Anaerobic Preparation and Solvent-Free Separation of Uranium Endohedral Metallofullerenes

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Received October 18, 1996. Revised Manuscript Received May 15, 1997[⊗]

Safe production, handling, and separation of depleted uranium endohedral metallofullernes in an oxygen-free environment is demonstrated. Films of C_{60}, C_{70}, and M@C_{60} are produced by subliming fullerenes from arc-produced soot onto a mass spectrometry target (with ca. 1% impurities of higher fullerenes). Also, films consisting of higher fullerenes (empty and full) and mostly devoid of C_{60} or C_{70} are made by subliming at higher temperatures. The temperature of the soot must be uniform and held constant during sublimation in order to produce high-quality films. M@C_{60} requires a slightly higher temperature for sublimation than empty C_{60}, the likely result of stronger interactions between M@C_{60} and its surroundings in the soot.

Introduction

Since the discovery of a method for bulk synthesis of the fullerenes,[1] research into the empty carbon cages has progressed rapidly, while investigations into endohedral fullerenes ("endos", colloquially) have moved at a slower pace. The main reasons for this discrepancy are that the endos typically comprise only 10% or less of all fullerenes produced and most are insoluble as well as air sensitive. Experiments in which soot containing a wide range of metallofullerenes is exposed to air results in the sublimation of only the special endohedral metallofullerenes Ln@C_{74} and Ln@C_{82} even though Ln@C_{60} is clearly the dominant metallofullerene in the soot.[2,3] Methods traditional in empty fullerene science, such as brushing the soot from an open arc chamber, Soxhlet extraction, and HPLC, cause most endos to disappear from the sample. To date, all the experimental work has centered on the unusual C_{82} endohedral fullerenes (e.g., Ln@C_{82}, a lanthanide atom within the 82-atom carbon cage) that can survive in air and organic solvents.[4] The exceptional behavior of the soluble endos likely reflects fundamental differences between their electronic structure and, for instance, M@C_{60}. Reports of necessarily different laboratory techniques for isolating the rest of the endos have not appeared.

Working with actinides presents additional difficulties. Actinide-containing compounds, especially when fine powders, must be contained to prevent skin contamination or uptake into the researchers' lungs. Purification of An@C_{82} by traditional solvent methods are less attractive because they would entail the creation of a large volume of mixed waste. Waste having a radioactive component and an otherwise hazardous component, such as an organic solvent, is termed mixed waste and is expensive to dispose of. A moratorium on its generation was in effect at Los Alamos National Laboratory (LANL) when this project was begun. Considering contamination control led to closed containers and dryboxes, which were easily designed for complete anaerobic handling of fullerenes and soot. The need to avoid mixed waste led to sublimation for the separation of fullerenes from soot, and the technique was pressed to include separation of fullerenes from each other. An early report of gradient sublimation using a crude apparatus[3] showed such poor selectivity that we were not confident with this approach. Separations based on sublimation followed by effusion down a temperature gradient of C_{60}/C_{70} mixtures did achieve ultrapure C_{60}.[5] Since sublimation is inherently simple and cost-effective, it merited a second try.

In this paper, a method for generating and working with fullerenes and fullerene soot anaerobically is presented, and its benefits displayed. Sublimation of fullerenes from soot at carefully controlled temperatures is shown to be an effective technique for the separation of mixed fullerenes into size groups. M@C_{60} (M = La, U) are separated from all other endohedral metallofullerenes by this method. Analysis of the samples was performed by laser desorption time-of-flight mass spectrometry (LD-TOF-MS) employing a nitrogen laser.

Experimental Section

A carbon arc fullerene generator was built along the lines of those well-known in the literature, with the additional feature of being able to transport the soot anaerobically into the drybox. The arcing chamber section is depicted in Figure 1. Not shown, the vacuum seals around the rods are made by ultra-Torr fittings to the water cooling hard copper pipe that also serves as the mount for the graphite rods. This arrangement allows a sliding feed for the rods. An airlock system on

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

(1) Kratschmer, W.; Lamb, L. D.; Fostiropoulous, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(2) Chai, Y.; Guo, T.; Jin, C.; Haufler, R. L.; Chibante, P. F.; Fure, J.; Wang, L.; Alford, J. M.; Smalley, R. E. *J. Phys. Chem.* **1991**, *95*, 7564.

