

CARBON ARC GENERATION OF C<sub>60</sub>

R. E. Haufler\*, Y. Chai\*, L.P.F. Chibante\*, J. Conceicao\*, Changming Jin\*,  
Lai-Sheng Wang, Shigeo Maruyama\*\* and R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Physics  
Rice University Houston, Texas 77251

\* Robert A. Welch Foundation Predoctoral Fellow.

\*\* RQI Visiting Fellow, Department of Mechanical Engineering, University of  
Tokyo, Bunko-ku, Tokyo 113, Japan.

## ABSTRACT

Generation of C<sub>60</sub> at a rate of more than 10 grams per day has been accomplished by operation of a carbon arc in an atmosphere of helium. Optimum yield of 15% was found to occur near 100-200 torr, but yields greater than 3% were found throughout the range between 50 and 760 torr. A model is proposed to explain the observed behavior based on competition between annealing of graphitic sheets to curve so that they minimize dangling bonds, and further rapid growth of these sheets in the gas phase to form giant fullerenes. In agreement with predictions of this model, laser vaporization of graphite targets was found to produce macroscopic quantities of C<sub>60</sub> only when performed in an oven above 1000 C.

## INTRODUCTION

In an earlier publication from this group at Rice [1], an efficient "contact arc" vaporization procedure was described which was capable of producing C<sub>60</sub> at the rate of roughly one gram per day. The purpose of the following discussion is to present an improved procedure which is now easily capable of producing a gram of C<sub>60</sub> in less than one hour. Additionally, we present a model for the formation of C<sub>60</sub>, C<sub>70</sub>, and the other fullerenes in condensing carbon vapors which offers an explanation of why such high yields are obtained under the conditions of a carbon arc or a resistively heated carbon rod in an inert atmosphere, and why this yield is much lower under the conditions of Q-switched laser vaporization. The model predicts that the yield of C<sub>60</sub> produced by laser vaporization will increase when the local gas temperature is increased. Results from such a laser vaporization experiment in an oven at 1200 C are reported here, confirming the predictions of the model.

In addition we present a plausible explanation of how, until recently, C<sub>60</sub> has managed to elude detection for the past 10,000 or so years of recorded human history.

### A NEW C<sub>60</sub> GENERATOR

Figure 1 displays a cross-sectional schematic view of the new C<sub>60</sub>/C<sub>70</sub> generator. Here two 6 mm diameter graphite rods (Ultra Carbon, "ultra F" purity), 15 cm long are mounted in a 25 cm cubic vacuum chamber such that they can be driven to meet each other in the center of the cube by two external threaded rod mechanisms. As shown in the figure, these rods pass through water-cooled high current electrical feedthroughs, good electrical contact being maintained by spring-loaded gimbal wheels. Each graphite rod is attached to the end of a 10 mm diameter stainless steel rod which passes through an o-ring seal fitting in the adjacent vacuum wall. On the outside these stainless steel rods are attached via electrically insulating nylon adaptors to two threaded rods, 24 turns per inch, which in turn pass through threaded blocks bolted on a fixed plate. Turning these threaded rods then results in the graphite rods on the inside of the vacuum chamber being driven at each other. The graphite rods turn with the threaded rods. Since both threaded rods were right-handed screws, and they were driven in opposite directions, and the effect of the screw motion was to rotate the two rods in opposite directions, thus helping to maintain even erosion of the rods as their ends were vaporized in the arc. Although the initial intent of this design was to facilitate full computer control of the gap between the graphite rods during vaporization, simple manual control was found to be adequate for the work described below.

