On the Formation of the Fullerenes [and Discussion]

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On the formation of the fullerenes

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The chemistry by which the closed-cage carbon clusters, C_{60} and C_{70}, can be formed in high yield out of the chaos of condensing carbon vapour is considered. Several mechanisms for this process that have been proposed are critically discussed. The two most attractive are the 'pentagon road' where open sheets grow following the alternating pentagon rule and the 'fullerene road' where smaller fullerenes grow in small steps in a process which finds the buckminsterfullerene (C_{60}) local deep energy minimum and to a lesser extent the C_{70} (D_{5h}) minimum. A clear choice between the two does not seem possible with available information.

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1. Introduction

The observation (Kroto *et al.* 1985) that the truncated icosahedron molecule, C_{60}^{BF} (buckminsterfullerene), is formed spontaneously in condensing carbon vapour was greeted by some in the chemical community with some doubt. It seemed incredible that this highly symmetrical, closed, low entropy molecule was forming spontaneously out of the chaos of condensing high-temperature carbon vapour. We still believe that the formation of C_{60}^{BF} in supersonic cluster beam sources must be a relatively minor channel, probably accounting for less than 1% of the total carbon. Thus when C_{60}^{BF} was finally isolated from graphitic soot (Krätschmer *et al.* 1990), it came as a surprise that the C_{60}^{BF} plus C_{70} yields were as large as 5%. Later yields have improved substantially, for example Parker *et al.* (1991) obtained a total yield of C_{60}^{BF} of about 20% with total extractable fullerene yields totalling 44% from a carbon arc soot. Thus conditions can be found where C_{60}^{BF} and fullerene formation in carbon condensation can hardly be called a minor channel.

Several proposals have been put forward to account for the formation of C_{60}^{BF} and the other fullerenes. Before reviewing these proposals, it seems appropriate to consider the key observations about fullerene synthesis, the kinds of carbon clusters possible, their energetics, and the thermodynamic and kinetics of carbon clustering.

2. Key observations on fullerene synthesis

(*a*) *Effect of buffer pressure in arc synthesis*

Krätschmer *et al.* (1990) vaporized graphite in the presence of He buffer gas, examined the soot collected and observed that the intensity of the UV and infrared absorption features characteristic of C_{60} were buffer gas pressure dependent. At a pressure of about 1.3×10^3 Pa (10 Torr), these features are absent, but are clearly

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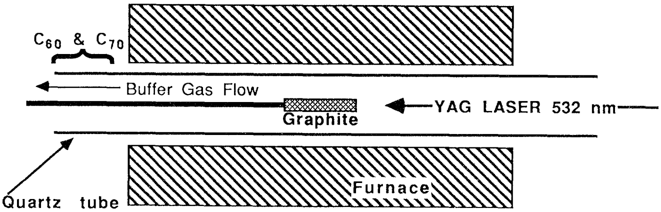

Figure 1. Tube furnace laser vaporization apparatus used by Haufler *et al.* (1991) to produce high yields of C_{60}^{BF}. The 532 nm doubled Nd: YAG pulse vaporizes C from the rotating graphite target into the inert carrier gas stream. The fullerenes condense just outside the oven on the tube wall.

present when the buffer gas pressure raised to 1.3×10^4 Pa (100 Torr). Extensive subsequent experiments by many groups indicate that C_{60}^{BF} yields depend only slightly on the buffer gas pressure between 10^4 and 5×10^4 Pa (100–400 Torr), but decrease rapidly at lower or higher buffer gas pressures.

(b) *Effect of wall temperature in laser vaporization*

Haufler *et al.* (1991) set up the apparatus shown in figure 1 to explore the effect of wall temperature on fullerene yields by laser vaporization. In this apparatus graphite is vaporized from the end of the graphite rod by a softly focused pulsed visible laser (Nd: YAG, 532 nm, 5-ns pulse, 300 mJ pulse^{-1}). When the walls of the tube are at room temperature no fullerenes are found in the resulting soot; only when the walls of the tube were heated to 1000 °C were any fullerenes obtained. As the furnace temperature was increased further, the yields increased reaching 20% C_{60}^{BF} at 1200 °C, which was the maximum temperature obtainable with this apparatus.

The observations by Krätschmer *et al.* and Haufler *et al.* can be interpreted as indicating that the processes forming C_{60}^{BF} require elevated temperatures for some time, i.e. involve reactions with substantial activation energies. In the Krätschmer *et al.* experiments, the higher buffer gas pressure confines the carbon vapour to a high temperature region near the heat source. In the laser vaporization experiments, a high temperature is supplied directly.

