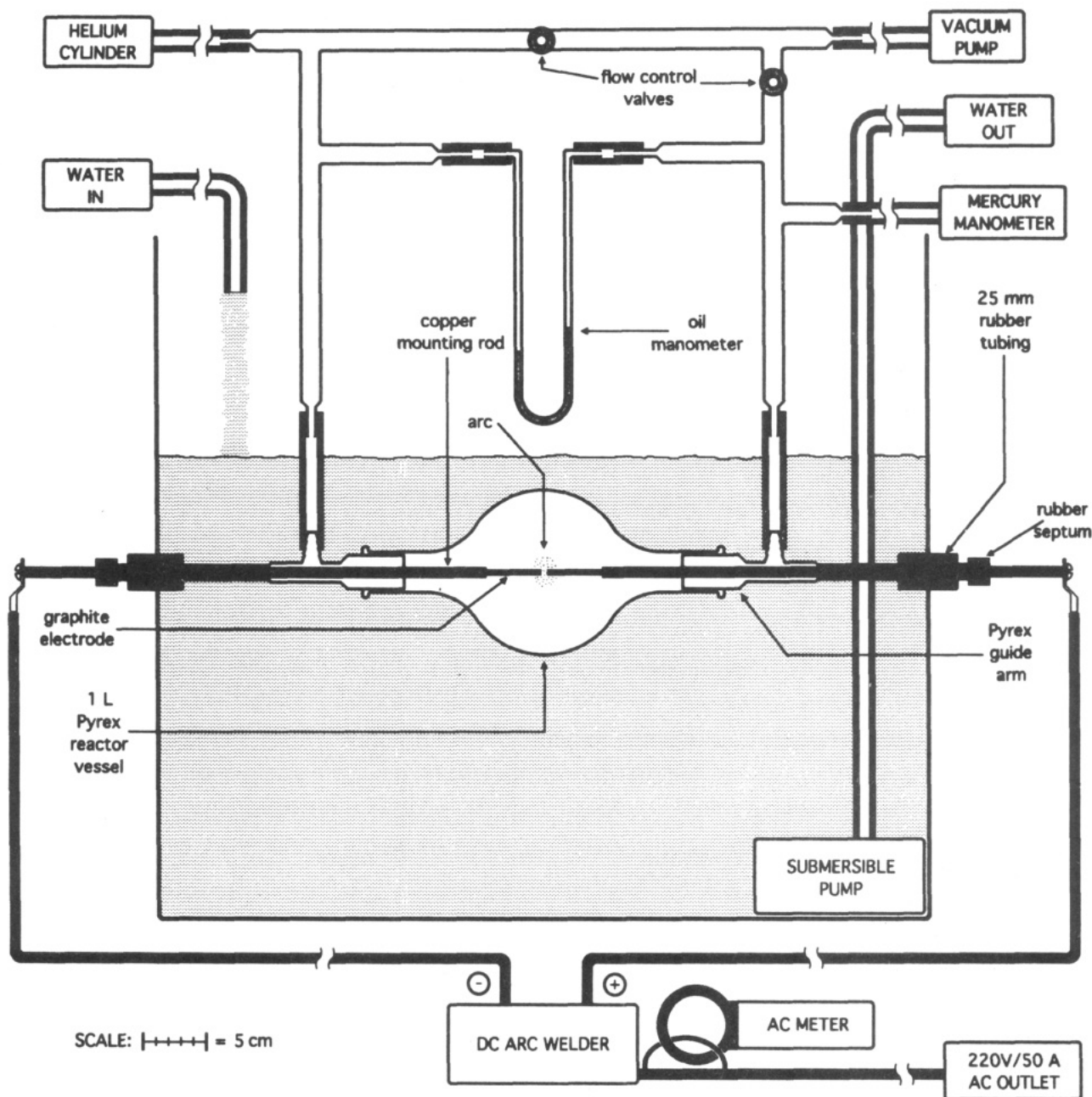
Figure 1.

a no. 2 hole punched through their center. These septa maintain a seal between the sliding copper mounting rod and the end of the Pyrex guide arm. The guide arm's vacuum take off adapters connect, via rubber tubing, to a gas manifold mounted above the reactor vessel (the outside diameter of the manifold tubing is 15 mm).

The entire vessel, except for the ends of the guide arms, is submerged in a cooling water bath made from a plastic storage container.[6] Two holes slightly less than 25 mm in diameter are made in the side of the storage container by heating an appropriately-sized glass tube in a gas flame and melting through the plastic. It is through these holes that the guide arms pass while water leaks are prevented by using rubber gaskets made from a short lengths of 25-mm rubber tubing. A submersible water pump is placed at the bottom of the cooling bath which helps to circulate the cooling (tap) water around the vessel and allows the

water to be removed from the bath as quickly as it flows in from a rubber hose at the top of the bath. If the water is not circulated and replenished in this manner, the bath tends to overheat, which can result in the vessel cracking.

The gas manifold above the vessel carefully monitors and controls the atmospheric conditions inside the vessel. Helium flows into the left side of the manifold and the gas is removed from the right sie of the manifold by a vacuum pump. The absolute pressure of gas in the vessel is monitored by a mercury manometer mounted on the right side of the manifold just above the reactor vessel. The pressure difference between the two sides of the vessel is an indication of the direction and magnitude of gas flow through the vessel and is measured by a silicon oil manometer (8 mm o.d.) mounted across the two sides of the manifold. The flow of the gas through the reaction vessel is controlled by two standard high vacuum Teflon-brand plug control valves. The central valve acts as a shunt, directing all or some of the helium flow through the vessel rather than across the top of the manifold. The valve on

(6) These storage containers are available at most department stores for approximately $10 and are made of a flexible plastic similar to plastic garbage containers.
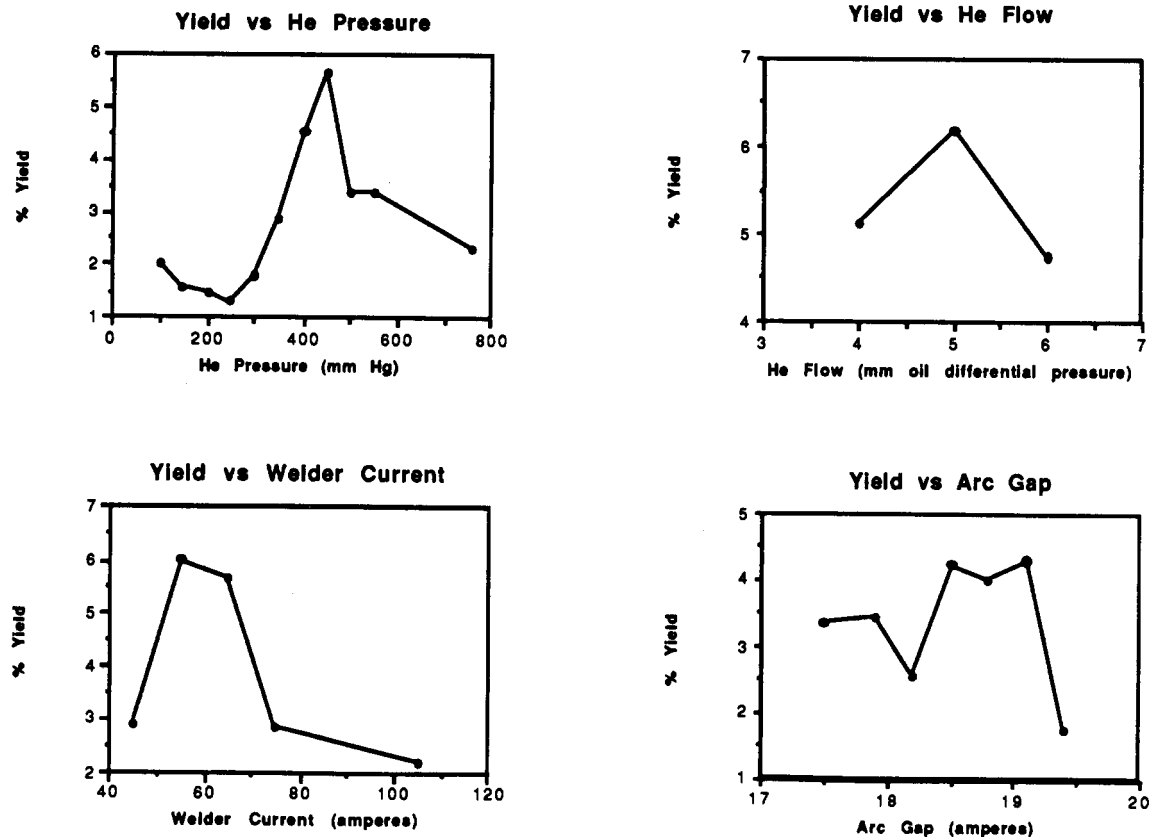
Yield vs He Pressure

Yield vs He Flow

Yield vs Welder Current

Yield vs Arc Gap

Figure 2.

the right side of the manifold controls the rate of helium flow out of the vessel and thus regulates the sensitivity of the shunt control valve.

The reactor is powered by a variable current AC/DC arc welder which is plugged into a standard 220 V/50 A wall outlet.[7] A clip-on digital AC current meter is attached to the input end of the arc welder to monitor the current.[8]

The apparatus described not only provides us with an inexpensive and easily fabricated fullerene reactor but also gives us the flexibility to adjust and optimize various reaction parameters in order to increase yields. We have determined that there are four easily adjusted parameters that must be maintained for high yields: (1) the absolute pressure, (2) the rate of helium gas flow through the reactor, (3) the current level of the arc as determined by the setting on the arc welding unit, and (4) the arc gap maintained by monitoring the current on the clip-on digital AC current meter. Other workers have dealt with some of these parameters but here we describe the control and optimization of all four parameters simultaneously (Figure 2). Optimization studies were done with inexpensive graphite welding electrodes.[9] We eventually started using

high purity graphite electrodes which doubled our yields.[10] Even with this change in electrode type, all the optimized reactor conditions given in Figure 2 hold for both sources of graphite except for the optimal arc gap measured in amperes on the clip-on digital AC current meter.

Helium pressure is the operating parameter that is commonly reported for the synthesis of fullerenes. Our studies have shown that there is a local yield maximum at about 150 mmHg but that the yield optimum occurs at 450 mmHg after going through a yield minimum at 250 mmHg. An optimized operating pressure of 450 mmHg is significantly higher than the operating pressures of 100–200 mmHg normally used by other workers;[3] however, a recent report suggested that optimal pressures for graphitic nanotube formation was in the range of 500 mmHg, similar to our maximum for C_{60} formation.[11] These pressures are monitored by a standard U-shaped mercury manometer and the pressures can be accurately adjusting by the low-pressure valve on the helium regulator.