(3) Yeretzian, C.; Wiley: J. B.; Holczer, K.; Su, T.; Nguyen, S.; Kaner, R. B.; Whetten, R. L. *J. Phys. Chem.* **1993**, *97*, 10097.

(4) (a) Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 981. (b) Bethune, D. S.; Johnson, R. D.; Salem, J. R.; de Vries, M. S.; Yannoi, C. S. *Nature* **1993**, *366*, 123.

(5) Averitt, R. D.; Alford, J. M.; Halas, N. J. *Appl. Phys. Lett.* **1994**, *65*, 374.

S0897-4756(96)00540-6 CCC: $14.00

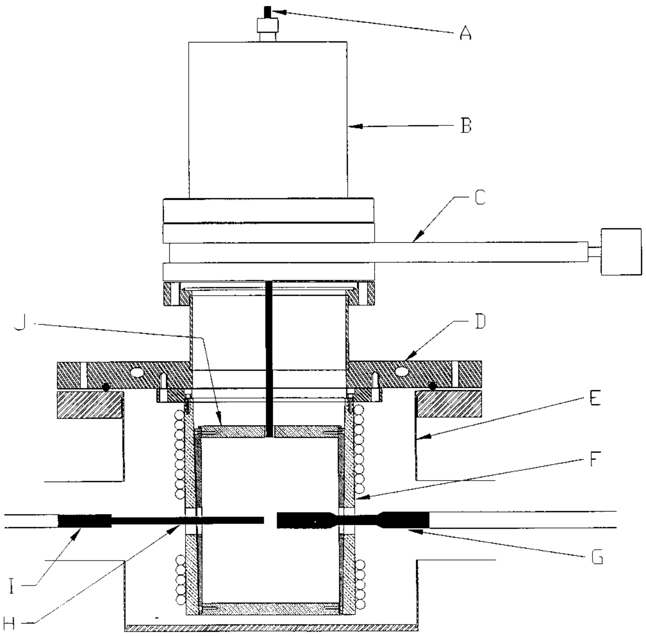

Figure 1. Arc reactor allowing anaerobic collection of soot: (A) two-piece stainless steel rod to raise/lower inner cylinder, slides through ultra-Torr fitting; (B) steel collection can; (C) 6 in. i.d. gate valve (MDC, Hayward, CA); (D) water-cooled 16 in. o.d. steel lid; (E) 12 in. i.d. steel outer chamber; (F) copper outer cylinder hung from lid with $^3/_8$ in. soft copper coils for water cooling; (G) $^5/_8$ in. graphite electrode screwed into water-cooled copper pipe; (H) rod to be consumed, press fit into mount; (I) $^1/_2$ in. o.d. graphite mount with tapered hole, screwed onto water-cooled copper pipe; (J) retractable inner copper cylinder which contains almost all of the soot, the top and bottom are formed $^1/_4$ in. thick copper disks held in place by counter sunk 4-40 brass screws.

the consumable rod side allowed for rapid replacement of spent or broken rods without venting the chamber. The maximum length of sliding rod that could fit through the airlock was six inches. The pressure was kept at 100 ±1 Torr of He. Use of an MDC pressure controller and a manually set needle valve on the vacuum pump manifold allowed the atmosphere in the arc chamber to be continually refreshed. Power was provided by an Airco ac arc welder capable of providing 500 A, but generally kept in the 100−200 A range, varying with the size of the rod to be consumed.