3. Energetics of carbon clustering

The structure and stability of carbon clusters has been of intense interest since the pioneering work of Pitzer & Clementi (1959). The general picture which has emerged is that for the smaller C_n clusters ($n < 10$) that linear structures generally are energetically most favoured. At about C_{10} these linear structures close into rings which presumably persist as the lowest energy form to about C_{20}. In the region C_{20} to C_{30} (the ‘forbidden zone’) it is unclear which structures are energetically most favourable. Above about C_{30}, the lowest energy structures up to several hundred carbon atoms appear to be the fullerenes.

Our focus is upon the fullerenes. In particular, the stability of C_{60} and C_{70} relative to the other fullerenes and to each other is of primary interest because these two species are the fullerenes produced in highest yield in carbon arcs and in combustion. Quite a few calculations mainly using various semi-empirical theories have been carried out to determine the stability of the fullerenes. Figure 2 shows the recent results of Scuseria's group (Strout *et al.* 1993), who carried out minimal basis set STO-3G SCF calculations on several fullerenes. The smooth curve fitted through

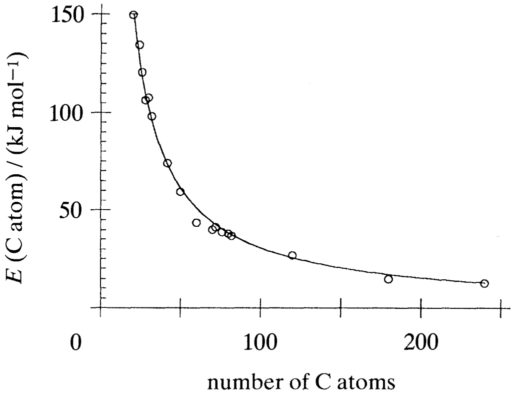

Figure 2. STO-3G restricted Hartree–Fock SCF energies per C atom of representative fullerenes relative to that calculated for single sheet graphite from the work of Strout *et al.* (1992). E/atom $= 3071/N_c$.

these energies shows that C_{60} and to a lesser extent C_{70} are, as expected, unusually stable. Note particularly that C_{70} is energetically more stable on a per carbon atom basis than C_{60}.

4. Thermodynamics of carbon clustering

A model for fullerene formation based on thermodynamic considerations would be much simpler than one based on kinetics. Fullerene formation might be modelled by supposing that small species are initially produced in a carbon arc at equilibrium with the electrode surface and that this carbon vapour diffuses through the inert gas into a cooler region where the equilibrium vapour density is much less than the actual density. There the fullerenes could be formed at thermodynamic equilibrium assuming that nucleation of graphite is kinetically forbidden. Then this equilibrium distribution could be quenched upon further diffusion into a cooler region. This model is highly attractive because it avoids any consideration of complex kinetics; unfortunately, it is demonstrably incorrect.

Slanina *et al.* (1989) have considered the thermodynamics of the fullerenes in carbon vapour, and their work demonstrates that the C_{70}/C_{60} ratio of approximately unity (ratios obtained vary roughly from 0.1 to 10) found in extracts from graphitic soot is incompatible with thermodynamic equilibrium being established between these two species when they were formed. In their work, the sum of the partial pressures of C_{60} and C_{70}, $\bar{P}_{60-70}$, at which the species are present in equal concentrations at equilibrium was calculated, and $\bar{P}_{60-70}$ is never larger than 10^{-13} bar below 5000 K. The observed C_{60} and C_{70} yields cannot be reached with such a small partial pressure of product. If the sum of the C_{60} and C_{70} partial pressures is raised, C_{70} rapidly becomes totally dominant at thermodynamic equilibrium.

5. Energetic effects and C_{60} isomers

Energetic and thermodynamic considerations can play a pivotal role in fullerene formation by providing a driving force for selecting C_{60}^{BF} and providing a large activation barrier to further reactions of C_{60}^{BF}. The potential surface minimum corresponding to buckminsterfullerene is very low in comparison with that of the other fullerene isomers of C_{60} (which in turn almost certainly have lower energies

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than non-fullerene C_{60} isomers). Further, the energy per carbon atom of C_{60}^{BF} is much lower than any isomer of C_{58} and C_{62} as is indicated in figure 2. Locally (in terms of carbon cluster size) C_{60}^{BF} is a deep potential well.

In addition, C_{60}^{BF} has no weak point for chemical attack, all C atoms being equivalent; and the structure contains no pairs of adjacent pentagons which would provide an already activated point of attack for the addition of smaller carbon clusters. This contrasts with all other fullerenes in the cluster size range near C_{60}^{BF} (up to C_{68}) which must have at least one pair of adjacent pentagons. Thus in comparison with its isomers and neighbours C_{60}^{BF} once formed is more resistant to chemical attack than any other fullerene. C_{60}^{BF} is a survivor (Heath *et al.* 1987). Once formed, it should not react rapidly under most conditions. Thus any formation mechanism that has a significant fraction of the clusters reaching C_{60}^{BF} can account for the high yields because clustering can be effectively stopped at C_{60}^{BF}. No equilibrium between C_{60} and C_{70} need exist and the problem of relatively too much C_{70} encountered with the purely thermodynamic considerations above need not arise.

