Self-Assembly of the Fullerenes

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Scanning tunneling microscopy has a way of conjuring up fanciful thoughts. While lecturing about C_{60} and the fullerenes recently, I visited one of the leading labs using this technique and looked at images of these hollow, nanoscopic geodesic domes of carbon, one at a time. Seeing such pictures it is easy to imagine a whole new world down there on the chemist's atom-by-atom length scale, and there are those who will view this world with the eyes and ambitions of a molecular architect, or a physicist, a materials scientist, or a chemical engineer. Are these the first elementary building blocks of a new carbon-based technology? Superconductors, semiconductors, fullerene-encapsulated atoms, doped fullerene cages, fullerene pendants on polymer chains, buckytubes, buckyfibers, open tubes (bucky-pipes?) used in an entirely new class of catalysts, etc.: one wonders how real such nanotechnological fantasies can become, and when.

This issue of *Accounts* constitutes something of a coming-out party for these new molecules in the chemical community. It is still too early to tell just how much of the carbon-based nanotech fantasy will become fact, but a tremendous amount has been learned over the past six years. At the time of this writing, over 700 research articles have appeared or are currently in press directly on the subject of the fullerenes. Of these, slightly more than 500 have been submitted since the Krätschmer–Huffman method[1] first made the fullerenes broadly available in the late fall of 1990. By now it is certainly not necessary to introduce this subject to the general chemical audience. Even for those who missed the research articles in the primary journals, there will be few who have missed all of the over 40 review articles[2–6] and 75 news pieces that have appeared by my informal count[7] in the public and scientific press. In a sense, Bucky and the fullerenes came preintroduced at birth. The six-year-old name, buckminsterfullerene,[8] in all its clumsy six syllables, says it all.

This initial Account deals with a central mystery of the fullerene story: How are they made? How can the fullerenes in general, and C_{60} in particular, possibly be made spontaneously in high yield simply by condensing carbon vapor in a special way? In fact we appear to have here a beautiful example of what has long been

recognized to be essential for a practical nanotechnology:[9,10] an efficient mechanism of self-assembly of architecturally useful structures on a nanometer scale. The mystery of how this happens in the case of carbon is still by no means fully resolved, but my colleagues and I have advanced one theory[3,5,11,12] that does appear to be consistent with all known facts. It has to do with dangling bonds and the ability of carbon atoms to interact with each other with an effective valence of 3.

The Making of the Fullerenes

The first recorded observation of the fullerenes was made using an apparatus similar to that shown in Figure 1. Here a pulsed laser beam (the green second harmonic of a Nd:YAG laser, 532 nm) is directed onto the surface of a rotating/translating graphite disk. Although the intensity of the laser is only enough to deposit a few tens of millijoules onto a 1-mm-diameter spot on the surface of the disk, it does this in an extremely short period of time: only 5 ns. This is sufficient to generate a plasma of carbon vapor over the irradiated spot in which temperatures over 10 000 °C are readily obtained. In order to cool this superhot plasma, and generate clusters, a burst of helium gas is used from a pulsed gas nozzle. As the carbon atoms and small radicals are cooled in this carrier gas, clustering reactions occur. By controlling the relative timing between the vaporization laser and helium gas pulses and adjusting the flow geometry, the residence time in the source can be extended to allow these growing clusters to "cook" in the soup of carbon radicals before the carrier gas expands out the end of the source and forms a supersonic free jet in a vacuum chamber. Collimated beams skimmed from this supersonic free jet then provide an excellent environment for probing both the size distribution and detailed nature of the carbon clusters by time-of-flight (TOF) mass spectrometry and

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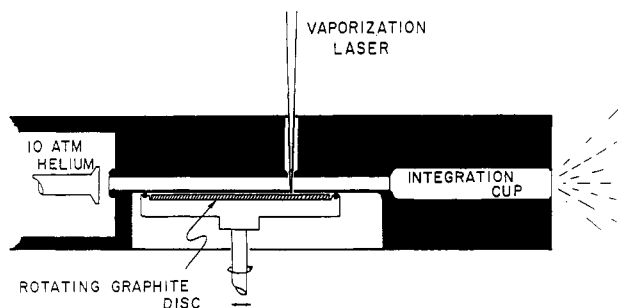
Figure 1. Supersonic carbon cluster beam source utilizing a pulsed laser to vaporize a graphite disk and a pulsed jet of helium to control clustering. Reprinted with permission from ref 8. Copyright 1985 Macmillan Magazines Ltd.

laser spectroscopy. The combination of laser vaporization with a pulsed gas flow permits the intermediate steps involved in carbon condensation to be studied in a controlled, systematic way. This fact beyond all others was what finally led to the discovery of the fullerenes.