The next condition that we investigated was that of helium flow through the reactor. By adjusting the flow control valves on the gas manifold and monitoring the differential pressure on the U-shaped silicon oil manometer, one can adjust the helium flow through the reactor from 0 mm (a static helium atmosphere) to greater than 30 mm oil pressure. A differential oil pressure reflects a net helium flow through the reactor from left to right. An optimum flow was found at 5 mm oil pressure. Pressures greater than 6 mm caused the soot to accumulate on the right side of the reactor and blew soot out of the reactor and into the manifold and vacuum lines. Pressures less than 4 mm gave extremely low yields and caused the soot

(7) The arc welder (Lincoln Electric model AC/DC 225/125) was purchased from a local welding supplier and cost approximately $300.

(8) The clip-on digital AC current meter was purchased from a local electronics distributor for approximately $100. The meter is attached around one of the two hot leads of the 220 V power cord attached to the arc welder. One can access these leads by carefully removing the outer power cord covering, exposing three wires, namely, the two colored hot leads and the one white ground lead. Care must be taken to not penetrate the insulation of these inner wires. The current meter is then clipped around one of the exposed hot leads. The metallic portion of the wires should never be exposed.

(9) Standard 3/16 in. copper-clad graphite electrodes (Arcair brand, $0.25/rod) were obtained from a local welding supply center. The copper sheathing was peeled off before use. Technical data sheets on these electrodes showed that a significant amount of the mass consisted of nongraphitic binders that probably caused the lower yields seen in the optimization study graphs.

(10) High quality graphite electrodes (Cat. #AXF-5Q1, $1.92/rod, 6 in. long, 3/16 in. diameter) were obtained from Poco Graphite, Inc., 1601 South State Street, Decatur, TX 76234.

(11) Ebbesen, T. W.; Ajayan, M. *Nature* 1992, *358*, 220.

to accumulate on the left side of the reactor. Observation of the arc through a modified reactor vessel equipped with a view port[12] revealed that under a static helium atmosphere the arc plume actually flowed from the positive to the negative electrode (this is the direction of the current flow). A slight helium flow in the opposite direction seemed to counteract this current flow and "balanced" the arc so that at the optimum flow of 5 mm, the soot stayed in the center of the reactor vessel rather than flowing out one side or the other.

The welder current was the next parameter that we investigated and it was adjusted to obtain an optimum fullerene yield. Our studies showed that a current of 55 A gave the best yields. Higher current increased graphite rod burn rates but decreased yields.[13] At currents lower than 55 A we had difficulty maintaining an arc.

Finally, varying arc gaps were investigated. Other workers optimized this parameter by setting the arc gap to a level where the arc was "brightest".[14] We sought to find a more objective criteria for determining arc gap and found that monitoring the current draw of the arc with the clip-on digital AC current meter attached to the arc welder was a convenient and reliable way of monitoring this parameter.[8] While using welding grade graphite rods,[9] an optimum arc gap of 2–4 mm (determined visually through the view port)[12] corresponded to a current reading of 18.5–19.0 A on the clip-on digital current meter. Using high purity graphite rods,[10] the optimum arc gap of 2–4 mm corresponded to a current reading of 6.6–7.2 A on the clip-on digital current meter.

A detailed experimental procedure is as follows. The two guide arms were removed from a 110 °C oven, the 25-mm rubber tubing gaskets were slipped onto the end of the arms, the manifold hoses were attached, and the two arm assemblies were inserted through the holes of the empty cooling bath. The reactor vessel was then removed from the oven, the two joints are well-lubricated with silicon grease, and the vessel was mounted between the two guide arms. Adjustments in the guide arms were made to ensure a tight fit between the ground glass joints. Two weighed high purity graphite electrodes[10] (6 in. long) were inserted into the ends of the two copper mounting rods, the rubber septa were slipped over the other ends of the rods, and the rod assemblies were then inserted into the end of the guide arms. The septa were adjusted so that they slip over the end of the guide arm and give a reasonable vacuum seal.[15] The chamber was then evacuated, and the reactor was attached to the arc welder with the screw connections. The cooling bath was filled with tap water and the water flow was adjusted so that when the submersible pump was turned on, there was no net flow of water out of the cooling bath. It is important that the reactor vessel is always covered with water to avoid cracking of the reactor. The system was then kept under

5 mm vacuum[15] for 20 min. Helium was then introduced into the reactor and the pressure was adjusted at the regulator until an absolute pressure of 450 mmHg was obtained as determined by the mercury manometer. The flow control valves were then adjusted until a diffrential pressure of 5 mm was reached in the silicon oil U-tube. The copper mounting rods were pushed in until the two graphite rods were centered in the vessel but were not touching. While wearing rubber gloves and welder's goggles, the arc welder was set to 55 A DC, and the AC current meter and the arc welder were turned on (*CAUTION*).[16] The right copper mounting rod was pushed in slightly so that the graphite electrodes briefly touched and established an arc. This right copper rod was then moved in or out until the current meter read 7.2 A. The rod was allowed to burn until the current meter read 6.6 A at which point the right copper rod was again pushed in until a 7.2-A reading was obtained. This process was then repeated. One only needs to adjust the right copper rod (the positive electrode) because the left electrode is never consumed. It takes from 2–3 min for the graphite rod to burn through the 7.2–6.6-A range. Slag (as observed through the view port of our test apparatus)[12] accumulates on the left electrode and must occasionally (about every 30 min) be removed. This is accomplished by turning off the arc welder, waiting 30 s for the electrodes to cool, and tapping on the left copper mounting rod with a glass rod which knocks the slag off the electrode. Failure to turn off the arc welder and wait for the electrodes to briefly cool before dislodging the slag can cause the vessel to crack when the hot slag hits the bottom of the vessel and induces thermal stresses in the glass. An entire 15-cm electrode was consumed in about 1.25 h. One must be careful to not burn the graphite rod down below 1.5 cm; failure to do this can cause the arc to jump to the copper mounting rod, melting the top of the copper rod and necessitating redrilling of the graphite rod holding hole. Additional graphite electrodes can be burned in the same run by turning off the welder, bringing the reactor up to atmospheric pressure, removing the right mounting rod and replacing the consumed graphite stub with a new rod, re-inserting the mounting rod, pumping the system down to 5 mmHg, bringing the atmosphere back to 450 mmHg, turning the welder back on, and initiating a new arc. One need not disassemble the apparatus nor empty the cooling bath during this procedure. About six rods can be consumed in an 8-h period. If more than eight rods are consumed in a single run, the guide arms tend to clog with soot and the reactor becomes inefficient.

When the run was complete, the reactor was taken apart and the vessel had the joints wiped free of grease with paper towels and hexane. One end of the vessel was capped with a 24/40 rubber septum, the flask was filled with 500 mL of toluene, and then the other end of the vessel was also capped with a 24/40 rubber septum which had a needle inserted in it to avoid pressure build-up in the vessel. The reaction vessel was then carefully shaken to dislodge most of the soot and facilitate suspension of the soot in the toluene. The vessel was then placed in a sonic water bath for 30 min (with the needle pointing up and out of the water). The black soot suspension was then filtered through a pad of Celite-521 in a fritted glass funnel to give a dark red-brown solution of crude fullerenes. The

(12) The apparatus with a view port had an additional 24/40 female joint placed at right angles to the guide arms in the center of the 1-L reaction vessel, directly above the point of the arc. A tube was made with a male 24/40 joint (20-mm diameter, 20-cm long tube including the male joint) at one end and a clear glass window attached to the tube with epoxy at the other end. This tube was inserted into the female joint such that the window points up and out of the water bath. It is through this window that we directly observed the arc. Welder's goggles are used when looking into the port at the arc to avoid eye injury. Use of a view port of this type will easily allow observation of electrodes and slag build-up.

(13) Wudl et al. had similar burn and yield observations when moving to a higher current. See ref 4b.

(14) Parker et al. observed that their optimum arc gap was 4 mm. See ref 4a.

(15) With our apparatus a vaccum of only 5 mmHg can be obtained. The rubber septa are most likely the weak points in our system and cause the leaks which prevents us from obtaining lower pressures.

(16) The apparatus poses risks of electrical shock similar to those risks incurred during ordinary arc welding. Accordingly, rubber gloves should be worn to avoid electrical shock while handling the exposed copper rods. The operator should wear rubber-soled shoes and only one hand should be in contact with the copper rod at any time. To avoid eye injury, welder's goggles should be worn when observing the arc.
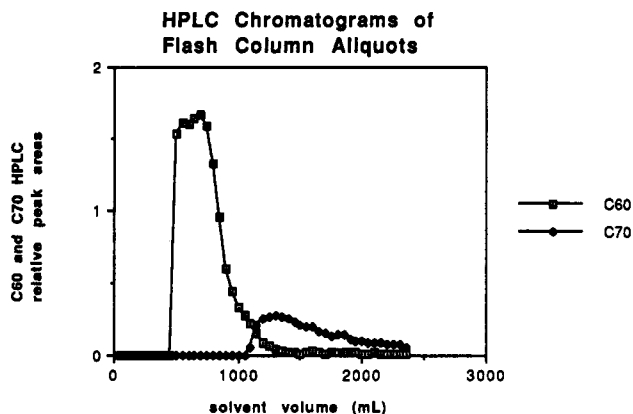
HPLC Chromatograms of Flash Column Aliquots

Figure 3.

solvent was removed from the crude fullerene extract by rotary evaporation to give a black powder. The black powder was suspended in diethyl ether and poured onto the top of a small plug of silica gel. The crude fullerenes are insoluble in ether and stay at the top of the column. While at the top of the column, the crude material was washed generously with ether and then flushed through the column with distilled toluene. The discarded ether washings removed the grease residues and the ubiquitous hydrocarbon side products of the fullerene reaction; the silica gel plug also acts as a fine filter to remove any soot that passed through the Celite pad. This filtered crude extract was then concentrated by rotary evaporation and weighed. We have found that this clean-up procedure is necessary for obtaining accurate weights of the crude soluble fullerene extracts and neglect of this type of purification will undoubtedly cause hydrocarbon and/or insoluble particulate to inaccurately enhance the reported crude yields. The weights of the consumed rods and the slag were obtained and subtracted from the initial weights of the rods to give a weight of the graphite that was consumed and converted into soot. The crude yield was then calculated from these values. A typical 1-rod run takes 78 min, burns 2142 mg of graphite, and produces 278 mg of soluble crude fullerenes, giving a crude yield of 13%. Yields reproducibly ranged from 11 to 14%. Thus an 8-h run that consumes six graphite rods will produce ~1.7 g of crude fullerenes from which ~1.0 g of pure C_{60} can be obtained by the following purification procedure.