As we shall see, most proposed formation mechanisms aim at directly producing C_{60}^{BF}. Is this necessary? Below we show that thermodynamics strongly favours C_{60}^{BF} over other isomers of C_{60} and in the subsequent section we conclude that at elevated temperatures the ring rearrangements necessary to interconvert isomers can overcome kinetic activation barriers. This opens the way to formation mechanisms which merely have to avoid skipping over C_{60} too often.

Thermodynamic equilibrium favours C_{60}^{BF} over the other C_{60} fullerene isomers because it is much lower in energy. Presumably the next most stable isomer of C_{60} has two pairs of adjacent five-membered rings with C_{2v} symmetry. This has been calculated to be 193 kJ mol^{-1} (2 eV) higher in energy (Raghavachari & Rohlfing 1992). This C_{60} isomer is a closed, rigid cage with similar vibrational frequencies, and hence similar vibrational partition function. It is similar in overall size with similar rotational constants. Thus the internal partition function of C_{60}^{BF} is smaller than this next most stable isomer of C_{60} by roughly a factor of thirty from the ratio of symmetry numbers (2/60). The result is that the equilibrium constant for the reaction

$$C_{60}(\text{two fused pentagon pairs}) = C_{60}^{BF}, \qquad (1)$$

is approximately 4000 at 2000 K. At lower temperatures the equilibrium will shift more towards C_{60}^{BF}. There are exactly 1812 fullerene isomers (Manolopoulos 1992; Liu *et al.* 1992), but the rest of these isomers will be higher in energy and should have negligible equilibrium populations.

6. Ring rearrangements on the fullerenes

Stone & Wales (1986) considered the ring rearrangement shown in figure 3*a*. They concluded that as a concerted process it has a Hückel four-centre transition state and thus will have a substantial activation barrier. The existence of such an activation barrier has been confirmed by the calculations of Yi & Bernholc (1992) who found activation energies in excess of 500 kJ mol^{-1} (5 eV).

However, a photofragmentation study of fullerene positive ions (O'Brien *et al.* 1988) provides some experimental evidence that ring rearrangements are reasonably facile. In these studies a positive ion was mass-selected, excited by an excimer laser, and the resulting fragment ions mass detected. Almost certainly these large ions

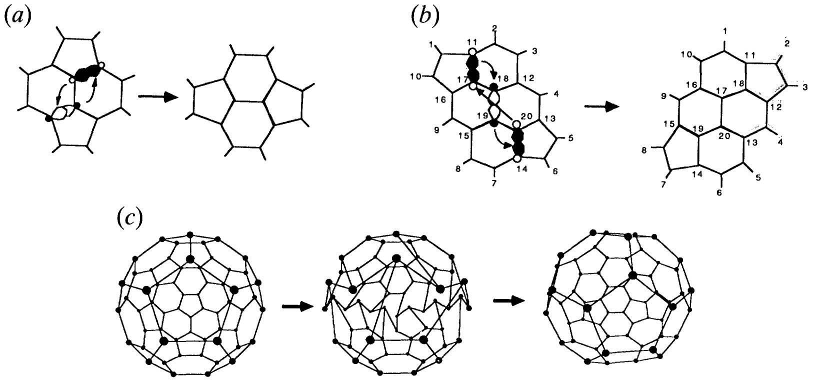

Figure 3. Schematic representation of some hypothetical fullerene ring rearrangement processes. (*a*) Stone–Wales rearrangement. (*b*) An allowed six-cycle rearrangement. (*c*) A global ring rearrangement on C_{60}. The reverse process is energetically favoured.

undergo rapid internal conversion so that the excitation energy is converted to vibrational energy. By varying the fluence of the excimer laser, the amount of energy deposited in the cluster can be varied. The time between excitation and observation of the charged fragment can also be varied. Figures 4 and 5 compare the fragmentation patterns with short and long times between excitation and observation. In figure 4, the time allowed for fragmentation is short (about 3 μs) and the fluence is high. In figure 5, the time allowed is longer (120 μs) and the fluence is lower. Thus the conditions of figure 4 favour unimolecular processes with large activation energies in contrast with figure 5 where unimolecular processes with lower activation energies are favoured. The loss of an even number of carbon atoms in the fragmentation is striking evidence that the cage structure is maintained. The fact that C_{60} is recognized as special in the observations at long fragmentation times is clear evidence that ring rearrangement processes must have a lower activation barrier than fragmentation.