The laser-vaporization supersonic cluster beam technique was originally developed[13] in 1980–1981 as a means of studying clusters of virtually any element in the periodic table, including highly refractory metals[14] and semiconductors such as silicon[15] and gallium arsenide.[16] In 1984 a group at Exxon was the first to use such an apparatus to study clusters of carbon.[17] Figure 2 shows the remarkable cluster mass distribution they obtained. The fullerenes are seen here for the first time as a distribution of clusters starting somewhere in the high 30s and extending out to well beyond C_{100}. Note that this fullerene distribution contains only even-numbered clusters, and it appears rather cleanly separated from an abundant distribution of smaller clusters in the C_2 to C_{25} size range by a region where there is little signal: a region in the carbon clusters we at Rice soon began to call the "forbidden zone".

The small 2–25-atom carbon cluster distribution had been seen many times before in less elaborate experiments[18,19] and had long been assigned to carbon clusters which had taken the form of linear chains (for the smaller ones) or large monocyclic rings.[20] But the large, even-numbered distribution had never been seen before. By early 1984 the laser-vaporization supersonic cluster beam technique had been used to study clusters broadly throughout the periodic table. Nothing like this even-numbered distribution had ever been seen for any other element, and this is still true today: carbon is absolutely unique.

As is now well-known,[2-6] the realization that the even-numbered distribution was due to carbon in the form of hollow geodesic domes came in supersonic beam

experiments at Rice University, where the supremacy of one particular member of this distribution, C_{60}, was made clear. As shown in Figure 3, it was the ability of the cluster source to be varied from one condition of condensation to another that provided the vital clue.

The Giant Fullerenes

Buckminsterfullerene, C_{60}, rapidly dominated the attention of experimentalists and theorists alike for the next five years. However, it is now clear that a bit more work to probe the nature of the larger carbon clusters would have been fruitful during those years. The original Exxon data, as well as that of our group at Rice, indicated that the even-numbered distribution went out to well past C_{100}, but none of the TOF mass spectrometers in use at the time could probe this higher C_n distribution at high mass resolution. It was clear that even-numbered clusters dominated the distribution to at least C_{200}, but odd-numbered clusters might have been present as well in substantial numbers.

Only recently has this situation changed. As part of a general effort to study large clusters in detail, we developed an apparatus which combines a laser-vaporization supersonic cluster beam source with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.[21] It is possible, using this new device, to study the giant carbon cluster distribution in detail at a mass resolution of better than 10^4 to 1. Figure 4 shows a typical FT-ICR mass spectrum of carbon clusters where this apparatus was optimized to trap positive carbon clusters in the $C_{300}{}^+$ to $C_{350}{}^+$ mass range.[21] As shown in the inset, there is very little indication of any clusters in this region with an odd number of carbon atoms. They all appear to be fullerenes. Depending on the detailed conditions back in the laser-vaporization supersonic nozzle, it was found possible to generate what appeared on first sight to be a small amount of odd-numbered clusters in this size range, but on detailed examination at high mass resolution, they were revealed to be due to doubly charged even-numbered clusters in the 600–700-atom size range.[22]

All these large clusters were shown to be giant fullerenes by what we have come to call the "shrink-wrap" test. In a series of photofragmentation experiments in 1986–1987, my colleagues and I were able to show that C_{60} and the other fullerenes in the 50–90 size range follow a bizarre fragmentation path.[23] Since closed fullerene cages are edgeless, either fragmentation must involve the breaking of many carbon–carbon bonds before a fragment can be removed, or there must be a concerted path to form a fragment while simultaneously generating the next smaller fullerene cage. Robert Curl and Sean O'Brien found such a concerted path for the ejection of a C_2 fragment,[23] and this is currently believed to be the primary photoprocess for all these fullerenes. It is a high-energy path which is forbidden in the Woodward–Hoffmann sense, but still for a closed fullerene cage it is "the only game in town". The consequence of this C_2 loss mechanism is that a fullerene

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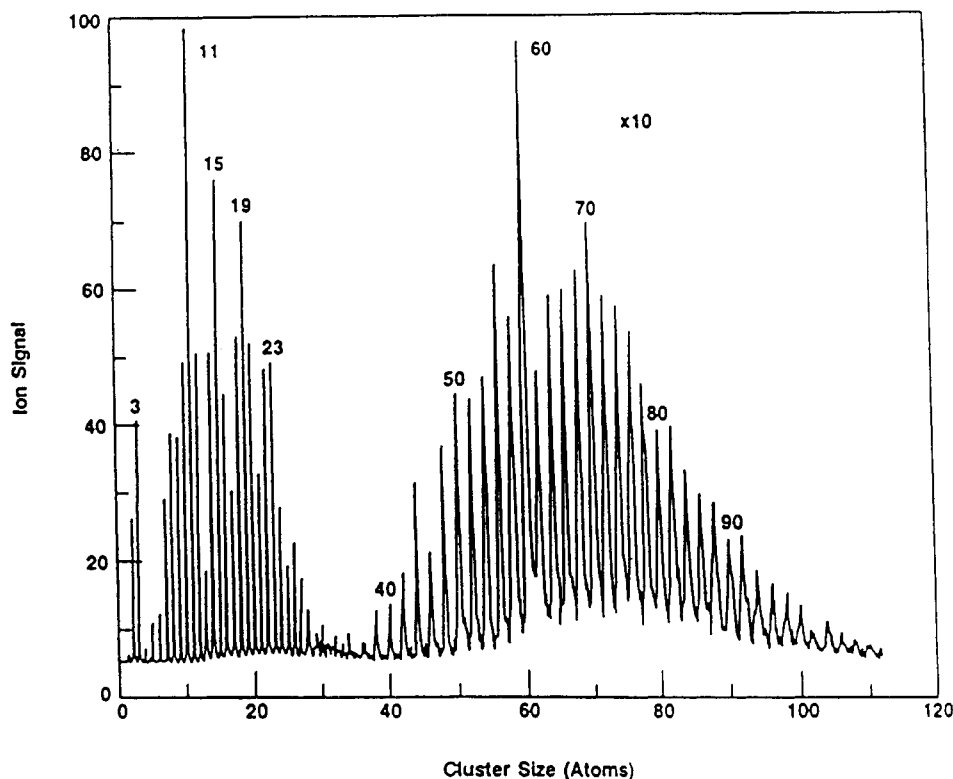
Figure 2. Time-of-flight mass spectrum of carbon clusters produced in a supersonic beam by laser vaporization of graphite. Reprinted with permission from ref 17. Copyright 1984 American Institute of Physics.