Three kinds of rods were vaporized. A $^1/_4$ in. diameter graphite rod of AXF-5Q quality from POCO Graphite, Inc. (Decatur, TX) was used for empty fullerene studies. Graphite rods doped with La at 0.5 atom % were received from TDA Research (Wheat Ridge, CO) and used to prepare the La metallofullerenes.[6] The uranium metallofullerene studies were performed using graphite rods doped with 0.55 atom % depleted uranium that were prepared at Los Alamos (U:C = 1:180). The uranium-doped graphite rods were made using fabrication procedures for uranium-loaded graphite fuel elements used in the space nuclear propulsion program.[7] These procedures were developed in order to ensure that the product had a homogeneous uranium distribution in the graphite, a uniform and predetermined density, and a precise posttreatment geometry. The fabrication uses graphite flour, a thermosetting resin binder, wood flour, and UO_2. The graphite flour was obtained from Great Lakes Carbon, Niagara Falls, NY, Grade 870 RL and had an average particle size of 5 μm. Varcum thermosetting resin from Varcum Chemical Division of Reichold, Inc., Niagara Falls, NY, was used. This resin is a partially polymerized furfuryl alcohol that was catalyzed by the addition of 4 wt % maleic anhydride. Wood flour burns out at relatively low temperatures and is used to create porosity that permits the gases from resin decomposition to escape without building up pressure that would cause defects. Depleted uranium in the form of UO_2 particles with average particle size of 5 μm was used. The graphite flour and wood flour were mixed and blended, the UO_2 was added and blended, and finally the binder was added and mixed by hand. The ratios of the ingredients were 6.76:2.77:0.0008:1 by weight of graphite flour:resin:wood flour:UO_2. A 60 in. rod was extruded onto a fixture that went directly to a curing oven. The extrusion pressure was 17.2 MPa and an extrusion die was used that resulted in a $^1/_2$ in. rod after curing. The extrusion was heat cured at 250 °C for 96 h and 850 °C for 72 h. The first heat treatment decomposed the wood flour and set the resin. Large volumes of gas are evolved during this cycle. The second heat treatment resulted in decomposition of the resin and further outgassing. A ∼15% volume shrinkage occurs during the two heat treatments. The final product is a $^1/_2$ in. diameter graphite rod containing 200 mg/cm^3 of UO_2 with a density of 1.8 g/cm^3. Uranium carbides are not formed during these heat treatments; such species require heat treatments above 2000 °C.[8] Although the arc reactor proved capable of arcing $^1/_2$ in. rods, most runs were performed with $^1/_4$ in. rods to alleviate difficulties in maintaining the proper alignment. These were made by machining down the $^1/_2$ in. rods.

After a run, the rods were withdrawn outside of the cylinders, and the inner cylinder (with the tapered outside) was pulled up through the gate valve into the can. The gate valve was closed, and the copper gasket seal between the valve and the chamber was broken. The valve and can were then taken into the antechamber of a Vacuum Atmospheres (Hawthorne, CA) glovebox. Deposits on the cold electrode were broken off and left at the bottom of the chamber. External surfaces on the now open arcing chamber were examined for contamination using both a hand held Eberline SP beta/gamma meter and an alpha probe. Typically, there was no evidence of soot escaping the inner cylinder, although it was impossible to view through the holes in the outer cylinder where the rods were fed in. A lid was placed over the chamber to prevent the stirring of any fine dust while not in use.

Once inside the glovebox, the can was separated from the gate valve and the inner cylinder lid was removed. The soot on the inside walls of the cylinder was then brushed onto aluminum foil. The foil was then rolled up for storage to prevent exposure to UV light. The glovebox atmosphere was Ar, where static electricity is much less of a problem than in a nitrogen atmosphere. An oxygen monitor continuously showed O_2 concentrations of less than 1 ppm.

Figure 2 depicts the simple sublimation apparatus. The gate valve accompanied the quartz soot container into the glovebox, where the soot was loaded in and the gate valve closed. Once out of the glovebox and mounted as shown, with all of the soot occupying a thin ($^1/_8$ in.) layer on the bottom of the hourglass, a chromel−alumel thermocouple was mounted with the tip pressed against the side of the quartz where the soot lay. Sublimation was performed under vacuum, with a typical operating pressure of 0.1 mTorr. Not shown, insulation fully sealed the top and bottom of the furnace. After sublimation, the apparatus offers flexibility in choosing what gets exposed to air during disassembly. Thus, parts could be returned to the glovebox for further handling. While the temperatures quoted below are correct for this apparatus, they may vary according to sublimer design and thermocouple placement.