There are other conceivable mechanisms for fullerene ring rearrangement in addition to the Stone–Wales process. Figure 3*b*, *c* shows some candidates. The Hückel six-centre transition state of figure 3*b* is an allowed concerted rearrangement, but the distortion required to reach the transition state is large. It should be noted that in figure 3*b* that atom 9 can be removed and atoms 15 and 16 linked converting their hexagon into a pentagon without really changing the mechanism. Likewise atom 4 could be removed. It is difficult to decide whether the cyclic rearrangement propagating around the molecule shown in figure 3*c* is an allowed concerted rearrangement. It is obviously a transition state in which many atoms move.

If ring rearrangements are facile at high temperatures, all that is required to obtain a high yield of C_{60}^{BF} is that the clustering should mostly pass through C_{60} and not skip over it, because the ring arrangements will lead downhill to C_{60}^{BF}. Indeed even if C_{60} is skipped over to C_{62} and perhaps even C_{63} and C_{64}, these clusters may dissociate back to C_{60}^{BF} at elevated temperatures. These dissociations remain endoergic (Stanton 1992), but because C_{62} has a much higher energy per C atom than C_{60}^{BF} they are less endoergic than typical fullerene dissociations, and entropy favours the dissociation. We will return the issue of whether C_{60} is likely to be skipped over in clustering.

Figure 4

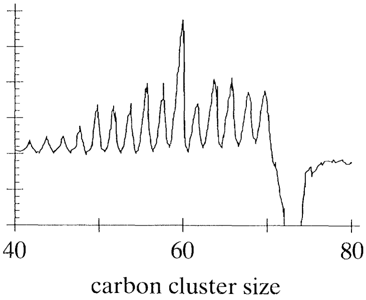

Figure 5

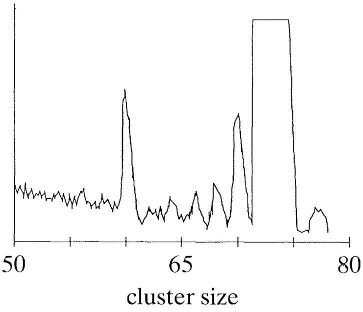

Figure 4. Photofragmentation pattern of mass-selected C_{74}^+ by ArF laser (15 mJ cm^{-2}) with about 3 μs allowed between the ArF laser pulse and mass selection of the fragment ions. Note that C_{60}^+ is only about twice as prominent as its neighbours. The C_{74}^+ peak is downwards because the data presented is the difference between excimer laser on and excimer laser off.

Figure 5. Photofragmentation pattern of mass-selected C_{74}^+ by ArF laser (15 mJ cm^{-2}) with about 120 μsec allowed between the ArF laser pulse and mass selection of the fragment ions. Note that C_{60}^+ is much more prominent than its neighbours.

7. Carbon cluster kinetics and structures

The small target in phase space presented by the C_{60}^{BF} has led several investigators to propose special kinetic pathways leading directly to C_{60}^{BF}. Some general consideration of carbon clustering can provide a basis for examining the specific proposals.

A simple model of clustering kinetics is suggested by the phrase, ‘everything that hits sticks’. One assumes that all clustering reactions are allowed, all are irreversible, and all have the same cross-section. If the clustering actually starts with atoms, this model is very unrealistic because the dimerization step, $2C \rightarrow C_2$, requires a three-body collision to stabilize the product. However, the saturated vapour over hot graphite consists largely of C_3 with C and C_2 the next most abundant species. The vibrational modes of the C_6 produced by dimerization of C_3 can temporarily store the energy released by formation of the new bond until the C_6 is stabilized by collision with the buffer gas; thus clustering can be initiated without three body collisions. Of the various refractory materials examined in cluster beam experiments, carbon clusters most rapidly because it starts with a primarily molecular vapour avoiding the three-body collision bottleneck (and because carbon forms very strong bonds).

Everything that hits sticks is readily integrated numerically. At intermediate clustering times, the resulting cluster distribution is approximately an exponential decay of cluster concentration with increasing cluster size. Major deviations from such a distribution can be interpreted as indications of size-dependent differences in reactivity.

Figure 6 depicts a carbon cluster distribution thought to be representative of a fairly early stage of clustering. It shows three distinct distributions consisting of some very small clusters with less than six atoms, an intermediate group from about seven to 22 atoms, and a heavy group from 36 atoms up. The first group, let us call it A, has both even and odd sizes and is dominated by the small clusters of three or less, the second group, B, has both even and odd cluster size and exhibits some rather marked almost periodic variations in intensity, and the last group, C, consists of only even clusters with C_{60} slightly more prominent.