does not so much fragment as evaporate C_2 off its surface. The result is a sequential shrinking of the fullerene cage as more C_2 species leave. For more highly excited fullerenes, an extension to the mechanism was found whereby C_4, C_6, or larger even-numbered linear chains can be lost from the fullerene cage,[23] a mechanism which may be responsible for the abundance of these chains in interstellar space.

Figure 5 shows an example of the application of this shrink-wrapping test to large carbon clusters. Here clusters in the C_{288} to C_{316} size range were selected by a technique called "SWIFT" which ejects all other clusters from the FT-ICR cell.[22] The small mass peaks appearing in this mass spectrum between the peaks for the large even-numbered carbon clusters were found under higher mass resolution to be due to doubly charged even-numbered clusters in the C_{574} to C_{630} size range, as discussed above. These selected clusters were then subjected to 100 pulses of a XeCl excimer laser beam at 35 mJ cm^{-2} fluence per pulse in the near ultraviolet (308 nm). The result, seen in the middle panel of Figure 5, is that the large clusters have fragmented by successive losses of C_2 and higher even-numbered units. What appear in this mass spectrum to be odd-numbered fragments in the C_{81} to C_{151} mass range turn out to be due to the generation of doubly charged fragments in the C_{162} to C_{302} size range by a process of thermionic emission from singly charged parent ions. This amazing process occurs on these clusters because their only fragmentation channel—C_2 loss—occurs at a significant rate only at such high levels of vibrational excitation that the cluster temperature is so high that electrons literally "boil off".[24]

The most vivid demonstration that these giant clusters are, in fact, giant fullerenes comes from following

the C_2 loss process all the way down to its bitter end. As the fullerene cage shrinks, the bond strain increases until, at C_{32}, it bursts. This has been found to be true for all (empty) fullerenes,[25] regardless of their initial size. By the late spring of 1990 such experiments at Rice had verified that effectively all the positive carbon cluster ions produced by laser vaporization of a graphite target in this apparatus up to at least C_{600}^+ were fullerenes.

This is an incredible result. Prior to 1985, as far as we are aware, no one had ever suggested that closed carbon cages would be formed spontaneously in a condensing carbon vapor. Now it turns out that there are readily obtainable conditions where this is effectively *all* that forms!

In the late fall of 1985 while my associates and I were trying to rationalize the formation of soccer-ball C_{60}, we came up with a mechanism[12] we called then the "party line". We had realized that C_{60} in our beam experiments was not the dominant product of the chemical "cooking" that was going on in the nozzle. Rather it was the sole survivor of a clustering process that was carrying out all other clusters up to sizes so large that we could no longer detect them. We imagined that the growth process that generated these fullerenes began with linear chains that grew by addition of other linear-chain carbon radicals to be large enough to take the form of monocyclic rings. And these rings, in turn, would grow through further additions of small carbon radicals until they were in the 25–35-atom size range where polycyclic networks began to be favored. However, these open graphitelike sheets would have many peripheral dangling bonds and would therefore be highly reactive, particularly compared to the smaller