LD-TOF-MS were performed on a standard reflectron time-of-flight instrument purchased from R. M. Jordan and turbopumped to an operating pressure of <10 nTorr. Both ionization and desorption were accomplished by a nitrogen laser, Model UV12 from Laser Photonics. The beam was

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(6) Cagle, D. W.; Thrash, T. P.; Alford, J. M.; Chibante, L. P. F.; Ehrardt, G. J.; Wilson, L. J. *J. Am. Chem. Soc.* **1996**, *118*, 8043.

(7) Davidson, K. V. AIP Conference Proceedings **1991**, *217*, 1015. Taub, J. M. Report LA-5931 available from NTIS, also available on the Internet using an Acrobat viewer at http://lib-www.lanl.gov/la-pubs/00374261.pdf.

(8) Pavone, D. Report LA-2096 available from NTIS, also available on the Internet using an Acrobat viewer at http://lib-www.lanl.gov/la-pubs/00318112.pdf.

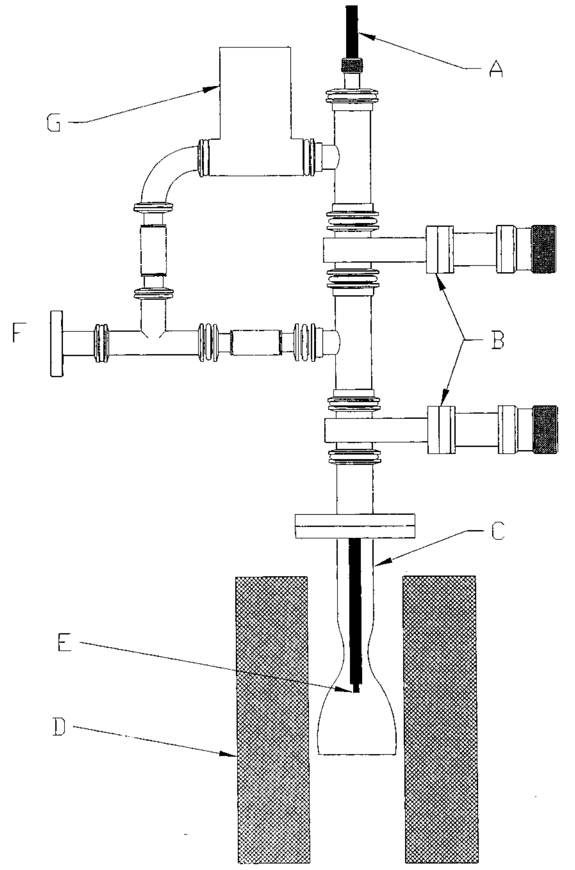

Figure 2. Simple sublimation apparatus: (A) retractable water-cooled rod; (B) 1.5 in. i.d. gate valves; (C) quartz soot container, 3.5 in. across bottom; (D) 1000 °C furnace; (E) mass spec target; (F) to vacuum pumps; (G) bellows valve.

Table 1. Ionization Potentials of Fullerenes[a]

molecule	IP[9]	IP[10]	no. of ArF photons to ionize	no. of N_2 photons to ionize
C_{60}	7.59 ± 0.02	7.78	2	3
C_{70}	7.48 ± 0.05	7.64	2	3
C_{76}	7.10 ± 0.10	7.14	2	2
C_{84}	7.15 ± 0.10		2	2
$Y@C_{82}$		6.22	1	2
$La@C_n$	6.3 ± 0.1		1	2

[a] ArF: 193 nm = 6.4 eV/$h\nu$. N_2: 337 nm = 3.7 eV/$h\nu$.

passed through a circular iris, several neutral density filters, and then a 50 cm focal length spherical focusing lens to give an elliptical spot. The beam energy was estimated as 15 μJ/pulse, but the fullerenes could undergo significant fragmentation if the power density was too high. So spectra were very sensitive to position of the lens, but (as the figures show) it could be located such that no fragmentation appeared. A Precision Instruments 9825 signal averaging PC card provided 16384 points at a 20 ns sampling rate and 16 bit transfer to the presentation software, TOFWARE (Ilys Software, PA). Typically, 1024 shots at 10 Hz were averaged. All spectra display singly ionized positive ions in the fullerene mass range with flight times on the order of 150 μs.