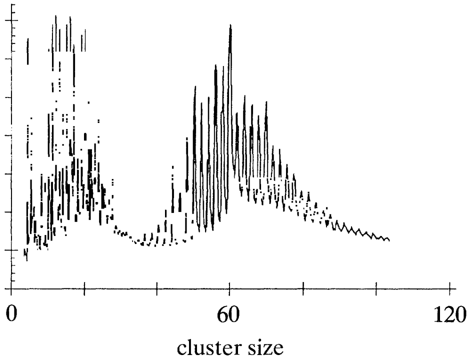

Figure 6. Typical carbon cluster distribution obtained in a laser vaporization supersonic beam source under relatively mild clustering conditions.

The most logical interpretation of the distribution is that clusters in the two low intensity regions, the 'gaps', are highly reactive while clusters in the high intensity regions are less reactive. The absence of odd clusters in the high mass region suggests that the odd clusters are much more reactive than the even ones. The high mass even clusters have been shown (Zhang *et al.* 1986) to be unreactive towards common reagents such as NO and are thought to be fullerenes. In laser cluster beam experiments with very little carrier gas, it is possible to produce cluster distributions near C_{60} with odd cluster intensities the same as those of the even cluster intensities with the C_{60} intensity hardly special at all. Presumably the carbon plasma expands so rapidly that clustering is stopped before the odd clusters react away. On the other hand, when clustering conditions are prolonged, high mass distributions, where C_{60} is essentially the only peak below C_{100} with appreciable intensity can be produced.

Recently, the ion drift tube mobility studies from Bowers' group (von Helden *et al.* 1991) have provided a means for separating carbon cluster ions with different structures because the reciprocal of the ion mobility is proportional to the collision cross-section. Thus a single cluster mass often consists of clusters with several different chemical structures and thus different cross-sections.

Such a mass-selected ion peak injected as a single packet into the drift cell separates into several peaks emerging from the cell at different times. The growth of collisional cross-section with size depends on the cluster shape, and thus in plots of inverse mobility versus cluster size the clusters can be grouped into chemical families which fall on a straight lines in the plot. Figure 7 shows such a plot of inverse mobility against cluster size for residual positive ion clusters from a supersonic excimer laser vaporization source. For a given cluster structure, a collisional cross-section can be fairly accurately calculated. Thus for a proposed structure a mobility can be calculated as a function of cluster size and compared with the mobilities of the families seen in figure 7. Thus a classification of components in the cluster beam by likely chemical structure emerges.

This classification scheme applies to positive *residual ions*, and we are interested in *neutral* clusters. Bowers' group (M. T. Bowers, personal communication) has also studied *residual anions* and find the essentially the same structural families but with quite different relative concentrations for a given mass and different ranges of cluster size where given families are important. Previous experience (O'Brien *et al.* 1986) indicates that the cluster distributions seen with residual *cations* is more similar to that of the *neutrals* than is the residual anion distribution. Thus the use of cation

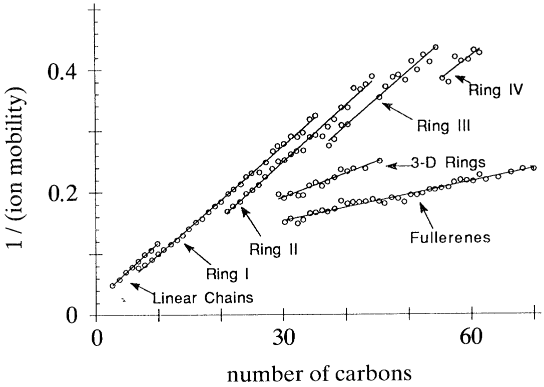

Figure 7. Reciprocals of the mobilities the carbon cluster cations as a function of cluster size from the work of Bowers and coworkers. The reciprocal of the mobility is proportional to collision cross-section which can be calculated from a model structure permitting the structural classification shown. Ring I is a single ring, ring II may be a planar bicyclic, ring III and ring IV may be one family and are guessed to be planar tricyclic rings. 3-D rings are guessed to be rings fused into a three-dimensional perhaps propeller-like structure.

distribution of figure 7 seems more appropriate to a discussion of the neutral distribution. The data in figure 7 were obtained under conditions where clustering was quenched at quite an early stage corresponding to the presence of odd peaks with intensities only somewhat less than the even peaks in the high mass region above 30 carbon atoms.