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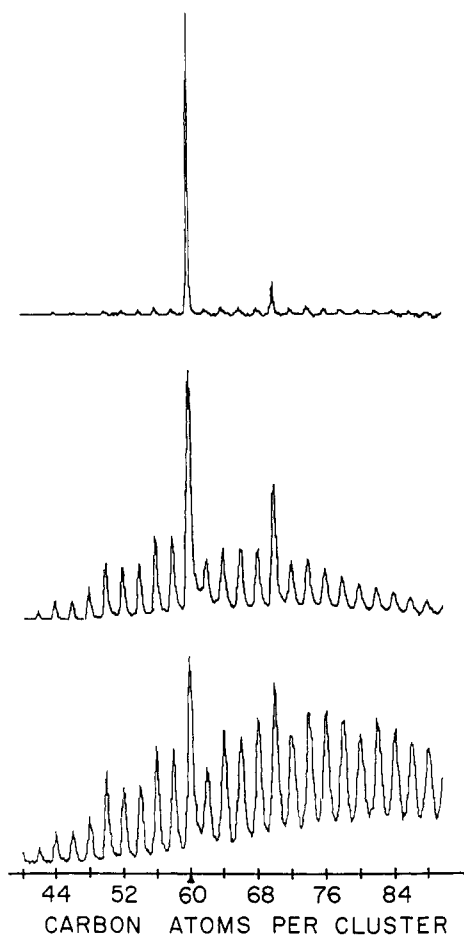(25) Weiss, F. D.; O'Brien, S. C.; Elkind, J. L.; Curl, R. F.; Smalley, R. E. *J. Am. Chem. Soc.* **1988**, *110*, 4464.

Self-Assembly of the Fullerenes

Acc. Chem. Res., Vol. 25, No. 3, 1992 **101**

chains, only two dangling bonds, one on each end. The high comparative reactivity of the open graphitic sheets with many dangling bonds then nicely explained the observed "forbidden zone" in the cluster distribution: their high reactivity made them low-abundance species in any "snapshot" of the chemical kinetics.

In order to explain the formation of fullerenes, the "party line" went on to suggest that some of the open graphitic sheets may rearrange to incorporate pentagons as well as hexagons in the bonding pattern. The pentagon would cause the sheet to curl and enable some of the peripheral dangling bonds to join. As more pentagons were included, the sheet would curl more, the strain energy of curving the "π" bonds of the sheet being more than offset by the formation of good σ bonds. We further realized that there would be a propensity to avoid adjacent pentagons in the growing, curling sheet since otherwise this would produce a locally anti-aromatic cycle in the polycyclic net, and it would also produce sharp corners in the net at the points of attachment.

However, at the time, even we regarded this process of pentagon incorporation to be relatively unlikely as the carbon radicals rapidly condensed. Perhaps once in every thousand or so times the sheet would happen to get enough pentagons in to allow it to close to form a small fullerene. Those that closed to form C_{60} would survive even the most intense subsequent exposure to carbon radicals and would stand out uniquely in our mass spectra. But the vast majority, we supposed, would simply grow too big to detect. Particularly in the presence of hydrogen, such as is encountered in sooting flames, we expected that the most likely object to be formed would be a spiraling object where the curving growth edge overran the opposite edge of the sheet, burying it inside.[12] While something like this spiral soot object may still be important in flames, it is clear from the most recent FT-ICR studies that it probably is not
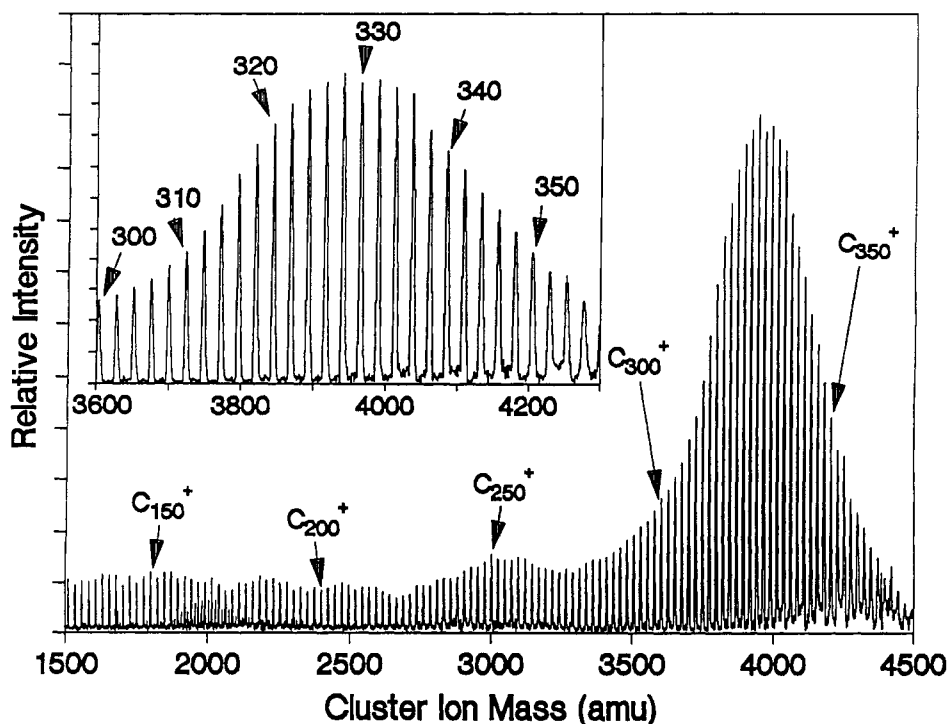