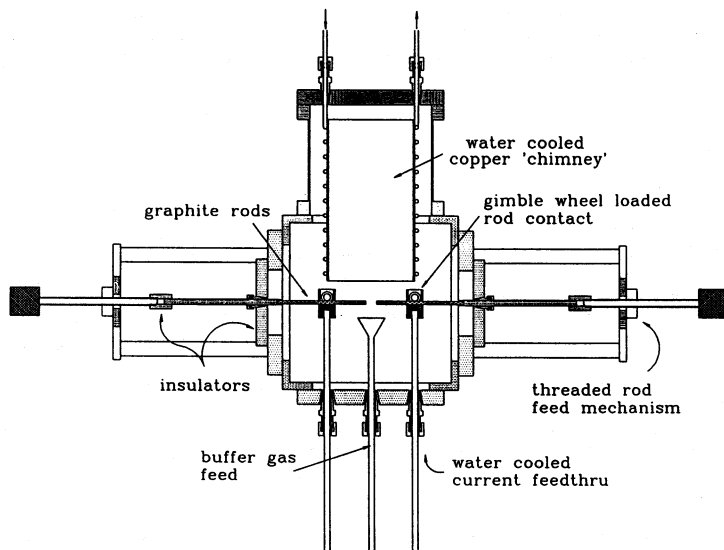


Figure 1. Schematic cross-sectional view of a carbon arc C<sub>60</sub> generator.

The power supply used to generate the arc was an ordinary welding power supply (Sears Craftsman 230/140 AC/DC "Infinite Amp" welding power supply) operated in the AC mode at a current setting of 150 amp. In practice the rods

were moved into contact after the power supply was turned on, and then backed off a few millimeters after the arc was initiated. When operating with 100 torr helium, the arc voltage at a current of 150 A was found to be typically 27 V rms (60 Hz), and only slowly dependent on the spacing of the arc gap.

As shown in Fig. 1, the buffer gas was brought into the vacuum chamber from the bottom via a tube which directed the gas flow at the region of the carbon arc. In order to remove water vapor and other gases evolved during the vaporization of the graphite rods, a constant flow was maintained. After an initial evacuation to below 50 millitorr with a mechanical pump, the chamber was back-filled to the desired operating pressure (typically 100 torr). The input gas flow was then adjusted to the desired value (typically 100 sccm). During operation with an earlier version of this apparatus it was found that a cooling water leak sufficient to leave a  $H_2O$  partial pressure of as little as 0.1 torr produced a drastic reduction in the  $C_{60}$  yield.

The result of generating a carbon arc under these conditions is to produce a large amount of a rather granular soot which uniformly coats all the inside surfaces of the chamber. Because of its granularity, it is easily removed from the deposition surfaces simply by brushing with a camel-hair or similar brush. In order to simplify the process of collection of this soot, and to moderate the infrared heating of the chamber walls which would otherwise occur due to light emission from the carbon arc, we have adopted the water-cooled copper "chimney" design shown in figure 1. Even in the absence of any directed flow from the incoming gas, the design of this chimney was configured so that natural convection currents would carry most of the soot upwards. In operation we found that roughly 50% of the soot moved up through the chimney so that it was deposited on the inside, and to some extent on the outside of this water-cooled structure. With the 100 sccm gas flow this collection efficiency was found to increase to 80%. We suspect that a somewhat more refined design would enable the entire collection operation to be completely separated from the vaporization region. In view of the likely formation of a wide range of polycyclic aromatic carcinogens as side products of this carbon arc operation, we feel the soot collection and subsequent processing deserves careful consideration.

#### RESULTS FROM THE NEW ARC SOURCE

The most significant result of operation of this new device was that the net yield of the  $C_{60}/C_{70}$  product obtained by Soxhlet extraction of the raw graphitic soot was found to be fairly insensitive to the gap between the carbon electrodes during the time the arc was running. Although we had previously believed [1] that there was something special about having the rods in some sort of near contact, this turns out not to be important. As would be expected, the rate of vaporization of the carbon rods was found to be a very sensitive function of the size of the electrode gap: the closer the better. Remarkably, however, the yield of  $C_{60}/C_{70}$  mixture upon extraction with toluene was found to be fairly insensitive to the length of this gap. Thus it was found that yields between 10 and 15% could be obtained both by keeping the rods at a 5 mm gap during the entire vaporization process, and by maintaining a <1mm gap by running the carbon rods at each other at a rate of over 3 cm per minute. Note this later figure corresponds in the case of a 6 mm OD graphite rod to a rate of vaporization of well over 1 gram per minute. At the 10-15% conversion rate into  $C_{60}$  that we typically achieved under these conditions, this corresponds to a  $C_{60}$  generation rate of nearly 10 grams per hour. In practice the task of loading new graphite rods, collecting the soot, and extracting the  $C_{60}/C_{70}$  soon became rate limiting. Under industrial conditions it appears likely that  $C_{60}$  and  $C_{70}$  will be readily manufacturable by such techniques in large (ton) quantities at low cost. This fact virtually