Table 1 gives a comparison of literature values for ionization potentials of various fullerenes and compares the number of photons required of the N_2 laser as compared to the more common ArF laser.[9,10] It is apparent that all fullerenes, with the exception of C_{60} and C_{70}, require two N_2 photons for ionization. In that respect, peak heights from higher empties and any endo are directly comparable as reflective of relative concentrations in the sample. This is an advantage over ArF ionization, which greatly exaggerates the presence of endos.

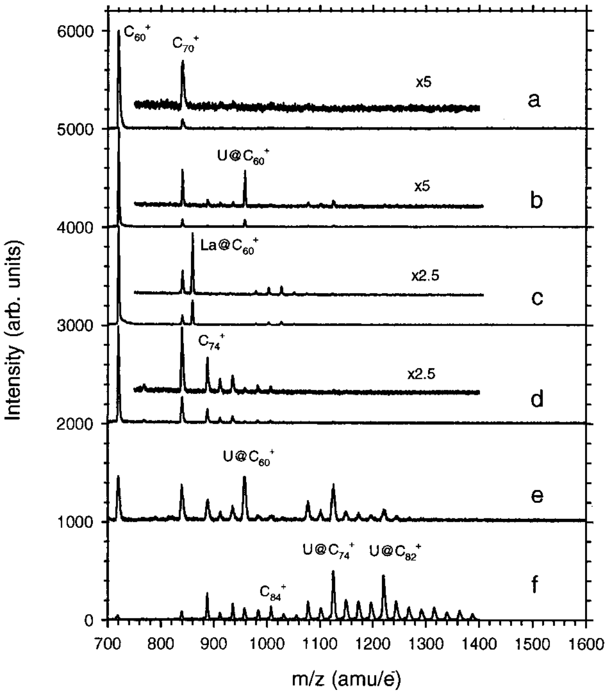

Figure 3. LD-TOF-MS spectra of the surface of sublimed films. All soots from which the films were sublimed are mixed metallo- and empty fullerene containing except (d), which is only empties. Sublimation temperatures and metals used in producing the soot are (a) 350 °C U; (b) 365 °C U; (c) 365 °C La; (d) 380 °C; (e) 510 °C U; (f) 680 °C U.

Results

In the first experiment, anaerobically collected soot from uranium-doped rods was placed in the sublimer and heated to a specific temperature. That temperature was held constant for an hour or two, producing a film of approximately 10−100 μm in thickness. The mass spec target was then withdrawn and placed into the LD-TOF-MS. Spectra of films produced at sublimation temperatures over the range 350−680 °C are displayed in Figure 3. Lower temperatures did not produce enough sublimed fullerenes to analyze. Since the laser desorbs only from the surface of the target, the data display only what sublimed onto the target last.

For comparison, the sides of the target of a 365 °C sublimation were scraped and sonicated into methanol. The solution was dripped onto a second target, which was heated to evaporate the methanol. This approach samples the entire thickness of the film rather than just the top layer. The analysis, shown in Figure 4, reveals a great drop of the $U@C_{60}$ peak intensity relative to the others as compared to Figure 3b where only the target surface was examined. It seems that the C_{60} sublimed first, coating the target, before other species begin to layer on. When a film created over a broad temperature range was resublimed, a disappointingly large fraction of the material did not leave the first target. This may be caused by the lower layers of the film having enough energy to be chemically reactive before the top layers

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(9) (a) Empty fullerene IPs from: Steger, H.; Holzapfel, J.; Hielscher, A.; Kamke, W.; Hertel, I. V. *Chem Phys. Lett.* **1995**, *234*, 455. (b) Endo IP from Hettich, R. L.; Ying, C.; Compton, R. In *Fullerenes: Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1994; p 1457.

(10) Nagase, S.; Kobayashi, K. *Chem. Phys. Lett.* **1995**, *228*, 106.