Comparison of figures 6 and 7, indicates that group A (the very small clusters of figure 6) must be linear, the second-group B must correspond to ring I, and the third group C must be, as already indicated, the fullerenes. Ring I species (B) and the fullerenes (C) have no dangling chemical bonds, thus accounting for their lack of reactivity. Ring II species have been assigned bicyclic structures and must be quite reactive as the ring II region overlaps the gap between 26 and 36 carbon atoms rather accurately.

For a given mass, von Helden *et al.* can measure the relative amounts of the various structures as they resolve into separate peaks in the drift cell. Under their clustering conditions, high mass clusters containing an odd number of carbon atoms are present in significant quantities implying that clustering has been quenched at an early stage. They find already C_{32}^+ a few percent of the fullerene structure which grows to 98% by C_{60}^+.

8. Proposed kinetic models for C_{60}^{BF} formation

We have already seen that any model accounting for C_{60}^{BF} and $C_{70}(D_{5h})$ formation must be a kinetic one with major pathway(s) leading directly to C_{60}^{BF}.

(*a*) *Special pathways based on particular intermediate size clusters*

Those proposing a kinetic model in this sense believe that the potential energy hole of C_{60}^{BF} viewed as a target is too small to hit (at least often enough to account for the yield) by a chaotic clustering with many pathways. There are two models which combine several intermediate size clusters into the C_{60}^{BF} cage. A model of C_{60}^{BF} formation proposed by Goeres & Sedlmayr (1991) combines napthalenic C_{10} units.

Quantum theoretical calculations by Scuseria's group (Strout *et al.* 1992) show that napthalenic C_{10} is much higher in energy than simple C_{10} rings (ring I). This seems fatal for the model because no matter how reactive a species is, any pathway where it reacts with itself will be minor unless the concentration of the species is high. The other model of C_{60}^{BF} formation building up from intermediate size clusters has been proposed by Wakabayashi & Achiba (1992). In this mechanism napthalenic C_{10} combines with ring C_{18} to form a building block 'open' fullerene C_{28} well on the path to C_{60}. (The process continues C_{18}, C_{12}, C_2 to reach C_{60}.) As mentioned above, it is unlikely that napthalenic C_{10} can ever be present in significant amounts. However, the Scuseria group calculations (Strout *et al.* 1992) suggest that when ring C_{10} is placed inside a C_{18} ring, it begins to distort in the direction of producing the appropriate C_{28} intermediate.

An argument against mechanisms utilizing particular intermediate size clusters can be based on the fact that a wide variety of intermediate size clusters are observed in carbon cluster distributions which ultimately will produce larger clusters. Thus it is hard to account for the high yields of C_{60}^{BF} when these other intermediates pathways, which presumably lead to other products, are present.

(*b*) *The pentagon road*

To account for the formation of C_{60}^{BF} as a minor channel in supersonic cluster beams, we proposed the following picture (Heath *et al.* 1987). When the carbon cluster size passes about 30 atoms, graphitic sheets begin to be formed. As smaller species are ingested by the graphitic sheet, it attempts to follow the low energy path minimizing the number of dangling bonds by including pentagonal configurations at convenient places among the hexagonal ones. The incorporation of pentagons allows the sheet to minimize energy by curling up, reducing the number of dangling bonds. In this older picture, the pentagonal configurations introduced in this way will generally form rather randomly, giving rise to a multitude of curved shell-like graphitic networks of various shapes and sizes. Occasionally a sheet will 'accidentally' form in which the pentagons are so distributed so that closure can occur. The ion mobility work of von Helden *et al.* provides some support for this model in that ions are observed between 30 and 4 atoms with intermediate mobility between the fullerenes and the rings. These mobilities suggest a three-dimensional (3D) structure and the species were called 'open' fullerenes by von Helden *et al.*

To account for the observed high yields of C_{60}, this picture can be modified (Smalley 1992) by emphasizing the reduction in the number of dangling bonds through the incorporation of pentagons and de-emphasizing the random incorporation of pentagons. It is well-known (Schmalz *et al.* 1986) that adjacent pentagons are destabilizing. Construction of a carbon cluster, by specifying that it grows by addition of five-membered rings with closest vertices separated by a pair of six-membered rings on each side of the connecting bond between the five-membered rings, leads directly to C_{60}^{BF}. In this picture, open sheets are growing by addition of small clusters to their open edges with constant annealing so that the growth units described above are maintained. The driving force for following this pentagon road is that it reduces the number of dangling bonds in comparison with a hexagonal sheet while avoiding the high energy adjacent pentagon structures. In this model, growth takes place by following a minimum energy path in the broad valley of these pentagon road structures.