Figure 3. Mass spectrum of carbon clusters produced by laser vaporization under conditions of increasing (bottom to top) chemical "cooking" in the supersonic nozzle. Reprinted with permission from ref 8. Copyright 1985 Macmillan Magazines Ltd.

monocyclic rings which had, at least formally, no dangling bonds at all or, when they opened to form linear

Figure 4. Mass spectrum of large carbon clusters produced by laser vaporization of graphite. Inset shows that there are few if any odd-numbered clusters present. Reprinted with permission from ref 21. Copyright 1990 American Institute of Physics.
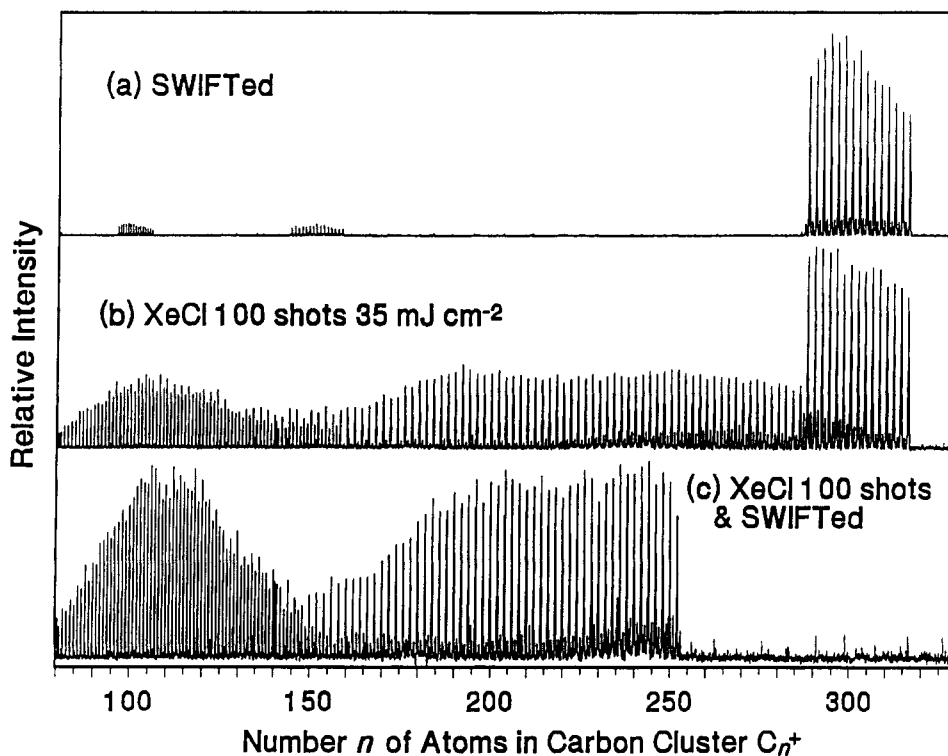
Figure 5. Mass spectrum of large carbon clusters (a) as initially selected and (b) after photolysis by 100 pulses of a XeCl excimer laser at 35 mJ cm^{-2}. Panel c shows the mass spectrum of C after the parent cluster ions were ejected from the ICR trap. Reprinted with permission from ref 22. Copyright 1991 Springer-Verlag.
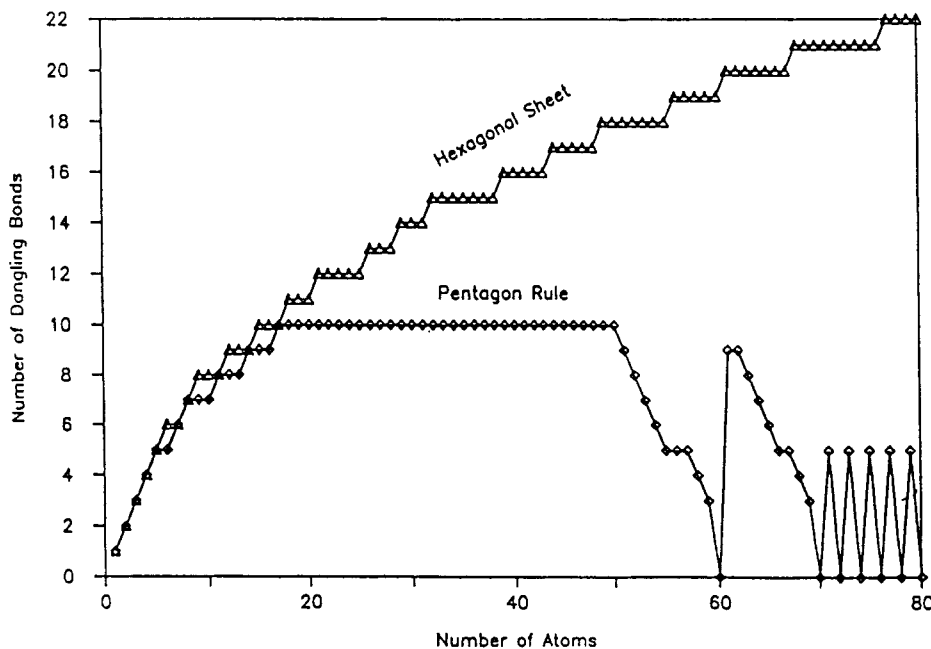

Figure 6. Number of dangling bonds in the best possible structure for a graphitic sheet with (top) all hexagons, compared to (bottom) those which obey the "pentagon rule" (as many pentagons as possible such that no two are adjacent), as a function of the number of atoms in the sheet. Reprinted with permission from ref 11. Copyright 1991 Materials Research Society.

significant in pure condensing carbon vapors. In a sense, we were too pessimistic about our own mechanism. Closure to form fullerenes turns out to be so facile that it is often by far the dominant process.