guarantees that C<sub>60</sub> and C<sub>70</sub> will have major materials applications in the not-too-distant future.

At this point only a cursory examination has been made of the variation of C<sub>60</sub>/C<sub>70</sub> yield as a function of buffer gas pressure and composition. In the case of helium, we find that the optimum pressure is in the range of 100 to 200 torr (10-15% yield), but yields as high as 3% may be obtained anywhere between 50 torr and 1 atm. Argon produces similar results, although the peak yields were reduced to 5%. Molecular nitrogen was found to work much less effectively, although some C<sub>60</sub> was produced at a yield of roughly 0.8%. We suspect this lower efficiency of operation in an N<sub>2</sub> environment is due to facile formation of N<sub>2</sub><sup>+</sup>, and atomic N in the plasma. We have no firm evidence yet that the velocity of gas flow over the carbon arc produces any substantial effect on the yield. In principle (see below) this flow velocity parameter may be another useful control on the yield and the overall process of condensation.

#### A MODEL FOR FORMATION OF C<sub>60</sub> AND THE OTHER FULLERENES

Five years ago, soon after the original realization in this laboratory that C<sub>60</sub> could be made extraordinarily special under some conditions [2], a model was proposed [3,4] to rationalize the formation of closed, spheroidal graphitic structures such as soccerball C<sub>60</sub> [5,6]. To most observers at the time, the most incredible aspect of the soccerball hypothesis was not that it involved a hitherto unknown aromatic structure. The hollow I<sub>h</sub> symmetry structure had been shown many years before [7,8] to be a perfectly reasonable form of carbon under the rules of bonding long since demonstrated to be valid for carbon. Instead, the most remarkable proposal seemed to be that any such high symmetry, and therefore low entropy, form of carbon would be produced spontaneously in a high temperature carbon vapor. After all, at high temperatures one expects the TΔS term of the free energy to dominate, and poorly organized, high entropy forms should be preferred. Yet here the most symmetrical of all possible molecules, C<sub>60</sub> in the form of a perfect truncated icosahedron, was postulated to be formed preferentially at extremely high temperatures.

On the other hand, one could argue that spontaneous formation of highly organized structures is actually quite common. Nature is full of examples of beautiful high symmetry forms which have appeared spontaneously out of randomness. Crystals of ice, or diamond, or any of a wide variety of minerals are examples. Alternatively (and perhaps more instructively) there are many sets of structures which appear on a computer screen when calculating cellular automata [9]. Here simple rules which apply only to nearest neighbors are found to lead ultimately, to overall structures of remarkably high symmetry and complexity.

In 1985 it was argued that a sort of nucleation and crystallization process may explain the efficient formation of C<sub>60</sub> [3,4]. The argument is much like the description of a rule for the state of the adjacent cells in cellular automata. Here with carbon condensing in a supersaturated vapor, the rule describes the stability of various alternative forms of graphitic carbon sheets as they grow in size. As first pointed out by Pitzer and Clementi in 1959 [10], the most favored form of small carbon radicals at high temperature in a carbon vapor is likely to be linear chains (which at these temperatures would perhaps more accurately be visualized as writhing carbon snakes). But beyond some length -- say 30 to 40 carbon atoms -- it is reasonable to expect these "snakes" would frequently sample the form of polycyclic aromatic rings, objects we refer to as "graphitic sheets". These structures have the advantage of substantially increasing the average coordination number of the