The crude material was purified on an activated charcoal/silica gel flash column.[17] A slurry of alkaline decolorizing carbon Norit-A (36 g) and silica gel (72 g) in toluene (200 mL) was poured into a typical glass flash chromatography column (38-mm diameter and 40 cm long) that had a cotton plug at the bottom of the column. The slurry was allowed to settle as the solvent *above* the stationary phase was allowed to drain under a 7.5 psi N_2 head pressure applied at the top of the column.[18] The stationary phase must not be allowed to become solvent free or else cracking of the stationary phase can occur. A saturated toluene (400 mL) solution of crude fullerenes (1.85 g) extracted from carbon arc soot was slowly poured

onto the top of the Norit-A/silica gel stationary phase. A 7.5 psi N_2 head pressure was applied, thus providing a ~16 mL/min elution rate. The deep purple-colored solution containing C_{60} started to elute from the column after 37 min. After 36 min more, the eluant was only faintly purple and collection of a second faction was then begun. The total volume of toluene needed for obtaining the C_{60} fraction (first fraction) was ~600 mL. After 3 min more, a red-brown band characteristic of C_{70} started to elute. A graph of aliquots analyzed by HPLC[19] shows the relative concentrations of C_{60} and C_{70} versus solvent volume (Figure 3). Removal of the solvent from the purple fraction afforded 1.16 g of crystalline C_{60} (63% of a possible 75% of C_{60} in extractable fullerenes) that was >99% pure by HPLC.[17,19] This represents a net yield of about 8.5% pure C_{60} based on the weight of the graphite consumed.[20] While the second band eluted from the column was red-brown, it did contain some C_{60}. One more smaller chromatographic run on the initial red-brown portion afforded 74 mg more of C_{60} and 120 mg of a sample that was ~1:10 in $C_{60}:C_{70}$ as judged by HPLC analysis.[18] Thus the combined yield of purified C_{60} after two columns was 67% of a possible 75% of C_{60} in extractable fullerenes.

Although we illustrated this purification procedure with 1.85 g of extractable fullerenes, it worked equally well on a smaller scale using the proportionately smaller stationary phases and solvent volumes. Norit-A alone as the stationary phase without silica gel as a co-phase worked excellently for C_{60} separations on smaller scales (i.e., 100 mg of crude fullerenes with 2.0 g of Norit-A); however, the silica gel prevents cracking of the stationary phase in the larger columns and allows for higher flow rates.

In summary, we have described and inexpensive and easily fabricated fullerene reactor of the arc discharge type. The apparatus described allows one to control various reaction parameters and optimization of the parameters gives reproducible runs of 11–14% crude yield. The crude material is purified on a activated charcoal/silica gel column to give a net pure C_{60} yield of 8.5% from consumed graphite.[20]

(17) Alkaline decolorizing carbon Norit-A was purchased from Fisher Scientific Company. Flash chromatography grade silica gel 60 (230–400-mesh ASTM, 0.040–0.063 mm particle size) was purchased from EM Science. A detailed description of this purification method and the purity of the C_{60} and C_{70} obtained was recently described. See: Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* 1992, *114*, 7917.

(18) *CAUTION:* Though we experienced no rupture of the glass under 7.5–10 psi pressures, we recommend utilization of this procedure behind a protective transparent shield to prevent injury if a rupture should occur.

(19) HPLC was done using an Alltech Econosphere silica gel column (250 mm × 4.6 mm i.d.) with 2% toluene in hexane at 1 mL/min using UV detection at 284 nm. The crude material showed a mixture of C_{60}, C_{70}, C_{84}, and possibly other higher fullerenes in a peak area ratio of 58.0, 38.9, 1.6, and 1.5, respectively. The retention times were 5.1, 5.9, 6.6, and 7.4 min, respectively, with base-line separation. Thus, at 284 nm, the extinction coefficient of C_{70} appears to be greater than that of C_{60}, therefore skewing detection in favor of C_{70}.

(20) In summary, 2142 mg of graphite consumed from one rod yields 278 mg of crude fullerenes = 13% (generally 11–14%) crude yield or yield of soluble extract. At 2142 mg of graphite consumed per rod × 6 rods per 8 h = 12.9 g of graphite that can be consumed in this apparatus per 8 h; 12.9 g of graphite consumed × (11–14% crude yield) = 1.42–1.81 g of crude fullerenes per 8 h; 1.42–1.81 g × 63% chromatographic recovery of pure C_{60} = 0.89 g to 1.14 g of pure C_{60}; 0.89–1.14 g of pure C_{60}/12.9 g of graphite consumed = 6.9–8.8% of pure C_{60} obtainable based on the mass of graphite consumed.

[9]See, for example, David J. Griffiths, *Introduction to Electrodynamics*, 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1989), pp. 416–426.

[10]A clearly explained derivation is also given in E. Bennett and H. M. Crothers, *Introductory Electrodynamics for Engineers* (McGraw-Hill, New York, 1926), pp. 614–620.

[11]See, for example, M. Mason and W. Weaver, *The Electromagnetic Field* (University of Chicago, Chicago, IL, 1929), pp. 285–300.

[12]See, for example, R. Becker and F. Sauter, *Electromagnetic Theory and Relativity* (Blaisdell, New York, 1964), Vol. 1, pp. 292–294.

[13]David J. Griffiths and Mark A. Heald, "Time-dependent generalization of the Biot–Savart and Coulomb laws," Am. J. Phys. **59**, 111–117 (1991).

[14]Tran-Cong Ton, "On the time-dependent, generalized Coulomb and Biot–Savart laws," Am. J. Phys. **59**, 520–528 (1991).

[15]See, for example, W. G. V. Rosser, *Classical Electromagnetism via Relativity* (Plenum, New York, 1968), pp. 29–42.

[16]See, for example, Oleg D. Jefimenko, *Electricity and Magnetism*, 2nd ed. (Electret Scientific, Star City, WV, 1989), pp. 514–516. See also Refs. 13 and 14.

[17]See, for example, Ref. 11, pp. 297–298 or Ref. 15, pp. 39–41.

[18]Examples on the use of Eqs. (4) and (5) are given in Ref. 16, p. 516 and in Oleg D. Jefimenko, *Causality, Electromagnetic Induction, and Gravitation* (Electret Scientific, Star City, WV, 1992), pp. 8–13 and 33–38.

[19]Examples on the use of the time-independent forms of Eqs. (4) and (5) are given in Ref. 16, pp. 101–106 and 305–357.

[20]One may think that by choosing the charge in the shape of a rectangular prism we limit the generality of our derivations. This is not so. Any charge distribution can be regarded as being composed of charges confined to small rectangular prisms: This is exactly what we do when we perform integration over a volume element (rectangular prism!) $dv' = dx' \, dy' \, dz'$.

[21]See, for example, Ref. 9, p. 417–419. Observe that this effect is not the same as the Lorentz contraction.

[22]See, for example, Ref. 11, pp. 285–286; also J. M. Aguirregabiria, A. Hernández, and M. Rivas, "The Liénard–Wiechert potential and the retarded shape of a moving sphere," Am. J. Phys. **60**, 597–599 (1992). Observe that this is not a relativistic effect.

[23]Observe that Eqs. (4) and (36) contain a *retarded gradient* of ρ and a *retarded time derivative* of **J**, rather than a gradient of *retarded* ρ and a time derivative of *retarded* **J**. This means that the gradient and the time derivative must be determined for the unretarded (stationary) ρ and **J** but must be used at the retarded position of the moving charge.

[24]See, for example, Roald K. Wangsness, *Electromagnetic Fields*, 2nd ed. (Wiley, New York, 1986), pp. 522–523; Edward M. Purcell, *Electricity and Magnetism*, 2nd ed. (McGraw-Hill, New York, 1985), pp. 238–241; Richard P. Feynman, Robert B. Leighton, and Matthew Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, PA, 1964), Chap. 26, pp. 9–10.

Production and separation of C60 and C70 as an undergraduate experiment

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Detailed instructions for producing and separating C_{60} and C_{70} are presented. The experiment involves elements of both physics and chemistry. After initial setup of the equipment, results are obtainable within a few hours. Additional experiments for observing physical properties of the fullerenes are suggested. A complete list of equipment is provided, with vendors and catalog numbers, for those wishing to duplicate the experiment.

I. INTRODUCTION

A large body of the present scientific literature is indirectly, if not directly, related to three scientific discoveries of the past 10 years, namely, scanning tunneling microscopy, high temperature superconductivity, and large cluster molecules; aspects of each of these discoveries already have been included in the undergraduate curriculum.[1-3] These inclusions add excitement to the laboratory experience by allowing students to work near the forefront of current research. This report provides a brief history of the discovery of C_{60} and C_{70}, molecules having only carbon atoms in a closed cagelike structure, and how they can be easily produced and chromatographically separated in a senior level experiment.

The first experimental evidence of C_{60} came in 1985 when Richard Smalley's group at Rice University, in collaboration with Harry Kroto of the University of Sussex, reported the presence of 60-atom carbon clusters in the mass spectra of laser-vaporized graphite.[4] They named the molecule "buckminsterfullerene" after Buckminster

Fuller, the famous architect and advocate of the geodesic dome for modern structures. However, about 2 years earlier Wolfgang Krätschmer of the Max Planck Institute of Nuclear Physics in Heidelberg and Donald Huffman from Arizona State University, in an effort to explain bands in the extinction spectrum of interstellar dust, had produced soot by striking an arc between graphite electrodes in a helium environment. They later found that their carbon dust contained both C_{60} and C_{70}, and that both molecules were soluble in benzene.[5,6] This was the needed breakthrough to allow easy production and separation of molecules now known as fullerenes.[4,7] The extractable mixture of molecules is composed of approximately 75% C_{60} (soccer ball structure) and 23% C_{70} (rugby ball), and the remainder contains larger molecules.[4]

In addition to graphite and diamond, fullerenes represent a new allotrope of carbon. Unlike diamond and graphite, however, which tend to absorb hydrogen due to reactions of dangling bonds on their surface with hydrogen containing species, fullerenes contain no unterminated
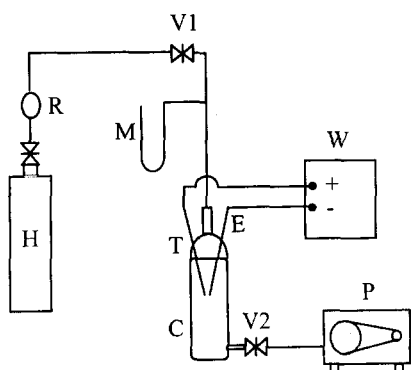
Fig. 1. Apparatus. H: helium cylinder, R: gas regulator, V1 and V2: valves, M: manometer, W: power supply, E: electrode, C: reaction chamber, T: reactor top, P: mechanical pump.