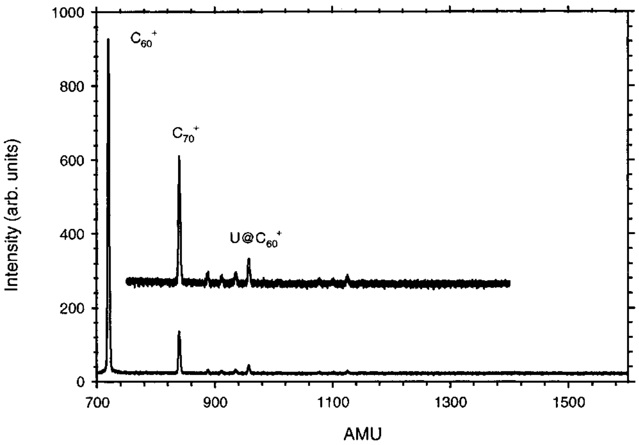

Figure 4. LD-TOF-MS spectrum of an evaporated film produced from the same sublimed sample as in Figure 3b. A portion of the sublimed material was homogeneously suspended in methanol, which was then evaporated onto a mass spec target. The spectrum shows the relative composition of all of the sublimed material, not just the material on the target surface.

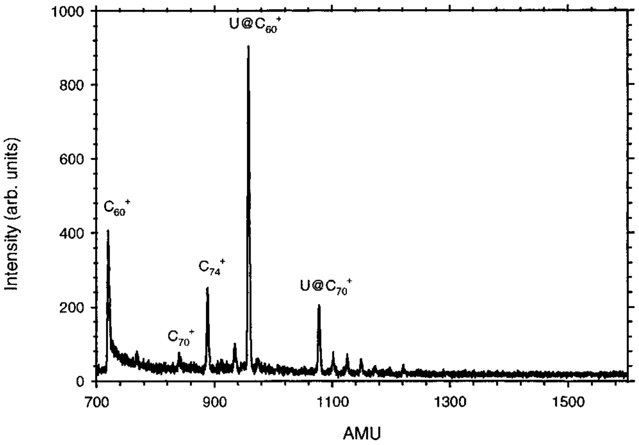

Figure 5. LD-TOF-MS spectrum from the face of sample 3b after dipping in *o*-xylene to remove most of the soluble material.

(consisting of lower vapor pressure fullerenes) are ready to take flight. Akin to photopolymerization, many fullerenes have enough energy when heated to react with each other, forming high molecular weight carbon networks instead of subliming. By subliming at a lower temperature (e.g., 350) first, to empty the soot of undesired fullerenes, and then proceeding to sublime at the desired temperature (e.g., 365 for M@C60), the film produced was more uniform.

A quick attempt was made to effect further separation by returning a 365 °C sublimed target to the drybox and setting it in sparged *o*-xylenes. The soluble fullerenes should be preferentially removed. The target was removed from the xylenes while there was still a little film left on its surface and then placed in the MS, with the result shown in Figure 5.

Discussion

From our perspective, a principle of success of the methods employed was that no detectable uranium contamination was ever discovered outside the arcing chamber and glovebox. This gives us the confidence to attempt more active nuclei in the future.

Uranium endohedral metallofullerenes form in similar relative abundance to their lanthanide analogues, with similar magic numbers: 60, 70, 74, 82, etc. However, the previously reported[11] $U@C_{28}$ species did not appear in our mass spectra, even when the unsublimed soot was analyzed. This is conceivably due to differences between the way the carbon/uranium vapor condenses after vaporization in the Los Alamos arc and the way it condenses in the heated buffer gas employed in the Smalley reactors. A uranium concentration that was too low may also play a role in $U@C_{28}$ not appearing; however the uranium concentration was at the lower bound of the uranium concentrations used in the Smalley reactors when $U@C_{28}$ was observed.

Although there are many reports of sublimation of C_{60}, C_{70}, and mixtures with or without higher empty fullerenes aimed at determining their vapor pressures,[12−15] the data from different groups do not converge well. This is thought to be a problem with the purity of the liquid-extracted samples because, after exposure to solvent, the solvent molecules show an incredibly high affinity for the fullerene lattice.[16] Despite discrepancies, previous works agree that smaller fullerenes have higher vapor pressures. A theory has been published that predicts sublimation enthalpies for fullerenes based on the number of carbon atoms per molecule.[17]

Conceptually, to change a fullerene solid into vapor, the balls must incur large translations in their lattice position. For C_{60} lattices, a variety of experiments determining the transport properties of the fullerene lattice reveal that interaction between the balls is exceedingly weak.[18] Since the observed extrinsic properties of the higher fullerenes C_{70}, C_{76}, C_{78}, and C_{84} closely parallel those of C_{60}, an analogy of weak intermolecular interaction in the lattice of these fullerenes seems reasonable. With the near absence of intermolecular forces, fullerene vapor pressures may be compared based on molecular properties, specifically, the total energy stored in the molecule. Energy is stored in the vibrations of a molecule, with the number of vibrations equal to thrice the number of atoms less six. Addition of a single metal atom to the molecule results in only a small increase in this energy.