carbon atoms. Yet they have the disadvantage of having a large number of unsatisfied "dangling" bonds in the sigma bonding framework around the periphery. Although we are conditioned to think of such objects as flat, very stable and rigid molecular structures, this conditioning comes from our experience with the related polycyclic aromatic hydrocarbons, PAHs. In the absence of hydrogen, a substantial fraction of the carbons in this structure are on the periphery of the sheet, and have at least one dangling sigma bond. As in the original proposal advanced in 1985 [3], we now believe it is the rearrangement of the bonding pattern to minimize these peripheral dangling bonds that leads to the formation of  $C_{60}$ .

For a small graphitic sheet there is a substantial advantage to be gained through the use of pentagons. Figure 2, for example, plots the number of dangling  $sp^2$  bonds in the optimum configuration of carbon atoms as a function of cluster size permitting (top) only six membered rings, and (bottom) as many five membered rings as possible with the extra condition that no two 5-membered rings share an edge. The uniform advantage of incorporating 5-membered rings evident in this figure is due to the fact that the incorporation of pentagons forces the network to curl, thereby decreasing the distance between dangling bonds, allowing some of them to join to form good carbon-carbon  $sp^2$  bonds. The disadvantage, of course, is that the "pi" network is no longer flat, and the degree of aromaticity of the resulting curled sheet will suffer as a result of the decreased overlap of the " $2p_z$ " orbitals. Even so, the curvature at any particular carbon center is not too severe (as long as two pentagons do not share a side), and it is expected that the advantage of curvature to the sigma framework far exceeds the reduction in stability of the "pi" bonding.

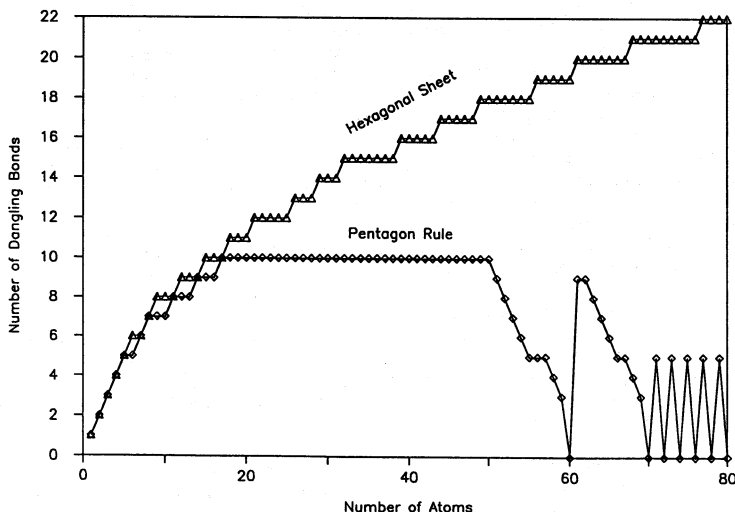


Figure 2. Number of dangling bonds in the best possible structure for a graphitic sheet with (top) all hexagons, compared to (bottom) as many pentagons as possible such that each pentagon is separated from all others by at least one hexagon, as a function of the number of carbon atoms in the cluster.

These judgements of the relative stability of curved versus flat bare carbon frameworks seem reasonable, but they have yet to be tested by detailed quantum chemical calculations. For the moment we will simply posit them as reasonable propositions. If they are true -- if the lowest energy form of any growing graphitic sheet in the 30-60 size range is the one that maximizes the number of non-adjointing pentagonal rings-- then the facile formation of  $C_{60}$  is readily understandable. Topologically,  $C_{60}$  is (uniquely) the structure one forms by following this minimum energy path. It is the smallest fullerene wherein the 12 pentagons are all separated from each other by intervening hexagons. The next smallest fullerene that obeys this rule is  $C_{70}$ .