Following the Pentagon Road

This mechanism we are now proposing[3,11] is basically the same as the old "party line", but with one critical new wrinkle: annealing. Specifically, we are suggesting that the energetically most favored form of any *open* graphitic sheet is one which (a) is made up solely of

pentagons and hexagons and (b) has as many pentagons as possible, while (c) avoiding adjacent pentagons. These three criteria we term the "pentagon rule". Figure 6 shows a comparison of the number of dangling bonds in such curved structures compared to the best possible hexagonal graphite sheets as a function of cluster size. Note that there is little advantage until roughly 20–30 carbons are assembled together, and that C_{60} is the first pentagon rule structure that can close.

If the assumption of the model is correct—that the pentagon rule structures really are the lowest energy
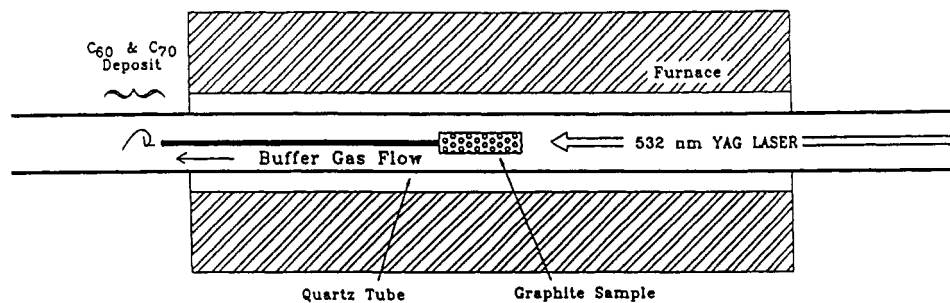
Figure 7. Cross-sectional view of apparatus to produce fullerenes by laser vaporization of a rotating graphite target in a tube furnace with a flowing inert carrier gas. Reprinted with permission from ref 11. Copyright 1991 Materials Research Society.

forms possible for any open carbon network—then one can readily imagine that high-yield synthesis of C_{60} may be possible. In principal all one needs to do is to adjust the conditions of the carbon cluster growth such that each open cluster has ample time to anneal into its favored pentagon rule structure before it grows further. We call this path through the kinetics the "Pentagon Road". It is a mechanism of graphite-sheet self-assembly that leads uniquely to C_{60}.

With this mechanism it is rather easy to explain our long-term failure to produce macroscopic amounts of C_{60} by laser vaporization of graphite using the techniques of 1985, and the subsequent stunning success of Krätschmer and Huffman. When using pulsed laser vaporization, one generates a hot plasma of carbon radicals which immediately after the laser pulse is of extremely high density, on the order of 10^{20}–10^{21} cm^{-3}. As a result, the growth rate of the open sheets is extremely rapid as this plasma begings to cool off by expansion. Since the surrounding carrier gas is at room temperature, the rate of cooling of this carbon vapor plume is extremely rapid, and within a few microseconds the temperature falls too low for the growing clusters to anneal. Under such circumstances most of the clusters grow out well beyond C_{60} before they incorporate enough pentagons (12) to close, and the result is a broad distribution of giant fullerenes. Enough C_{60} is produced to be detected by sensitive TOF mass spectrometers, but far too little to be detectable as a colored extract of the resultant soot in benzene.

In the Krätschmer–Huffman (KH) method,[1] carbon radicals are produced simply by slow evaporation of the surface of a resistively heated graphite rod. Here the carbon vapor density is far lower than that in pulsed laser vaporization and therefore so too is the rate of carbon cluster growth. Most critically, however, the rate of cooling of the condensing carbon vapor is much slower in the KH method. By adjusting the pressure of helium buffer gas around the evaporating graphite rods, one has at least coarse control over this rate of cooling and the rate of cluster growth. After the KH method was introduced,[1] it was found that a simple ac or dc carbon arc would produce C_{60} and the other fullerenes in good yield as well,[11] and this is now the method used commercially. Even though such a carbon arc maintains a high degree of ionization of the carbon vapor between the electrodes, and the vaporization mechanism differs markedly from that of a resistively heated carbon rod, the optimum helium pressure for C_{60} formation is found to be nearly the same. This suggests that it is not the vaporization method that matters; rather, it is the conditions pertaining while the carbon vapor condenses. By adjusting the helium buffer gas

pressure, one controls the rate of migration of the carbon vapor away from the hot graphite rod and thereby controls (at least crudely) the effective temperature and carbon radical density in the region where clusters in the size range near C_{60} are formed.