Fig. 3. Electrode assembly.

carbon–carbon bonds, and so are rather unreactive. At present fullerenes are the only known pure and finite forms of solid carbon.

II. APPARATUS

A schematic diagram of the apparatus needed to make fullerenes is shown in Fig. 1, and a detailed drawing of the reaction vessel is shown in Fig. 2. The vessel consists of two main parts, a hemispherical Pyrex glass cover and a cylindrical stainless steel chamber. These parts are joined and held together by a high temperature O-ring seal and a reaction flask clamp. The glass cover allows one a view of inside the chamber. There are three inlets on the cover; a 12 mm (o.d.) nipple along the central axis for feeding helium into the system, and two opposing socket joints at 20° off the central axis for the electrodes to pass. The cover assembly is best purchased from a custom glass shop since careful annealing is required to withstand the temperature gradients produced by the arc.[8] The metal reaction cham-
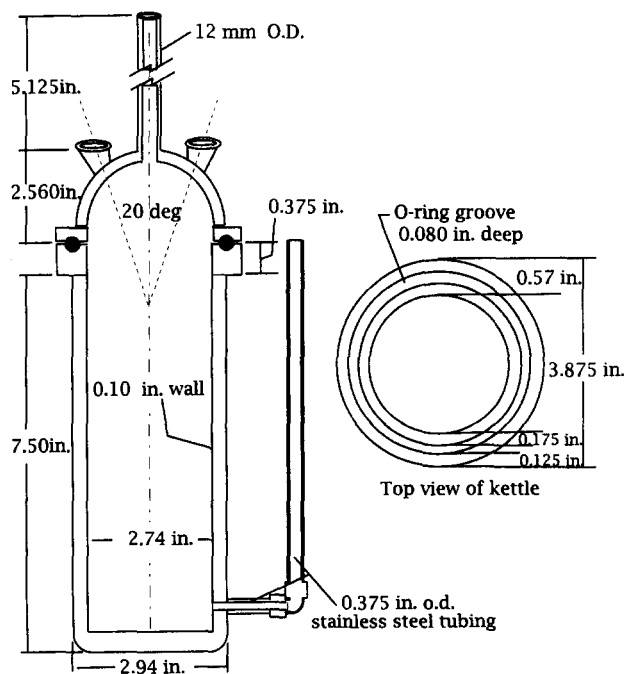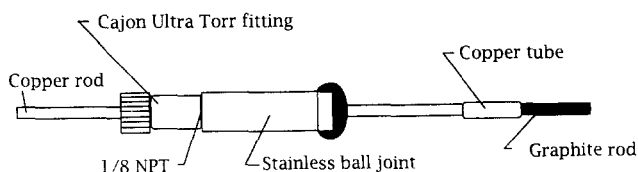

Fig. 2. Reaction chamber.

ber is rather simple and can be made locally. The parts are either welded or silver soldered together. Our chamber is welded and is comprised of an O-ring flange, a cylindrical body, an end cap, and a 3/8 in. nipple near the capped end of the cylinder for evacuation. The diameter of the chamber is determined by the size of the glass flange and accompanying O-ring seal used in making the cover. A book on designing and making vacuum apparatus is best consulted by those having little experience in such matters.[9] An all glass chamber is available,[8] however, in our experience, a glass system is easily broken and costly to replace.

The electrode assembly consists of four components; (1) a stainless ball joint, (2) an O-ring seal assembly, (3) a 1/4 in. (o.d.) copper rod, and (4) a 1/4 in. (o.d.), 3 in. long, spectroscopic-grade graphite electrode. Details of the assembly are shown in Fig. 3; part numbers and references to vendors are listed in Table I. For the copper electrode to completely pass through the O-ring seal assembly, the diameter of the outlet must be enlarged by drilling, and a piece of 1/4 in. (i.d.) copper tubing can be silver soldered to one end of the copper rod for holding the graphite electrode. (A low-temperature solder is not appropriate because of the intense heat produced by the arc.) Two layers of Teflon tape wrapped around the threads of the O-ring assembly will prevent leaks and seizing after being threaded into the ball joint.

A frame made of aluminum rods and clamps secured to a table top or wall, is recommended for supporting and anchoring components of the apparatus. This type of frame affords easy vertical adjustment of the chamber which is needed since it must be submerged in an ice–water bath for cooling during operation. The remaining parts, primarily assorted valves and fittings, can usually be purchased from local suppliers of compressed gases, or vendors of plumbing and refrigeration supplies. The valves should operate easily and those having Teflon or O-ring packing are preferable. Rubber vacuum hose can be used for the gas lines. A power supply with a current output of about 80 A dc is needed for the arc. Both ac and dc supplies are acceptable,

Table I. Special component parts list.

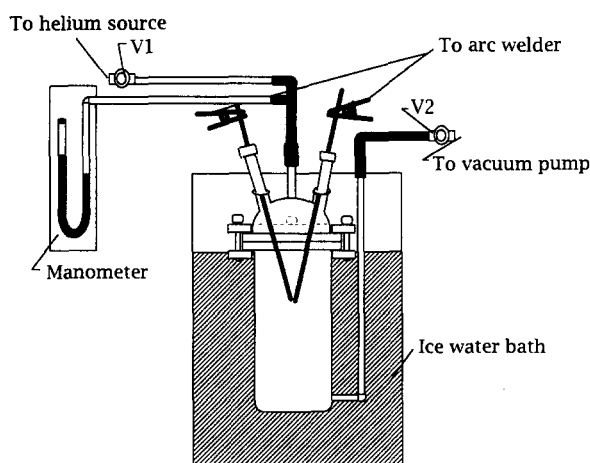| Description	Part No.	Reference
Cajon ultra Torr	SS-4-UT-A-8	16
Ball joint	7658-20 size 18/9	12
Manometer	8722-10	12
Pyrex cover		8
Chromatography column	EG 56787-06	8
Clamp		8
Graphite rods 99.9995%	14738	17
Aluminum oxide, activated, neutral, Brockmann I	19 997-4	18

Fig. 4. Diagram of assembled apparatus.

however, more current is needed for an ac supply. Also, a relatively small vacuum pump is adequate which need not pump below 1 Torr (mm Hg). A mercury manometer, or other device capable of measuring absolute pressure in the 100 Torr range, is required to measure the chamber pressure.

III. PROCEDURE

Thoroughly degrease and clean all parts before assembly. Washing in a labware cleaning solution followed by rinsing in distilled water and then in 2-propanol gives good results. Apply a thin film of silicone vacuum grease to the ball joints, O-ring seals and nipples over which vacuum hoses are fitted. Take care not to apply too much grease, which may result in slippage of the hoses and/or contamination of the chamber during arcing. After assembly, the reaction chamber is clamped to the supporting frame such that it hangs in a bucket that can be filled with ice and water to just below the O-ring flange as illustrated in Fig. 4. If desired, the tip of the graphite electrodes can be tapered with a pencil sharpener to effect a more reproducible arc path. When the electrodes are adjusted properly, they can be brought into contact about 5 cm below the flange and it is not possible to touch the metal wall of the chamber with either electrode. A small wad of glass wool is placed in the outlet nipple to prevent graphite particles from going into the vacuum pump. After connecting the gas and pumping lines, evacuate the reaction chamber and check for leaks by closing the valves and monitoring the chamber pressure; the vacuum seals are satisfactory if the pressure does not increase more than 1 Torr over a period of about an hour.

Use the following procedure to adjust the helium flow through the reactor. First, turn on the vacuum pump and reduce the pressure in the chamber as much as possible with valve V1 closed and V2 open. Second, adjust the helium pressure regulator for about 3 psig, close V2, and then slowly open V1 while monitoring the pressure as a function of time. Finally, with the pressure increasing at a rate of 10 Torr s^{-1} or less, adjust V2 to maintain an absolute pressure of about 100 Torr. The goal is to have a low helium flow-rate while maintaining a pressure of about 100 Torr in

the chamber. Later, after producing fullerenes, the effect of flow rate and chamber pressure on fullerene production can be determined.

With the power supply connected to the electrodes and the bucket filled with ice and water to the level of the metal flange on the chamber, the system is ready for operation. With the current selector switch at 75 A, an arc may be struck between the graphite rods. Insulating gloves should be worn for hand protection, and welder's goggles are necessary to protect the eyes from the intense radiation. View the arc through the glass lid and keep the graphite electrodes as close as possible without touching. If the tips are too far apart, the helium will ionize and the soot produced will contain no detectable amounts of fullerenes. The arc should not be maintained for more than 1 min, otherwise, the O rings in the electrode assembly are in danger of melting. Remember, the electrodes are not cooled by the ice–water bath. While arcing, the pressure initially increases for a few seconds and then returns to 100 Torr. After each arcing cycle let the system cool for about 10 min. and, if necessary, adjust the pressure during the cooling cycle. Also, the length of the electrodes extending into the chamber can be adjusted by pushing the rods through the O-ring seals. After 10 cycles of arcing and cooling, the chamber can be opened and the soot content can be measured. To achieve this close V2 and allow the chamber to fill slowly with helium. Siphon the water from the bath, allow 30 min. cooling time to reach ambient temperature, and open.

The soot can be either swept from the reactor into a beaker using a clean camel hair brush (synthetic bristles can generate static electricity which may damage the fullerenes), or extracted by pouring about 10 ml of toluene directly into the reactor. In either case, vinyl or nitrile gloves should be worn, and the work done inside a fume hood. Toluene extraction is probably the most efficient means of removal. Since the fullerenes are soluble in toluene, the material remaining in the reactor will be primarily insoluble graphite.

If fullerenes are present, the solution is a dark reddish-brown. Of the molecules in the solution about 75% are C_{60}, 23% are C_{70} and the remaining 2% contains other masses.[4] The soot–toluene concentration can be increased by evaporating some of the toluene. This is accomplished by gently boiling the solution for a few minutes, using a hot plate inside a well ventilated fume hood and observing usual safety precautions. After cooling to room temperature, strain the solution through filter paper or, better yet, a glass fretted funnel to separate the fullerenes from the graphite particles. Fullerenes may also collect on, and be extracted from the glass wool used to prevent soot from entering the vacuum pump.