Quantum chemistry calculations agree that a metal inside the fullerene cage donates several valence electron to the cage.[19,20] This is expected to result in increased electrostatic interaction between the endo and

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(11) Guo, T.; Diener, M. D.; Chai, Y.; Alford, M. J.; Haufler, R. E.; McClure, S. M.; Ohno, T.; Weaver, J. H.; Scuseria, G. E.; Smalley, R. E. *Science* **1992**, *257*, 1661.

(12) Popovic, A.; Drazic, G.; Marsel, J. *Rapid Commun. Mass. Spectrosc.* **1994**, *8*, 985.

(13) (a) Pan, C.; Chandrasekharaiah, M. S.; Agan, D.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1992**, *96*, 6752. (b) Pan, C.; Sampson, M. P.; Chai, Y.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.* **1991**, *95*, 2944.

(14) (a) Mathews, C. K.; Sai Baba, M.; Lakshmi Narasimhan, T. S.; Balasubramanian, R.; Sivaraman, N.; Srinivasan, T. G.; Vasudeva Rao, P. R. *J. Phys. Chem.* **1992**, *96*, 3566. (b) Ibid. *Fullerene Sci. Technol. 1* **1993**, 101.

(15) Abrefeh, J.; Olander, D. R.; Baloch, M.; Siekhaus, W. *J. Appl. Phys. Lett.* **1992**, *60*, 1313.

(16) Milliken, J.; Keller, T. M.; Baronavski, A. P.; McElvany, S. W.; Callahan, J. H.; Nelson, H. H. *Chem. Mater.* **1991**, *3*, 386.

(17) Ruoff, R. S. *Chem. Phys. Lett.* **1993**, *208*, 256.

(18) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *J. Mater. Res.* **1993**, *8*, 2054.

(19) Chang, A. H. H.; Ermler, W. C.; Pitzer, R. M. *J. Chem. Phys.* **1992**, *94*, 5004.

its surroundings. Since the observable properties of the M@C_{82} fullerene show unique behavior among endos, and the M@C_{60} and M@C_{70} species seem especially reactive,[3] the intermolecular interactions may vary widely cage to cage. Ignoring any interfullerene interactions, adding an atom to the cage may be expected to lower the vapor pressure because of the extra intrafullerene vibrations, but the effect of a single atom, compared to the existing 60, should be quite small. So an increase in enthalpy of sublimation for an endo of a given size versus the same size empty fullerene is expected and should be tied to the strength of intermolecular interaction.

In Figure 3a, the lowest temperature sublimation reveals C_{60} contaminated with some C_{70}. The presence of C_{70} may be due to the formation of an azeotrope.[10] By moving the temperature up slightly to 380 °C (Figure 3c) using soot without metals, the fullerenes C_{74}, C_{76}, and C_{78} appear as a group. Intermediate temperatures were not successful in further separating them. The presence of C_{74} was reported in earlier sublimation experiments where the soot was air exposed[3] but is never observed in solvent-extracted fullerenes. The mixed solid shown in the mass spectrum (Figure 3d) is currently under study to elucidate the nature of C_{74}.