A rough indication of the temperature range needed for annealing the open graphite sheets into their favored pentagon rule structures comes from measures of the temperatures needed to perform similar 5 $\leftrightarrow$ 6 ring rearrangements in polycyclic aromatics such as aceanthrylene, acephenanthrylene, and fluoranthene. In 1986 Scott and Roelofs[26] found such interconversions to proceed rapidly in the gas phase at 1100 °C. The most direct and relevant measurement, however, was obtained using the simple apparatus shown in Figure 7. Here a graphite target rod was mounted so that it was suspended in a quartz tube inside a furnace. A vaporization laser (Nd:YAG, 532 nm, 5-ns pulse duration, 300 mJ/pulse) was focused with a cylindrical lens to a 1-mm-wide, 1-cm-long line on the end of the target rod, and this rod was rotated slowly so that the laser smoothly eroded the end of the rod without digging a deep trench. Helium or argon carrier gas was passed slowly down the quartz tube so that any C_{60} and other small fullerenes would be transported out of the oven.

The results were quite vivid.[12] When the tube furnace was kept at room temperature, the laser vaporization was found to produce a black soot which when slurried with benzene or toluene and filtered revealed no visible trace of fullerenes in solution. The same remained true when the furnace was heated to 500 °C. But at 1000 °C we observed a significant yield of soluble fullerenes by this test. This yield was found to increase at higher furnace temperatures. By 1200 °C, the maximum temperature available with this particular furnace, the measured yield of C_{60} was well over 20% by weight of all the vaporized carbon. The optimum annealing temperature for the formation of C_{60} from a laser-vaporized graphite target is therefore probably a bit higher, perhaps 1300–1500 °C.

Other Possible Mechanisms for Efficient Self-Assembly

Of course there must be hundreds of mechanisms whereby a fullerene like C_{60} can form. The above Pentagon Road mechanism is just one of these. But it may be the only one compatible with the single most important fact yet discovered: the overall yield of C_{60} can be extremely high: certainly as high as 20% of all the condensing carbon vapor, and there are reports of much higher yields. This is the central mystery. It is

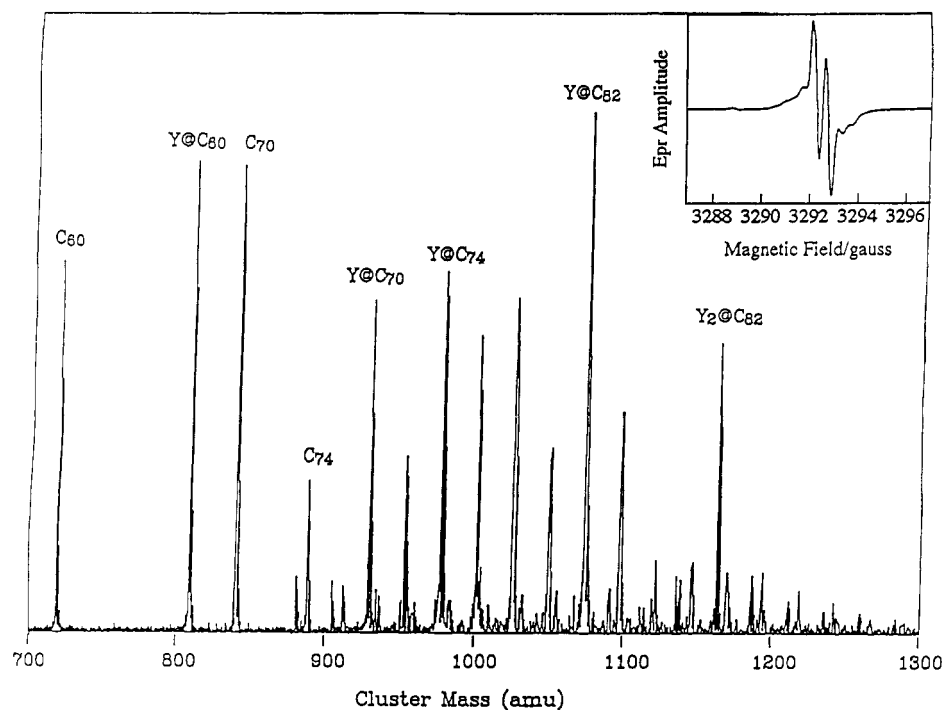(26) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461–5465.

Figure 8. Mass spectral analysis of a sublimed film of fullerenes containing yttrium metallofullerenes, $(Y_x@C_n)$, prepared by laser vaporization of a graphite/yttria (Y_2O_3) composite rod in a tube furnace at 1200 °C. The inset shows the EPR spectrum of the toluene solution of $(Y@C_{82})$ and $(Y_2@C_{28})$. Reprinted with permission from ref 35. Copyright 1992 Elsevier (Amsterdam).

explained by the above Pentagon Road mechanism as a consequence of effective annealing of the open graphitic sheets to their lowest energy form a rate faster than their growth. But it is not clear yet if there are any other viable explanations.