Under these presumptions, it is clear that the yield of  $C_{60}$  will be optimized whenever the clusters in the size range of 60 atoms have the maximum opportunity to anneal to their most favored form during the growth process. This, in turn, requires that the clusters spend the longest possible time in an environment of sufficiently high temperature that their bonding pattern can change. Considering the high bonding energy of carbon, this temperature may be exceedingly high. In a recent publication [11] concerning formation and photofragmentation (and thermionic emission) of giant (>300 atom) fullerenes in a Fourier transform ion cyclotron resonance (FT-ICR) apparatus it is argued that this temperature for facile bond reorganization and annealing is in the range of 2000-3000C. An interesting aspect of this FT-ICR work is that it revealed that with the exception of the small carbon chains and rings in the 2-30 atom size range, effectively *all* the clusters produced by laser vaporization in a helium atmosphere were fullerenes, with the majority of the clusters being giant fullerenes made up of more than 300 atoms. The process of closure of the graphitic sheets to form fullerenes is therefore much more facile than originally anticipated [3,4].

This line of reasoning leads to a simple explanation of why a buffer gas is necessary in order to have a substantial yield in the formation of  $C_{60}$  from resistively heated carbon rods such as first reported by Kratschmer, Fostiropoulos, and Huffman [12,13]. Without this buffer gas the small carbon radicals diffuse so far from the hot rod surface that the local temperature is too cool to anneal the growing clusters. They simply keep growing to form, large, rather amorphous graphitic sheets which deposit and polymerize together on the walls. With a small buffer gas pressure the carbon radicals still diffuse away from the hot carbon rod and most clusters continue to be formed in a zone which is too cool to effectively anneal to the optimum curled geometry during growth. Most clusters then grow in the gas phase as slowly curling graphitic sheets, building well past 60 atoms in size before they finally close to form giant fullerenes.

Alternatively, with too much buffer gas the carbon radical concentration will be so high in the region around the rod that growth of the graphitic sheets is too fast. Even though the temperature is quite high in this narrow region, annealing still can not keep up with the growth process. Again, the clusters under these conditions will generally build well past 60 before they have a chance to curve and close.

Thus there should be an optimum buffer gas pressure for concentrating the fullerene product distribution into the most favored structure,  $C_{60}$ . Since the effect of the buffer gas is primarily to adjust the rate of diffusion of the small carbon radicals away from the point of vaporization, this optimum pressure should be expected to depend on the nature of the buffer gas (its mass and collision cross-section) and the rate of its hydrodynamic flow past the source of the carbon vapor.

An interesting side branch of this line of argument is that it predicts that pulsed laser vaporization (with a Q-switched laser) is likely to be a very inefficient means of producing  $C_{60}$ . In such a circumstance, all the carbon radicals that are ever going to be involved are produced within the first 5 nanoseconds. While the local temperature of this laser-produced plasma is very high, it exists only in a very thin layer above the carbon target, and persists only for a fraction of a microsecond. In later microseconds the temperature of the laser plasma falls abruptly as it expands adiabatically into the surrounding comparatively low pressure carrier gas. While the local temperature rapidly falls below the range necessary for facile annealing of the growing graphitic sheets, much of the condensation has yet to occur. Most of the carbon then ends up in the form of what we have come to call "giant fullerenes", with very little in the form of  $C_{60}$ . In fact, this large distribution of fullerenes extending out to well over 1000 carbon atoms has been observed ever since the first laser vaporization experiment of carbon in a supersonic cluster beam source by Rohlifing, Cox, and Kaldor [14]. Our model for the optimization of  $C_{60}$  yield simply explains this observation of giant fullerene production as a result of too-rapid cooling of the laser-vaporized plasma.