The C_{60} and C_{70} can be separated by liquid–solid chromatography using a column packed with active alumina;[10,11] good separation is obtained using a 10.5 mm (i.d.) burette as the column having a packing length of 20 cm.[8,12] Careful packing of the column is essential in order to obtain better, and more reproducible separation of molecular weights. This is done by first filling the burette with solvent (1:19 toluene–hexane by volume)[10] and then adding the alumina powder. (A small wad of glass wool should be pushed to the bottom of the burette to keep alumina from entering the stopcock.) After the column is filled to within 3 cm of the top with alumina, open the

stopcock while adding solvent to the column until the total volume has exchanged, then close the stopcock when the solvent level is slightly above the top of the alumina. The solvent level should never be allowed to go below the level of the alumina. Finally, a layer of clean sand, about 3 mm high, can be added above the alumina to reduce swirling when solvent is pipetted into the column during use. Insert a cork stopper in the top of the burette and store safely until needed for separating the fullerenes.

To separate the fullerenes, add hexane to the extracted fullerene-rich toluene; the toluene/hexane ratio should be about 1:2 and the solution well mixed. Open the stopcock of the column and allow the liquid level to fall just below the level of the sand. With the stopcock closed, gently pipette fullerene solution into the burette to obtain a band 3–4 mm high. Open the stopcock and when the last of this solution reaches the top of the alumina column, start adding more of the toluene–hexane solvent mixture, always keeping the liquid level well above the sand. This ensures that no "dry regions" are present in which fullerenes could collect, thus reducing the yield. The fullerenes will separate as they move through the column. The leading colored band of C_{60} will be magenta followed by an orange band of C_{70}.[3,7] The extent of the separation depends on the length of the column and the ratio of toluene to hexane.[7] The separated fullerene solutions are collected in sealable glass containers.

The solvent can be removed from the fullerenes by gently heating the solution as mentioned earlier. The fullerenes will crystallize as the solvent evaporates, and may be redissolved as required in the same or other solvents. Indeed, the small fullerene crystals formed and can be viewed with an optical microscope, if a few drops of solution are added to a clean glass slide and allowed to evaporate.[5]

The infrared spectrum of the fullerenes may be obtained by dissolving the crystals in spectroscopic grade n-hexane and adding the solution to a disposable IR sample card,[13] or a KBr substrate, and allowing the solvent to evaporate. Chung and Sternberg have provided an extensive discussion of the mathematics of C_{60} and why there are only 4 absorption bands in its IR spectrum.[14,15] This is primarily due to the high degree of symmetry in the molecule. Other physical properties of fullerenes that could be measured in a senior level laboratory include Raman shifts,[14] UV–vis spectroscopy,[7] and powder x-ray diffraction profiles to demonstrate the fcc structure of crystallites grown from solution.[19–21]

IV. CONCLUSION

With the simple method described above, C_{60} and its fullerene cousins can be produced in the student laboratory. The apparatus is inexpensive and easily assembled. The materials produced by this system can be used for a variety of studies. These include various spectroscopic techniques to determine their composition, e.g., nuclear magnetic resonance, Fourier transform infrared, and mass spectroscopy.

Safety concerns: as a matter of convenience, the safety precautions suggested throughout the text are again summarized and should always be observed. Rubber or vinyl gloves are to be worn when manipulating the electrodes during the arcing process, and welders' goggles worn to protect the eyes from the intense radiation. All the compounds, hexane, toluene, and carbon black, are slightly toxic by inhalation and can be absorbed upon contact with skin, therefore, vinyl or nitrile gloves are to be worn and a fume hood used during extraction and separation of the fullerenes.

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C$_{60}$ and C$_{70}$ Made Simply

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C$_{60}$ and its fullerene relatives are now known as a radically new form of elementary carbon. Colorful, deformable, reducible and molecular, fullerenes are unlike diamond and little like graphite. Diamond is colorless, without equal in hardness, largely inert and macromolecular. Graphite is black, soft, largely inert and macromolecular. Fullerene carbon cages share, however, delocalized π bonding with the carbon planes of graphite. Fullerenes can now be prepared by rather simple methods as we shall describe in detail in this paper.

In 1985, Kroto, Heath, O'Brien, Curl, and Smalley at Rice University provided the first experimental evidence for C$_{60}$ and proposed that its molecular structure was that of a truncated icosahedron, the familiar form of a soccer ball (1). Their initial evidence for C$_{60}$ and its congeners came from mass spectra of species that had been vaporized into a helium beam from graphite with a pulsed laser in a high vacuum system. At first, the idea that new forms of elementary carbon existed with the whimsical name buckminsterfullerenes seemed fanciful to many. Doubt lingered in the absence of bulk samples of fullerenes that could be more fully characterized. Further mass spectrometric evidence in support of the C$_{60}$ structure soon came from Smalley's laboratory (2), and a number of theorists predicted properties of fullerenes. Yet, a method for preparing isolatable samples of fullerenes remained elusive.

In mid-1990, Krätschmer, Fostiropoulos, and Huffman reported the preparation of crude samples of C$_{60}$ and ^{13}C$_{60}$ in carbon dust as indicated by the infrared spectra of these materials (3). They had vaporized graphite by resistive heating in an inert atmosphere in a bell jar system. In a second paper they reported mass spectra, X-ray diffraction data and UV-VIS spectra of the mixture of fullerenes that had been extracted in benzene solution (4). Smalley and co-workers were soon reported to have made fullerenes in bulk by a related carbon arc method. A full report of the new synthetic work in the Smalley group appeared before the end of the year (5). Meanwhile, *Chemical and Engineering News* carried a descriptive account of the isolation of samples of C$_{60}$ and C$_{70}$ (6). This article contained color photographs of solutions of C$_{60}$ and C$_{70}$, which had been purified by column chromatography on alumina, and included a report of the single-line ^{13}C NMR spectrum.

Encouraged by the account in the *C&EN* article, we decided to attempt to prepare crude C$_{60}$ and to purify it.[1] Our first reactor was built from an organic chemist's three-necked flask. Because removing graphitic soot from the flask was frustrating, we modified the reactor as described below.

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[1] *Historical Note.* In mid-October 1990, A. R. J. proposed attempting to make C$_{60}$ as a January Term 1991 project. The appearance of the *C&EN* article shortly thereafter encouraged us to begin designing an apparatus for this purpose. Richard Smalley's seminar talk at Oberlin in the fall of 1989 also had stimulated our interest. Awareness of C$_{60}$ had preceded Smalley to Oberlin, however. In 1988–1989 Roy Jacobson had sponsored work on organic synthesis directed toward building up this molecule. In the mid-1980's he had done much work directed toward this synthesis as a graduate student with Orville Chapman at UCLA.

[2] The reaction kettle was fabricated at Eagle Laboratory Glass Co., 1912 East 337th Street, Eastlake, OH 44095.

Although fullerene samples are now available commercially from Aldrich Chemical Co. and Strem Chemicals, useful amounts can be prepared locally with the apparatus described here. Moreover, this apparatus is suitable for use in an undergraduate synthesis laboratory. Once prepared, the crude graphitic soot can be purified and subjected to NMR, UV–visible and vibrational spectroscopic examination. Useful ^{13}C NMR spectra can be run on the crude extract of fullerenes.

Procedure

Reaction Kettle

Figure 1 shows the reaction kettle that is the heart of the simplified apparatus for generating a crude mixture of fullerenes by the carbon arc method. This reactor was fabricated from two borosilicate-glass tubes of 8.0-cm outside diameter fitted with flanges made for an O-ring seal.[2] The top of the kettle has an inlet tube in the center for the supply of helium gas and two diagonally mounted ball joints for the electrode assemblies. The electrodes follow the paths of the dashed lines. These ball joints provide flexibility for aligning the electrodes. The outflow tube for helium gas exits on the side near the bottom to reduce clogging with graphitic soot. This outflow tube is strengthened with a glass rod crossbrace. A standard double C-clamp system is used to hold the kettle together at the flanges. The two graphite-rod electrodes meet at a depth that is well below the region of the O-ring seal and that is cooled by a surrounding ice bath.

Electrode Assembly

The construction of the electrode assembly is shown in Figure 2. The electrode lead must carry a large current, be
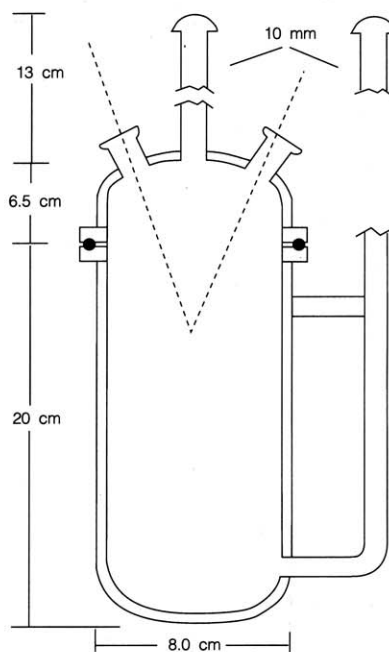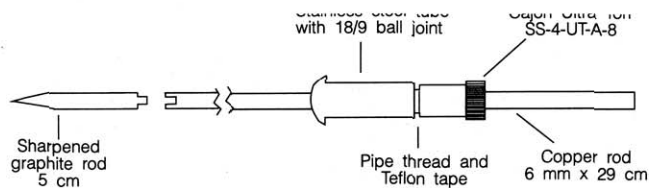

Figure 1. Reaction kettle.

Figure 2. Electrode assembly.

Figure 3. Overall reaction system.

adjustable in and out through a vacuum-tight seal and be terminated with a graphite rod. The 29-cm length of 6-mm (1/4-in.) copper rod is polished to present a smoother surface to the O-ring seal and is drilled out at one end to provide a receptacle for the graphite rod. The vacuum seal is made from a Cajon Ultra Torr fitting (SS-4-UT-A-8). The O-ring, which is Viton and rated to 200 °C, is held in place with a knurled nut. The other end of the Cajon fitting is drilled through to an inside diameter of slightly more than 1/4-in., turned down some and then machined to a 1/8-in. NPT pipe thread. The other part of the electrode lead-in is a stainless steel tube that terminates in a 18/9 ball joint on one end. The other end of the stainless steel tube is machined to receive the 1/8-in. pipe thread on the modified Cajon fitting. Ace Glass (Vineland, NJ) supplies the stainless steel tube with the ball joint. Teflon tape on the pipe thread gives a vacuum seal. The graphite rod is 1/4-in. diameter Ultra "F" Purity spectroscopic grade supplied by Ultra Carbon Corp. (P.O. Box X924, Bay City, MI 48708). The 5-cm length of graphite rod is machined on one end to fit snugly into the drilled-out end of the copper rod. Such a simple coupling works well. The other end of the graphite rod is shaped in a pencil sharpener.