One of the most difficult problems to get around is energetics. From a wide variety of calculations,[27-30] it is increasingly evident that C_{60} is not energetically favored over C_{70}, the larger fullerences, or bulk graphite. The larger the fullerene, the more contiguous six-membered rings will be present, and the closer its electronic structure will be to that of the more highly aromatic, delocalized graphite. If cluster growth in the condensing carbon vapor produces fullerenes larger than C_{60}, there is little reason for them to get smaller. High-yield formation of C_{60} must therefore be due to some particularly efficient path in the kinetics of cluster growth before the clusters get too large.

One might argue that C_{60} and the other fullerenes are made not from graphite sheets that build up by addition of small carbon radicals but rather by curling and closing of preformed sheets ripped off the original graphite target. Although we originally believed this may be going on,[8] this mechanism of fullerene formation has been disproven by a variety of experiments.[31-33] The most compelling have involved studies of the isotope distribution of C_{60} produced from 1:1 mixtures of

pure ^{12}C and pure ^{13}C graphite powders.[32,33] These experiments make it quite clear that C_{60} under the conditions of the high-yield carbon arc synthesis is formed by the aggregation of small carbon radicals.

At the moment, the only other mechanism that has been proposed that appears close to explaining high-yield formation of C_{60} is one suggested recently by Heath.[33] Here the assumption is that the graphitic sheets do grow from small carbon radicals, but they do not stay open. Instead they close to form fullerenes as soon as possible (possibly starting with C_{28}). These small fullerenes violate the pentagon rule since they have adjacent pentagons. However, since they have zero dangling bonds, the expectation is that they may, in fact, be the lowest energy structure. In this model, C_{60} is a special stopping place in the growth kinetics since it is the first which avoids the highly reactive adjacent-pentagon configuration.

This all-fullerene growth model predicts that it would be difficult to generate endohedral metal fullerene complexes during the growth. These fascinating $(M@C_{60})$ carbon-caged metal species (the "@" symbol is used to designate that the M atom is located at the inside of the C_{60} cage)[34] have long been a challenge to produce in bulk form. Small amounts appeared to be produced quite readily in the laser-vaporization cluster beams,[5] but for nearly a year after the KH method was introduced, it appeared that something may be barring the macroscopic synthesis of these species by similar techniques. Heath's all-fullerene growth model suggests that synthesis of a metallofullerene such as $(La@C_{60})$ in high yield in the gas phase would be difficult since the La atom is too large to fit on the inside of the very small fullerenes such as C_{32}, and once the fullerene is

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closed it may be difficult to insert it from outside.

Yet it is now clear that these $(M@C_n)$ species can be produced rather readily. The laser–furnace apparatus was used to produce the first macroscopic samples of endohedral metallofullerene complexes.[34] For example, Figure 8 shows the mass spectral analysis of a material produced in this quartz tube furnace by laser vaporization of a composite graphite/Y_2O_3 rod at 1200 °C.[35] In addition to $(Y@C_{60})$, it contains significant amounts of higher $(Y@C_n)$ fullerenes, including the first metal cluster to be trapped inside a fullerene cage, $(Y_2@C_{82})$. Once it was clear that these materials could be made, it was found that a simple extension of the carbon arc method could make them as well.[34] The EPR spectra of $(La@C_{82})$ and $(Y@C_{82})$ have recently been reported for room temperature solutions,[35,36] and it seems likely that a wide range of such $(M_x@C_n)$ species may ultimately be available.

Self-Assembly of Higher Fullerenes: Helical Buckytubes

The Pentagon Road open graphitic sheet growth mechanism therefore appears to be the only mechanism advanced thus far which fits the known facts for the formation of C_{60}. It is, however, by no means proven, and even if it were, there are many other aspects yet to explore. For example, how about the larger fullerenes? Is there something in this self-assembly mechanism when it misses C_{60} that explains the structure and relative formation rates of the higher fullerenes? One of the most fascinating such problems, just recently emerged, is the striking discovery by Sumio Iijima of the largest fullerenes yet observed: micron-long concentric "buckytubes" in which the hexagons are arranged in a helical pattern.[37] They appear to grow like whiskers out from the negative electrode of a dc carbon arc. Are these whiskers nucleated by cylindrical fullerenes formed in the gas phase by graphitic sheets that missed the C_{60} and C_{70} cage closings and grew for a while as tubes? There is much here for physical chemists to ponder, in both experiment and theory.

For *real* chemists, though, there are further and probably much more important challenges. Given such nicely self-assembled carbon soccer balls, rugby balls, and small tubes, for example, can a chemical technology be developed to open them up and reassemble the concave pieces in useful and controlled ways? Can we polymerize buckypipes to form buckyfibers? Can we make new carbon-based 3D networks that outdo zeolites? After all, self-assembly is only a start.

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