When endo-containing soots are sublimed, M@C_{60} begins to appear on the target at 365 °C (Figure 3b,c). Noting the nearly complete absence of other M@C_n, it seems that the single temperature sublimation technique is (surprisingly) successful at isolating M@C_{60} from other M@C_n. The low temperature at which M@C_{60} takes flight would seem to indicate that the strength of intermolecular forces in the soot are increased by only a few kcal/mol. Qualitatively, M@C_{60} has a higher vapor pressure than C_{74}, C_{76}, or C_{78} and lower than C_{60}. The higher fullerenes and the M@C_{60} are about equally dilute in the soot, and first-order molecular connectivity theory[15] predicts the enthalpy of sublimation for C_{76} to be about 50 kcal/mol versus about 40 kcal/mol for C_{60}. The temperatures for sublimation of U@C_{60} and La@C_{60} are about the same (Figure 3b,c), showing that, for endos, the vapor pressures are not dependent on the mass of the molecule. The films analyzed in Figure 3b,c may be thought of as M@C_{60}-doped C_{60} (with C_{70} contamination). The electrochemistry of M@C_{82} suggests that endos will be facile electron donors.[21] Thus, the film characterized in Figure 3b,c might exist as *n*-doped C_{60}, where the dopant has the same unusual size and shape of buckminsterfullerene.

An attempt, involving straying from the solvent-free path, was made to further improve the purity of the films. By dipping the target with film into sparged *o*-xylene in the glovebox (only a few milliliters were required), the M@C_{60} can be further concentrated. In Figure 5 it is seen that C_{70} has dropped into the baseline and become barely detectable, while M@C_{60} now appears larger than C_{60}. (However, it requires more photons to ionize C_{60} than M@C_{60}, so C_{60} remains the major constituent of the film.) After this exposure to relatively dry solvent, the M@C_{60} could not be resublimed, possibly due to reaction upon heating with residual solvent (whose low mass fragments could be detected in the mass spec).

At the highest temperatures, as in Figure 3f, the C_{60} and C_{70} have been mostly removed from the soot, and only higher fullerenes (empty and full) remain. From Table 1, the relative peak heights in the mass spectrum for empties and endos should be directly comparable because the same number of photons is required to ionize each of them. The large relative intensities of the U endos is in agreement with an earlier report of uranium having a special ability to form endohedral fullerenes.[9] Even after optimizing the concentration of lanthanum, the MS peak heights were not half as large as those for U (relative to the empties). Creating materials of this composition may be useful for applications where the specific fullerene cage around the metal is unimportant, only that most of the material consist of fullerene-caged metal atoms.

High-temperature sublimation may also be a way to preconcentrate higher fullerenes prior to HPLC separation. Although the expensive PYE columns can separate individual higher empties in a single step (or Ln@C_{82} in two steps),[22] preconcentration via sublimation of higher fullerenes in the injected mixture will result in increased amounts of isolated material per injection. While sublimation as described here is still a batch process, the size of the batch may be very large compared to the size of an HPLC injection. Older, less expensive columns require a preconcentration injection prior to isolation of specific higher C_n or M@C_{82}. Sublimation, saving the high-temperature fraction, can replace the preconcentration step and has the advantages of avoiding solvent usage and reducing both labor and column time.

Conclusions

Safe production and manipulation of actinide containing fullerenes has been demonstrated using anaerobic handling techniques. Sublimation of empty and endohedral metallofullernes has proved its utility as a technique for separation of fullerenes into cage-size groups. This allows the preparation of films containing only C_{60}, C_{70}, and M@C_{60} as well as films greatly enriched in higher fullerenes relative to C_{60} and C_{70}. The temperatures required for sublimation of M@C_{60} indicate that its enthalpy of vaporization is a few kcal/mol higher than C_{60}, the likely result of stronger interactions between M@C_{60} and its environment in the soot.

Acknowledgment. The authors would like to thank J. M. Alford and N. V. Coppa for fruitful discussions and “B.” J. McFarlan for technical assistance.

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(20) (a) Laasonen, K.; Andreoni, W.; Parrinello, M. *Science* **1992**, *258*, 1916. (b) Nagase, S.; Kobayashi, K.; Kato, T.; Achiba, Y. *Chem. Phys. Lett.* **1993**, *201*, 475.

(21) Suzuki, T.; Kikuchi, K; Oguri, F.; Nakao, Y.; Suzuki, S.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron* **1996**, *52*, 4973.

(22) Funasaka, H.; Sugiyama, K.; Yamamoto, K.; Takahashi, T. *J. Phys. Chem.* **1995**, *99*, 1826.