Reaction System

Figure 3 presents the overall assembly of the reaction system. The system consists of a two-way stopcock for controlling the inflow of helium gas, a closed-end manometer for monitoring the pressure of helium, the reaction kettle, a section of tubing for filtering with glass wool, and an exit stopcock. Helium gas of standard commercial quality is supplied at a few psi above atmospheric pressure. The manometer, which contains mercury and has a range to 200 torr, is placed in the inlet system to prevent clogging with graphitic soot. The tube in the outflow side that is packed lightly with glass to wool help reduce the amount of graphitic soot that reaches the mechanical vacuum pump. A *Welsh Duo-Seal 1400B two-stage mechanical pump* equipped with an exhaust filter is satisfactory, and attachment through rubber vacuum hose is sufficient. The reaction kettle up to the level of the flange is surrounded by a plastic bucket filled with ice and water. A light-colored plastic bucket is desirable because light from the arc can be seen.

Silicone grease is used on stopcocks and on the various joints. Electric current is AC from a welder's "buzz box". This supply uses a 30-A, 110-V circuit and provides up to 100 A AC. A current of 10 A is insufficient to produce fullerenes with the present apparatus. While a current of 35 A is sufficient, a faster rate of production occurs with 100 A.

- **Safety Concerns.** Several safety considerations dictated the setup and handling of the apparatus. Concerns have been expressed about possible carcinogenic properties of the condensed ring, aromatic fullerenes. The fullerenes also are known to be efficient sensitizers of the formation of highly reactive singlet O_2 (7). Thus, the whole assembly including the vacuum pump was placed in a good hood. As a precaution against contact with fullerenes and accidental contact wi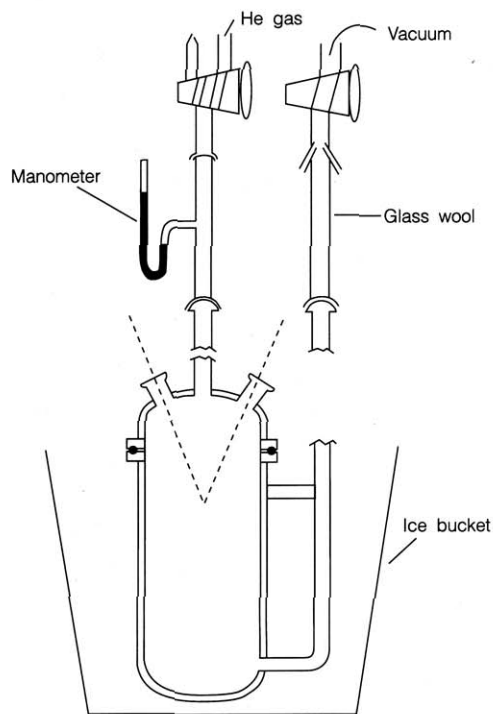th the high power electrical system, substantial rubber gloves were worn when working with the apparatus. In addition, welder's-quality eye protection was employed.

Carrying Out the Synthesis

With the whole system assembled and the graphite electrode tips just touching, the system was pumped to a good vacuum and filled with helium. This sequence was repeated two times. The bucket surrounding the reactor was filled with ice and water. Then, with a slow flow of helium achieved by setting the inlet stopcock, the outlet stopcock was adjusted to bring the pressure down to a steady reading of about 100 torr. The arc was struck. The electrodes were moved slightly apart to give the whitehot arc that produces high yields. After about 2 min at 100 A, the graphite rods are red hot, and the electrode assembly must be allowed to cool for a while to protect the O-ring seals before striking the arc again. It is not necessary that the graphite tips be reshaped for each round of arcing. With 12 min of arcing, about 0.15 g of soot is produced. When a sufficient amount of graphitic soot has collected in the lower part of the reaction chamber and the electrodes have cooled somewhat, the outflow stopcock is closed and the helium pressure is allowed to rise to a few psi above atmospheric. *Excess helium pressure is released through the* two-way inlet stopcock. For removing the graphitic soot, a camel's hair brush is recommended. Otherwise, with a plastic bristle brush a troublesome static charge forms.

To separate the fullerenes from the crude product of graphitic soot, this material is treated with toluene in a Soxhlet extractor. Soon after the white Soxhlet thimble with the crude black product in the bottom comes in contact with some toluene, a reddish-brown extract climbs the walls of the thimble. After extraction into toluene solution, the mixture of fullerenes is deep red-brown in color. About 20% is extractable. After rigorous removal of toluene with a RotoVap and final vacuum drying, the mixture of *fullerenes is ready for UV-VIS and NMR examination.* UV-VIS spectra can be run in hexane of spectroscopic grade. NMR spectra are conveniently run in benzene-d_6, in which

the fullerenes are much more soluble than in hexane. Observing the single ^{13}C line due to C_{60} at 143.2 ppm with respect to external TMS was straightforward on a 200-MHz FT NMR spectrometer. Observing the 5 lines of the less abundant C_{70} was challenging (8, 9). The proton-decoupled ^{13}C NMR spectrum also contained innumerable weak lines in the saturated hydrocarbon region.

The crude mixture of fullerenes can be separated by chromatography on an alumina column. The alumina was activated, neutral, Brockmann I, standard grade, ~150 mesh, 58 Å (Aldrich Chemical Co.). A quick and fair separation can be achieved on a 1.1-cm (i.d.) column of 10-cm packing length with a 1:2 toluene-hexane solvent. The separation of the leading magenta band of C_{60} is essentially complete. A distinct orange band of C_{70} is obtained, but its UV-VIS spectra shows some tailing of C_{60}. Relatively speaking, the UV spectrum of C_{60} is much stronger than that of C_{70}. The converse is true for the weaker visible spectrum of the two species (9, 10). A complete separation of C_{70} from C_{60} can be achieved on an alumina column of twice the length with a 1:19 toluene–hexane solvent mixture (see also 10, 11). With relatively less toluene in the solvent, the amount of crude fullerene separated in each step is reduced, however. A bright yellow, strongly adherent band also was found on the alumina. The spectrum of this material showed strong aromatic absorption in the UV but was not characterized further. Higher molecular weight fullerenes have been extracted at higher temperatures with solvents such as 1,2,4-trichlorobenzene (12).

Other properties of fullerenes that could be studied as part of a student laboratory program are its infrared spectrum (13), its cyclic voltammogram (10), its effectiveness as a photosensitizer of molecular oxygen (7), and its susceptibility to the Birch reduction to form $C_{60}H_{36}$ (5).

Acknowledgment

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component (τ = 4.7 ns). This τ value is consistent with previous (room temperature) estimates of donor–acceptor center to center distance of 25 Å. The most important result is that the simplified kinetics at room temperature argue that any structural states of the complex which are trapped at 77 K are largely equilibrated at 300 K within 5 ns. This result suggests that motion at the cytc/ccp interface can be quite rapid and offers experimental support for the rapid restricted dimensional diffusion model of the cytc–ccp complex suggested by Brownian dynamics.[8] With this information now available, more detailed insight into the nature of the binding sites in principle could be obtained by comparing the decay distributions for the native systems with those for site-specific mutants.[9,10] Such studies are in progress.

Characterization of the Soluble All-Carbon Molecules C_{60} and C_{70}

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We report on the further physical and chemical characterization of the new forms of molecular carbon, C_{60} and C_{70}. Our results demonstrate a high yield of production (14%) under optimized conditions and reveal only C_{60} and C_{70} in measurable quantity, in an 85:15 ratio. These two new molecular forms of carbon can be completely separated in analytical amounts by column chromatography on alumina. Comparison among mass spectra obtained by the electron impact, laser desorption, and fast atom bombardment (FAB) methods allows a clear assessment of the composition of the mixed and pure samples, and of the fragmentation and double ionization patterns of the molecules. In addition, spectroscopic analyses are reported for the crude mixture by ^{13}C NMR and by IR spectroscopy in KBr pellet, and for pure C_{60} and C_{70} in solution by UV–vis spectroscopy.

Introduction

In a surprising recent development, Krätschmer et al.[1] have shown that certain all-carbon molecules are produced in large quantities in the evaporation of graphite and can be isolated as soluble, well-defined solids. The major species was identified as molecular C_{60} through mass spectrometry and by comparison of the infrared spectrum with theoretical predictions for the celebrated truncated-icosahedron structure, which had earlier been proposed to account for cluster beam observations.[2] The solid material, described as a new form of elemental carbon in a nearly pure state, has a disordered *hcp* lattice of packed quasi-spherical molecules, but determination of the precise molecular structure awaits diffraction from well-ordered crystals.

Kroto et al.[3] have followed this announcement with a partial chemical separation of the soluble all-carbon molecules generated by the same procedure. They used mass spectrometric evidence to conclude that other air-stable C_n molecules are present (n = 62, 64, 66, 68, 70). They reported that chromatographic separation yields C_{60} and C_{70} in a 3:1 ratio, in contrast to the 2–10% of C_{70} estimated in ref 1. The reported ^{13}C NMR spectrum of the C_{60} fraction, in particular, evidently confirms the existence of a species with all 60 carbon atoms chemically equivalent (proposed structures as shown in Chart I).