#### A TEST OF THE $C_{60}$ FORMATION MODEL

We have performed one simple but rather demanding check of the predictions of this model. Since it suggests that the reason for the low yield of  $C_{60}$  from Q-switched laser vaporized carbon is a failure to anneal the growing clusters because the cooling is too rapid, we have built an apparatus where the vaporization occurs in a heated zone. Figure 3 shows a schematic of this apparatus. As shown in the figure, a 1.25 cm diameter rod of graphite was rotated within the bore of a quartz tube furnace. A slow (10 sccm) flow of argon gas at 500 torr was maintained over the target while a Nd:YAG laser doubled into the green (532 nm, 300 mJ per pulse at 10 Hz) was focussed to a 1mm by 10 mm line on the radius of the end of this rotating graphite rod. We found that at temperatures from 20 to 500 C, this apparatus produced no perceptible amount of  $C_{60}$  when tested by UV/VIS spectroscopy of benzene extract or by mass spectrometry of the material volatilized from a heated probe, two techniques we have generally found to be quite reliable [1]. Meijer and Bethune have recently published evidence that  $C_{60}$  and  $C_{70}$  can be made under these conditions in sufficient yield to be seen by laser microprobe techniques [15]. We suspect their sample actually was composed of a distribution of much larger fullerenes, with only a negligible amount of  $C_{60}$ . Their laser microprobe mass spectra is characteristic of laser photofragmentation of larger fullerenes [5,11].

On the other hand, once the temperature of the graphite rod region was raised to over 1000 C, a readily apparent red-brown ring of sublimed  $C_{60}$  was observed to form on the cold down-stream surfaces of the quartz tube of this apparatus. The material composing this ring was easily brushed off the quartz tube. It was found to readily dissolve in toluene, and give the typical UV-visible absorption spectrum of a  $C_{60}/C_{70}$  mixture. Roughly 100 mg of this material were produced in 3 hours of operation of the apparatus, corresponding to a yield of roughly 10% of the vaporized carbon. The yield was found to be highest at the maximum temperature limit permitted in this apparatus (1200 C). Higher temperatures may result in even better yields.

In addition to providing an impressive verification of the model we have proposed for  $C_{60}$  growth, this new laser vaporization technique within a hot oven may lead to an effective means of incorporating a variety of refractory metal atoms into the inside of fullerene carbon cages in high yield [1,3,5,6].

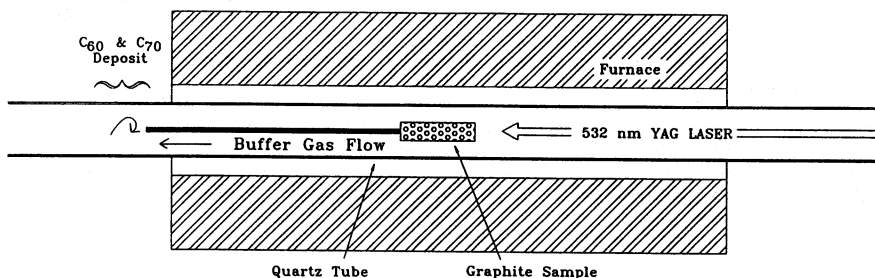


Figure 3. Cross-sectional view of apparatus to produce  $C_{60}$  by laser vaporization of a rotating graphite target in a tube furnace with a flowing argon carrier gas.

#### WHY HASN'T $C_{60}$ BEEN ISOLATED BEFORE? THE ENTRAPMENT OF $C_{60}$ .

This model for the formation of fullerenes and the role of a buffer gas in optimizing the yield of  $C_{60}$  also contributes to an explanation of why  $C_{60}$  has remained hidden for so long. Following the original proposal that the mechanism for generation of the fullerenes may also be involved in the nucleation of soot [4],  $C_{60}$  and the other fullerenes were detected in substantial abundance in sooting flames by Homann and co-workers [16, 17]. Therefore it appears that  $C_{60}$  and the fullerenes form readily whenever carbon is condensing in the gas phase. It must have been formed even in the first wood fires on earth. Homann's experiments reveal that  $C_{60}$  survives far up into the flame, with no indication of thermal decomposition or reaction with the various radicals and other active species in the reducing region of the flame. Our laser vaporization experiments in the tube furnace at 1200 C (which is near the temperature of a sooting flame) also confirm that  $C_{60}$  is stable under these conditions. Yet it turns out that  $C_{60}$  does burn quite readily in oxygen [18] to form  $CO_2$ . Ordinarily, in a candle flame for example, the  $C_{60}$  together with the other fullerenes and soot particles are burned back to  $CO_2$  and  $H_2O$  as they pass through the top of the flame and mix with air. If it were not for this fairly facile oxidation in air,  $C_{60}$  would certainly have been detected tens of thousands of years ago. It would have covered the ceilings of ancient cave dwellings.