This model would be made more tangible if the 3D ring (or open fullerenes) seen in figure 7 could be identified with pentagon road structures, but obviously they cannot. By approximately thirty-six atoms the inverse mobility of the 3D ring species is already more than that of C_{60}^{BF}. The pentagon road species inverse mobilities would approach that of C_{60}^{BF} as their size approached 60. Thus there is no direct experimental evidence for the existence of pentagon road species in the structures found by ion mobility probing. However, it is important to realize the importance of a cluster structure to the main kinetic pathway is not measured by its concentration, but by the flux going through it. Thus a highly reactive species (and the pentagon road species are expected to be very reactive) may be present in very small concentrations and thus be very difficult to detect, but still carry most of the kinetics.

(*c*) *The fullerene road*

Heath (1991) has proposed that fullerenes form at cluster sizes of about forty and grow by the addition of small clusters, e.g. C_2 until C_{60} is reached. To have a growth mechanism which finds C_{60}^{BF} structure with its isolated pentagons, he proposed that the addition of small clusters to the fullerene cage proceeds in a manner which removes adjacent pentagons. This idea is attractive because adjacent pentagons are a high-energy site and thus are likely to be more susceptible to chemical attack. Heath proposed some specific mechanisms for attack by C_2 that remove adjacent pentagons. However, his mechanisms require rearrangements of the part of the fullerene cage not shown in his diagrams and it is not clear how reasonable these rearrangements can be made. Heath's picture of fullerene growth as the synthetic route to C_{60} can be modified by postulating that ring rearrangements take place more rapidly than growth and remove adjacent pentagons when possible as this lowers the energy.

A fullerene path picture of clustering leading to large C_{60}^{BF} yields emerges. The conditions needed when the cluster sizes approach the critical fullerene region are a moderately high temperature and a relatively low carbon density. As clusters sizes grow above 30 atoms, fullerenes begin to form. They grow in size either by additions of smaller clusters to the cage or perhaps by opening and reclosing. Odd clusters, of course, cannot have a fullerene structure, but are expected to be very fullerene-like in structure. When odd clusters are formed, they are expected to be very reactive and easily converted to fullerenes by loss or abstraction of a C atom. When a C_{60} cluster is formed, it is either a fullerene or almost a fullerene. Ring rearrangements on the C_{60} remove adjacent pentagons and lead downhill in energy until the C_{60}^{BF} isomer is found. By the arguments discussed above, once found C_{60}^{BF} is much less reactive and is effectively removed from the reaction scheme. The C_{60} atom cluster size is rarely skipped over because reactions where an intermediate size cluster adds to a fullerene require extensive reorganization of the fullerene, and therefore have a low rate. However, reactions in which an intermediate size cluster reacts with a fullerene to produce the next larger size fullerene expelling a smaller intermediate are not excluded. In C_{61}, C_{62} up to possibly C_{64}, there is some chance that the very hot cluster will lose C, C_2, C_3 or C_4 and revert to C_{60}; otherwise once past C_{60} the slide down the energy curve of figure 2 continues with another chance at C_{70} that the growing cluster can fall into the $C_{70}(D_{5h})$ potential well and be trapped.

Clustering at very high temperatures, as with high buffer gas pressures in graphite vaporization, is unfavourable to C_{60} formation because C_{60}^{BF} itself becomes more reactive under such conditions. If the temperature decreases too rapidly, as with low buffer gas pressures in graphite vaporization, clustering takes place so rapidly that C_{60} is often skipped over and the reorganizations, needed to find the C_{60}^{BF} minimum, do not compete with further clustering.

At the time that Heath proposed his fullerene mechanism, no macroscopic samples of endohedral metallofullerenes had been synthesized; he naturally argued that this fact supported the fullerene growth mechanism over the pentagon road. It is impossible to introduce a metal atom into a closed shell, whereas a metal atom could nestle into the cup formed by the pentagon road. However, since that time many metallofullerene species have been synthesized, and this fact appears, at least at first glance, to argue strongly against the closed fullerene growth mechanism. There are three ways that the fullerene road could be made compatible with the fact of endohedral metallofullerene synthesis: the metal atom attaches to the cluster before a closed fullerene is formed, the metal atom in some way can eat into a closed fullerene, or the synthesis of endohedral metallofullerenes is by a mechanism entirely different from that of the empty fullerenes. Of these possible escape routes for the fullerene growth mechanism, early attachment seems most plausible. In the pentagon path mechanism, as the cluster following the pentagon rule is closing, the doorway for entrance of the metal becomes smaller. Thus, it is unlikely that the metal attaches at the last stages if the pentagon road is the correct mechanism, and both mechanisms seem to require fairly early metal attachment.