This paper describes the further physical and chemical characterization of these two new forms of molecular carbon.[4] Our results include the high-yield production (14%) of soluble material under optimized conditions, consisting of only C_{60} and C_{70} in measurable quantity. These have been separated in analytical amounts by column chromatography and have been characterized in pure or mixed forms by a combination of electron impact, fast atom bombardment (FAB), and laser desorption mass spectrometry. Spectroscopic characterization is reported including the ^{13}C NMR spectrum and the infrared absorption spectrum for the crude

CHART I
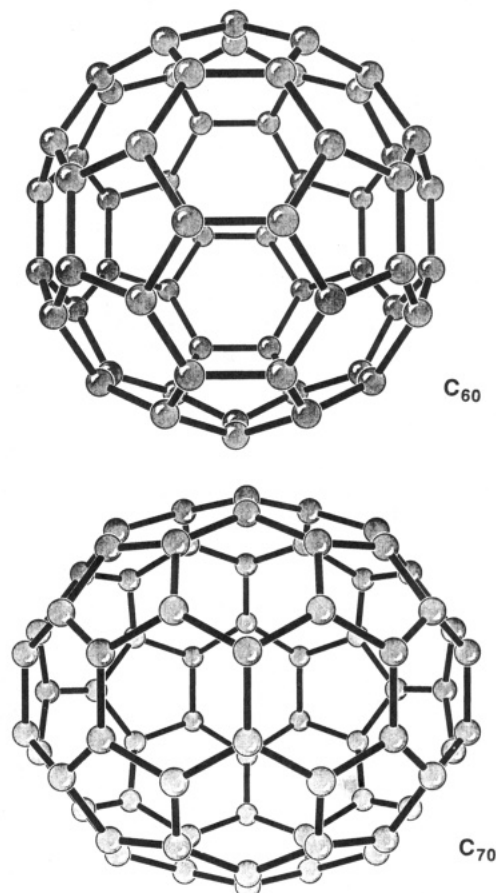
C_{60}/C_{70} mixture, and the UV–vis spectrum of pure C_{60} and C_{70} in solution. All five peaks of C_{70} in the ^{13}C NMR spectrum are

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unambiguously found.

Preparation Method and Chromatographic Separation

Two sets of samples have been used in the experiments described below, i.e., one prepared in Heidelberg,[1] used in the earlier stage of this work, and samples newly collected in Los Angeles. We now describe in more detail the method used and yields obtained in the latter preparations. The samples have been prepared following closely the method described by Krätschmer et al.[1] A carbon rod is evaporated by resistive heating under partial helium atmosphere (0.3 bar). The best results were obtained from high-uniformity graphite rods (Poco Graphite, Inc., Type DFP-2, <4 μm grain size, 0.8 μm average pore size). The rods are 1/8 in. diameter and emit a faint gray-white plume when heated by a current of 140–180 A. The sootlike material, collected from the partial evaporation of rods onto a glass shield surrounding the electrodes, is extracted with boiling benzene or toluene to give, after filtration, a brown-red solution. Evaporation yields a brown-black crystalline material in 14% yield (30 mg, identified below to be C_{60} and C_{70}). This yield is higher than reported earlier (ca. 1%,[1b] or "up to 8 percent"[3]) and is believed to be related to the graphite quality and the higher He pressure used. Further evaluation of these methods and yields will follow in a subsequent paper. Chromatographic filtration of the concentrated solution of "crude" material on silica gel with benzene can be performed, but the material obtained remains identical, in all aspects (same C_{60}/C_{70} ratio, no other constituents), to the crude material obtained from the benzene extractions.

Separation of the mixture of C_{60}/C_{70} proved to be a challenging task, particularly because of the poor solubility of the material in most organic solvents. While the solubility in benzene is about 5 mg/mL at 25 °C, the compound is soluble with difficulty at the same temperature in chloroform, dichloromethane, tetrachloromethane, diethyl ether, tetrahydrofuran, n-hexane, n-pentane, and n-octane. The mixture of C_{60}/C_{70} dissolves appreciably better in boiling cyclohexane, from which small black cubes crystallize out on cooling. The material did not melt below 360 °C in a sealed tube; the resulting sample redissolves in benzene, showing no sign of decomposition.

Analytical thin-layer chromatography on silica gel indicated some separation with n-hexane or with n-pentane as eluents, but not with cyclohexane. Analytical HPLC performed with hexanes (5-μm Econosphere silica, Alltech/Applied Science) gave a satisfactory separation (retention times 6.64 and 6.93 min for C_{60} and C_{70}, respectively, at a flow rate of 0.5 mL/min; detector wavelength, 256 nm), indicating the content of C_{70} to be approximately 15% for the Los Angeles samples. Two other minor peaks, possibly other unidentified C_n species, were observed (retention times 5.86 and 8.31 min), but they constituted less than 1.5% of the total mass.

Column chromatography with hexanes on flash silica gel gave a few fractions of C_{60} with ≥95% purity, as determined by HPLC, along with later fractions containing mixtures of C_{60}/C_{70} in various ratios. Because of the poor solubility of C_{60} and C_{70} in these alkanes, only limited amounts of pure C_{60} were made available this way, in insufficient quantity for a reliable ^{13}C NMR spectrum to be measured (see below). However, column chromatography on neutral alumina with hexanes gave an *excellent* separation in analytical quantities. Thus, pure fractions containing C_{60} (99.85%) and C_{70} (>99%) were obtained, as indicated by mass spectrometric measurements described below.
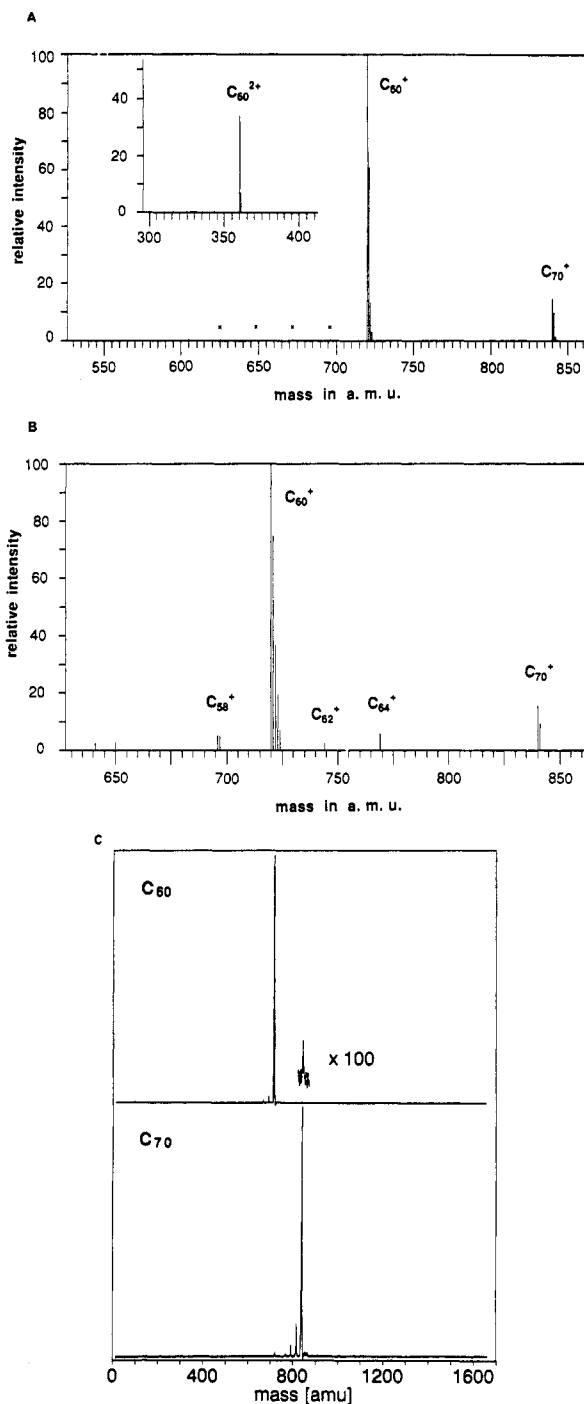
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Figure 1. (A) EI MS spectrum of the C_{60} and C_{70} mixture at 70 eV, with a source temperature of 340 °C. Peaks marked with an × are for the ions of C_{58}, C_{56}, C_{54}, and C_{52} at $m/z = 696, 672, 648$, and 624, respectively. The insert shows the C_{60}^{2+} ion of the same sample. The C_{70}^{2+} ion which also appears in the spectrum is not shown. (B) FAB MS spectrum of the C_{60} and C_{70} mixture with NOBA as the matrix. (C) Laser desorption mass spectra of *pure* C_{60} (above) and C_{70} (below).

Mass Spectrometric Characterization

The 70-eV EI mass spectrometric measurements of the C_{60}/C_{70} mixture's vapor at a source/probe temperature of 340 °C gave exceptionally clean spectra for the samples (Figure 1A). The C_{60}^+ ion at $m/z = 720$ and the C_{70}^+ ion ($m/z = 840$) are dominant, each with precisely the expected isotopic patterns. The next larger peaks are the doubly charged species C_{60}^{2+} and C_{70}^{2+}, at about one-third of the base-peak intensities, indicating that they must be very stable species as well. At lower ionization energy (16 eV), the doubly charged peaks disappear. From several EI spectra, the average ratio of C_{60} to C_{70} was determined to be 87:13, in striking accordance with the HPLC and the ^{13}C NMR esti-

mations (see below). It seems possible that previous estimates[1a] of the C_{70} content ($\sim 2\%$) of the crude C_{60} samples might have resulted from selective sublimation during the preparation of samples for IR and mass spectrometry. To examine this possibility, we have recorded the apparent abundances of the two molecules as the source/probe temperature is increased from 240 to 340 °C and find that the composition of the vapor changes from >99% C_{60} to the above ratio between 260 and 320 °C. A full analysis of the sublimation properties of these species will be reported separately.

The 70-eV EI spectrum of Figure 1A also contains peaks of C_{58}, C_{56}, C_{54}, and C_{52} at m/z = 696, 672, 648, and 624, respectively, corresponding to the expected fragmentation pattern.[5] Because they fail to appear at 16 eV, they must presumably result from fragmentation of the $C_{60}{}^+$ ion, yet their low abundance (0.8% summed together) suggests a very high stability to the carbon cage of C_{60}.

The fast atom bombardment (FAB) mass spectra of the *same* material were again astonishingly simple (Figure 1B), revealing only C_{58}, C_{62}, and C_{64} species besides the $C_{60}{}^+$ and the $C_{70}{}^+$ ions. No peaks were found beyond m/z = 840/841/842 (up to m/z = 1200), thus indicating the absence of higher mass C_n species. In agreement with the EI spectra of the high-temperature vapor, the FAB results indicated the C_{60}/C_{70} ratio to be 87:13. However, the minority species are more abundant than in the EI spectra and are probably the result of intermolecular reactions/fragmentations in the *m*-nitrobenzyl alcohol (NOBA) matrix used in FAB MS.