However, in the case of sooting flames where the fuel to oxygen ratio is sufficiently high that the soot does escape oxidation at the top of the flame,



it seems virtually certain that  $C_{60}$  must escape as well. Therefore the conclusion appears inescapable that  $C_{60}$  must have been generated and trapped with the soot even from the first fires on earth. Since it has yet to be identified in ordinary soots, it seems likely that  $C_{60}$  must be somehow trapped inside the soot particles.

We have reported above that one can make  $C_{60}$  in significant yield even with a simple carbon arc at 1 atmosphere pressure. From a historical perspective, this result at first seems incredible. While in comparison to flames this sort of electrical device is fairly novel in human experience, it is still quite old. Its roots stretch back to the early history of electricity. Carbon arcs were under study by Sir Humphry Davy within a few years after the invention of the electrochemical cell by Alessandro Volta in 1800. Extended operation of these unprecedentedly bright light sources was first made possible by the discovery of magnetic induction by Michael Faraday in 1831. Their application in lighthouses was one of the first practical uses of man-made electric power [19]. It is therefore natural to wonder why  $C_{60}$  hasn't been detected in such arcs until now.

For most of the intervening years since Davy, failure to observe  $C_{60}$  is rather easy to understand: carbon arcs were typically generated in air, where  $C_{60}$  and other carbon materials would have mostly been burned up as they left the arc. However, starting with the development of vacuum techniques early in this century, the generation of carbon deposits in vacuum and low pressure inert gases has been a standard technique for at least several decades. We now know that  $C_{60}$  must have been formed there too, and the question of why  $C_{60}$  remained undetected in this circumstance until 1990 still needs resolution. We suspect the answer is similar to the case of sooting flames -- it also involves entrapment.

The FT-ICR experiments mentioned above [11] suggest that essentially everything made when carbon condenses in an inert atmosphere is a fullerene. However, unless there is an inert buffer gas of the appropriate pressure, the great majority of these fullerenes will be very large, and only a small fraction of one percent will form  $C_{60}$ . Even so, this small amount of  $C_{60}$  should have been quite detectable. We believe the root cause of the problem of detecting  $C_{60}$  under these conditions has been the nature of the larger fullerenes. Although they are all large enough to space out the pentagons with intervening hexagons, these large fullerenes are still much more susceptible to free radical attack than  $C_{60}$  and  $C_{70}$ . The reason is that the strains of closure of the graphitic sheet in these molecules becomes increasingly concentrated at the corners of the pentagonal rings [2,3,5,6,20]. Most of the giant (>300 atom) fullerenes are fairly well described as roughly icosahedral particles, with the 12 pentagons forming the vertices of the icosahedron. The nearly flat triangular facets of these huge icosahedral molecules are made up of hexagonal sheets which curve nicely around the edges of the icosahedron, and meet at the vertices in the form of these pentagons [21]. Our point is that the fairly sharp corners which pertain to the pentagons in this structure leave the carbon atoms here with bond angles rather close to the tetrahedral bond angle. These carbons are close to a state of  $sp^3$  hybridization, and should therefore be active sites for chemical attack and polymerization with other fullerenes.