9. Comparison of the two mechanisms

The pentagon road and the fullerene road are both fairly plausible mechanisms for the formation of C_{60}^{BF} in high yield in condensing carbon vapour. Both explain the need for an elevated temperature for effective fullerene formation: the pentagon road to bring about annealation to the isolated pentagon networks before further growth; the fullerene road to overcome activation barriers to fullerene growth and ring rearrangements. Both seem to require the presence of small carbon clusters for growth by addition of small clusters to growth elements in the 30+ to 58 carbon atom range, although each can be modified to eliminate the requirement for the presence of small clusters by adding mid-size clusters to the growing species with the rejection of part of the mid-size cluster.

The two mechanisms are qualitatively different. In the pentagon road mechanism, the chemistry is carried by highly reactive, high-energy species that are never present in very high concentration, but through which most of the chemistry passes much as combustion is carried by free radicals. Note that if growth of the pentagon road species involves very small carbon species, that both reagents have high energy and are highly reactive as in a radical–radical process. In the fullerene road, the fullerene reactants are the most stable clusters of their sizes and there is a great deal of experimental evidence that they are indeed present in high concentration. There is also evidence that they are reacting.

Under the wrong clustering conditions the C_{60}^{BF} yield can be very small. For example, buckminsterfullerene is not very prominent in the distribution shown in figure 6. Yet there is abundant evidence that the even number species larger than about 34 atoms are predominantly fullerenes in distributions where C_{60} is not prominent. These readily formed smaller fullereness disappear when clustering is prolonged at elevated temperatures leaving only C_{60} and C_{70} as survivors. There must be a reasonably facile mechanism by which closed fullereness can grow (and shrink) at high temperatures so that the smaller fullereness which are known to form can be destroyed and replaced by C_{60}^{BF} and larger fullereness.

It is known (Howard *et al.* 1991) that C_{60}^{BF} is produced in hydrocarbon flames in good yield. In the flame, the dangling bonds at the edge of a pentagon road sheets can be satisfied by H atoms removing the driving force to curvature. However, this observation is not fatal to the pentagon road mechanism, because the temperature is probably high enough to make the CH bonds labile and there are free radicals present capable of extracting H atoms from the sheet edge.

The chemistry of two mechanisms is very different, yet it is not easy to design an experiment that will reliably differentiate between them. Methods for synthesizing C_{60}^{BF} under more controlled conditions, such as the laser vaporization, heated flow tube of figure 1, and some means of *in situ* monitoring of the concentrations of the species present during growth are needed. Possibly the addition of small quantities of unsaturated hydrocarbons such as acetylene to the buffer gas flow would be illuminating since at 1200 °C HCCH would be expected to heal the dangling bonds on the edges of the growing sheets removing the driving force for curvature and stopping the growth. Acetylene might be less likely to hinder the growth of fullereness, but could hinder their formation.

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Discussion

R. C. Haddon (*AT & T Bell Laboratories, U.S.A.*). Presumably, as the fullerenes grow, by any of these mechanisms, they do so by one carbon at a time?

R. F. Curl. That is one of the questions to which we would like to know the answer. The small species you have present are C_1, C_2 and C_3 with, possibly, larger less reactive rings. I think growth occurs either by adding C_2, which is not too attractive, because it's a reactive species that is not present in high concentration, or by adding a C_3 atom and then 'spitting' out a carbon atom. In the fullerene growth mechanism you have to maintain the integrity of the cage when you add to it. You may add a C_3 molecule, form an imperfect cage, and then add another C_3 to form a perfect cage, if you use the species present in the highest concentration, C_3.

R. C. Haddon. So in that mechanism you actually avoid odd membered fullereness?

R. F. Curl. I would prefer to avoid them, but I am not sure they can be avoided, because the most logical reagent is C_3. You either have to spit out a carbon atom, which is a high-energy process, or you can tolerate the odd ones, which then turn out to be very reactive and immediately go on to the next step. The big problem that you have with the 'fullerene road' theory, is that you don't want to jump over C_{60}. Say you have large quantities of polyacetylene rings, and you take C_{56} and a 10 membered polyacetylene type ring, and you stick it on, you jump way over C_{60}. If this is to be a plausable mechanism, you have to have some way of sticking on part of a C_{10}, so that you don't jump over the big hole in the road that corresponds to buckminsterfullerene.

R. C. Haddon. Do you regard these intermediates as fluxional, so that the carbon atoms get totally redistributed throughout the molecule as they get added? Based on the isotope experiments, there has to be some sort of randomization going on.

R. F. Curl. I assumed in the isotope experiments that randomization was probably occurring in the vaporization step; that is, you obtain such small fragments on vaporization, that a random situation develops. It would be useful to think of an experiment where you started with a smaller fullerene, say all ^{12}C, and then brought in another which was all ^{13}C, and see how that randomized, but I think that the randomization in those processes may occur in the very first steps.