The laser desorption method is less destructive than the FAB method, but shares the feature of not requiring a continuous, long-time heating of the sample.[6b] Accordingly, the very clean LD mass spectra of C_{60} and C_{70} (Figure 1C) were obtained by time-of-flight analysis of the ions desorbed when 266-nm laser pulses were directed into a pulsed He jet flowing over the sample. On the crude mixture of C_{60}/C_{70}, it was found that all features of (0–2000 amu) except C_{60} and C_{70} vanished at the lowest laser fluences, and these exhibited the same ratio (88:12), within experimental uncertainty, as found in the high-temperature EI mass spectra. When applied to the samples of C_{60} and C_{70} separated by column chromatography on alumina, the C_{60} fraction was found to have a purity of 99.85%, with C_{70} as the residual. On the other hand, the C_{70} fraction had a purity of >99%; the minor peaks, corresponding to C_{68}, C_{66}, C_{64}, and C_{60}, are found by careful analysis of the laser-fluence dependence to all be fragmentation products of C_{70}. In particular, the relative intensity of the C_{60} peak increased directly with increasing laser fluence, thus demonstrating that it results from the fragmentation of C_{70}.

Carbon-13 NMR Spectra

The crude samples of C_{60}/C_{70} obtained from our two sources were independently investigated by ^{13}C NMR and gave identical results. Since it was expected that the spin–lattice relaxation time of the ^{13}C nuclei would be quite long, an inversion recovery experiment was performed to obtain a rough estimate of T_1. Thus, it was determined that T_1 for C_{60} was ≥20 s. The samples of C_{60}/C_{70} were dissolved in an excess of benzene-d_6 and evaporated at 25 °C until saturation was achieved. Using a 30-deg pulse and a 20-s pulse delay, a total of 5780 accumulations obtained over 32 h on a Bruker AM 360 instrument (90.56 MHz) gave a spectrum with an acceptable signal/noise ratio, showing clearly the presence of C_{60} and C_{70} only (Figure 2B). Thus, the peak corresponding to C_{60} is observed at 143.2 ppm (cf. ref 3), and the peaks at 130.9, 145.4, 147.4, 148.1, and 150.7 ppm are attributed to C_{70}, the number of carbons and the 10/20/10/20/10 peak ratio being as expected for the proposed molecular structure.
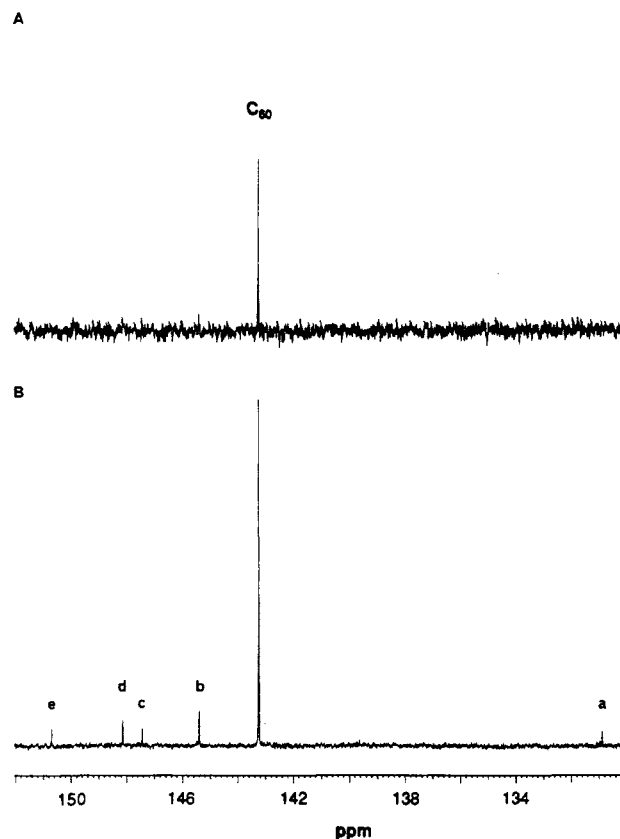
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Figure 2. (A) ^{13}C NMR spectrum of a C_{60} and C_{70} mixture in benzene-d_6 at 296 K after 484 accumulations with a 2-s delay between 30-deg pulses. (B) Same sample after 5780 accumulations with a 20-s delay between pulses. Peaks labeled a, b, c, d, and e are assigned to C_{70}. Both spectra are plotted from 130 to 152 ppm.

The ^{13}C NMR spectrum shown in Figure 2A was performed on the same sample with only 484 accumulations with a 2-s delay between pulses. Thus it is possible to see the single C_{60} peak in a very short time during the experiment. This demonstrates that erroneous interpretations about the purity of the sample can be made if too few accumulations or a less sensitive instrument is used.

With relaxation times for the ^{13}C nuclei of C_{60} and C_{70} being probably very similar, an estimate of the ratio of the two compounds (Figure 2B) by comparison of the peak heights was expected to give a good estimate of the composition of the compound. Thus, the ratio was determined to be 82:18, in reasonable accordance with the HPLC and mass spectrometric determinations described above.

As expected, the proton NMR spectra of the samples dissolved in benzene-d_6 were devoid of any absorptions besides the C_6D_5H peak at 7.15 ppm and a few impurities at 0.3–1.4 ppm, also present in neat solvent.

Optical Absorption Spectra

In ref 1, the optical absorption spectrum in the ultraviolet and visible region was reported for the sublimed C_{60}/C_{70} mixture as a neat solid film. In our work, the spectra of pure C_{60} and C_{70} were recorded in *n*-hexane. Figure 3 shows the absorption spectra in the 200–800-nm region for C_{60} (99.85% purity) and C_{70} (>99%) at 25 °C. Compared with the spectrum of ref 1, one observes small hypsochromic shifts of the peak maxima of C_{60} and alterations in relative intensities as a result of removing the C_{70} contaminant. In addition, the spectrum of pure C_{70} appears to be distinct from any previously reported, including the brief list of maxima given for a sample of unstated purity in ref 3.

Absorption by C_{60} begins with an abrupt onset of 635 nm, followed by several bands of varying width (centered at 621, 598, 591, 568, 540, and 492 nm), and a highly transparent region at 420–440 nm. The structure of the visible absorption spectrum
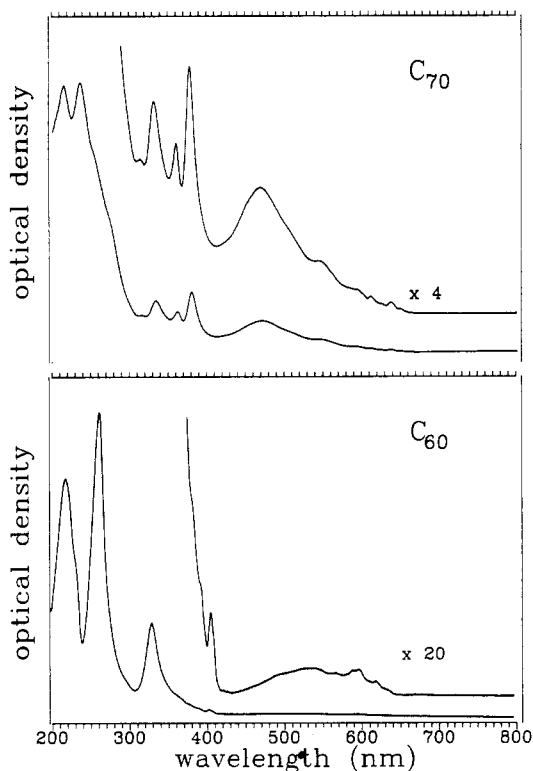
Figure 3. (A, top) Electronic absorption spectrum of dilute C_{70} in hexanes at 25 °C. The insert is the spectrum of the same sample at 4× concentration. (B, bottom) Electronic absorption spectrum of dilute C_{60} in hexanes at 25 °C. The insert is the spectrum of the same sample at 20× concentration.

is suggestive of vibrational structure from one or two forbidden electronic transitions. The combination of transparency in this blue region and in the red (>635 nm) gives dilute solutions a distinct purple color to the eye. A second onset leading to stronger absorption occurs in the form of a band at 404 nm, with a shoulder at 408 nm. These are followed by distinct shoulders at 396, 391, 377, and 365 nm, also suggestive of vibrational structure, appearing on a strong rise toward the first major maximum at 328 nm. The ultraviolet region is dominated by this feature and two other strong broad bands peaking at 211 and 256 nm, the former with a shoulder at 227 nm.

Based on these results, it seems unlikely that neutral C_{60} is the carrier of the interstellar 220-nm absorption band,[7] as the 255-

and 330-nm peaks are not concurrently observed.

Absorption by C_{70} begins with a weak onset band at 650 nm, followed by a series of peaks (637, 624, 610, 600, and 594 nm) superimposed on a gradually rising continuum leading to stronger maxima at 544 and 469 nm. A broad minimum covers the blue-violet region, and maxima of intermediate strength appear in the near-ultraviolet region at 378, 359, and 331 nm. Following a weaker maximum at 313 nm, very strong absorptions appear with three shoulders leading to the dominant bands at 236 and 215 nm. Dilute C_{70} solutions are orange-red in color. Detailed comparison of the spectra indicates no coincidences between C_{70} and C_{60} bands, as would be expected from the purities stated above.

The FT-IR spectrum of the C_{60} and C_{70} mixture performed with a conventional KBr pellet showed the four strongest bands for C_{60} at 1430, 1182, 577, and 527 cm^{-1}, as observed previously by Krätschmer et al.[1] In addition, the strong peak at 673 cm^{-1} mentioned by these authors was present, together with a smaller peak at 795 cm^{-1}.

Conclusion

The new molecular forms of carbon, C_{60} and C_{70}, were prepared following the method of Krätschmer et al.[1] in a consistently high yield (14%).[1] The benzene-soluble material extracted from the graphite evaporation product is predominantly constituted of C_{60} and C_{70}. Three independent methods, namely HPLC, mass spectroscopy, and ^{13}C NMR, demonstrate that these two compounds are present in a ratio near 85:15. The two compounds can be separated by column chromatography on alumina, allowing as for now the purification of minute quantities of pure C_{60} and C_{70}. Support for the proposed symmetrical cage structures (fullerenes) of C_{60} and C_{70} is inferred from the simplicity of the ^{13}C NMR spectra and the strong presence of the C_{60}^{2+} and C_{70}^{2+} ions. Attempts at the X-ray determination of the C_{60} molecular structure are now actively pursued.[6]

Note Added in Proof. The soluble byproduct (HPLC retention time 8.31 min) has since been isolated and determined to be C_{84} by laser desorption MS. The ^{13}C NMR spectrum of *pure* C_{70} (in 1,1,2,2-tetrachloroethane-d_2) has *only* the five lines at 131.0, 145.4, 147.5, 148.2, and 150.8 ppm.

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