We suspect that the extractability of  $C_{60}$  from graphitic soot prepared under an inert gas may be rather non-linear. When the gas conditions are such that only a small percentage of the carbon ends up as  $C_{60}$ , these molecules will be buried in a film of larger fullerenes which will have polymerized together. As one heats or agitates this loosely polymerized matrix it is likely that further reactions between the fullerenes will occur, resulting in the opening of the closed fullerene cages and the production of a highly

involved, interconnected amorphous graphitic structure with C<sub>60</sub> tightly trapped inside. It is only when the buffer gas conditions are adequate to funnel 10-20% of the condensing carbon vapor into formation of C<sub>60</sub> and C<sub>70</sub> that sufficient channels to the outside result in the final carbon particles through which these special fullerenes can be efficiently extracted. There is, therefore, something of a percolation problem intrinsic in the recovery of C<sub>60</sub> from these graphitic soots.

If this model is correct, there may be ways of intercepting the larger fullerenes before they react with each other, thereby passivating the pentagons. This, in turn, would give rise to a new class of molecules which could be separated into narrow size ranges by chromatography, and then reacted under controlled conditions by removal of the passivating groups.

The model also leads to the notion that it may be possible to recover "ancient buckyballs" by selective leaching of old soots, and the carbonaceous material in meteorites.

#### ACKNOWLEDGEMENT

We thank D. S. Bethune for useful conversations, and for communication of the results of his group prior to publication. This research was supported by the National Science Foundation, the Office of Naval Research and the Robert A. Welch Foundation.

#### REFERENCES

1. R. E. Haufler, J. Conceicao, L. P. F. Chibante, Y. Chai, N. E. Byrne, S. Flanagan, M. M. Haley, S. C. O'Brien, C. Pan, Z. Xiao, W. E. Billups, M. A. Ciufolini, R. H. Hauge, J. L. Margrave, L. J. Wilson, R. F. Curl, and R. E. Smalley, *J. Phys. Chem.* **94**, 8634 (1990).
2. H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature*, **318**, 162 (1985).
3. J. R. Heath, S. C. O'Brien, Q. Zhang, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Tittel and R. E. Smalley, *J. Am. Chem. Soc.* **107**, 7779 (1985).
4. Q. L. Zhang, S. C. O'Brien, J. R. Heath, Y. Liu, R. F. Curl, H. W. Kroto, and R. E. Smalley, *J. Phys. Chem.* **90**, 525 (1986).
5. R. F. Curl and R. E. Smalley, *Science* **242**, 1017 (1988).
6. R. E. Smalley "Supersonic Carbon Cluster Beams" in Atomic and Molecular Clusters, E. R. Bernstein, editor, *Physical and Theoretical Chemistry Vol. 68*, Elsevier Science, 1-68 (1990).
7. E. Osawa, *Kagaku* **25**, 854 (1970).
8. D. A. Bochvar and E. G. Gal'pern, *Dokl. Akad. Nauk SSSR* **209**, 239 (1973).
9. Essays on Cellular Automata, A. W. Burks, editor (University of Illinois Press, Urbana, 1970).
10. K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.* **81**, 4477 (1959).

11. S. Maruyama, M. Y. Lee, R. E. Haufler, Y. Chai, and R. E. Smalley, *Z. Physik D*, in press.
12. W. Kratschmer, K. Fostiropoulos, and D. R. Huffman, *Chem. Phys. Lett.* 170, 167 (1990).
13. W. Kratschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature* 347, 354 (1990).
14. E. A. Rohlfing, D. M. Cox, and A. Kaldor, *J. Chem. Phys.* 81, 3322 (1984).
15. G. Meijer, and D. S. Bethune, *J. Chem. Phys.* 93, 7800 (1990).
16. Ph. Gerhardt, S. Loffler, and K. H. Homann, *Chem. Phys. Lett.* 137, 306 (1987).
17. Ph. Gerhardt, S. Loffler and K. H. Homann, *Twenty-Second Symposium (International) on Combustion, The Combustion Institute (1988)*, pp 395-401.
18. S. Hwu, unpublished results.
19. see, for example, M. Luckiesh, Artificial Light (Century Co Publishers, New York, 1920).
20. H. W. Kroto, and K. McKay, *Nature* 331, 328 (1988).
21. H. W. Kroto, *Science* 242, 1139 (1988).