# Mechanism of Fullerene Formation

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In 1985, Kroto et al. made the surprising discovery that $C_{60}^+$ was unusually stable among the gas-phase carbon ions produced by laser vaporization of graphite.[1] They hypothesized that this stability resulted from its truncated icosahedron structure and dubbed the ion "buckminsterfullerene" after the famous architect. Many gas-phase experiments and theoretical investigations that followed supported this claim, and the soccer-ball structure of $C_{60}$ was finally confirmed in 1990, when Krätschmer and Huffman discovered a method for making macroscopic quantities of $C_{60}$ and other larger "fullerenes" via resistive heating of graphite.[2] Krätschmer and Huffman's finding opened up new avenues for research and discovery. In addition, it presented a mechanistic puzzle to physical and organic chemists: How can such highly ordered compounds as the fullerenes form in significant yields in the entropic conditions of graphite vaporization? And why do these conditions produce more $C_{60}$ than any other all-carbon molecule?

Before the bulk isolation of fullerenes, Smalley and co-workers postulated a mechanism which they called the "party line" for fullerene formation in their laser-vaporization/molecular-beam source.[3] In this scenario, small carbon particles would come together to form linear species, which would react with other linear species to make rings. Further addition of small linear chains would increase the size of the rings until they reached the 25−35-atom range. The party line mechanism assumes that, in that size domain, polycyclic networks resembling open graphitic sheets become thermodynamically most favorable. Smalley and co-workers hypothesized that these graphitic sheets are more reactive than rings or linear chains because they have more dangling bonds, and that to minimize the number of dangling bonds, the polycyclic network incorporates some pentagons, causing curvature. Occasionally, one of these cuplike pieces of graphite gathers enough pentagons in the right places to force it to close into a hollow cage, thereby forming a fullerene.[3]

Smalley and co-workers developed this theory to explain the observation of $C_{60}$ ions in their initial cluster beam experiments. In these studies, only a small fraction of the carbon vapor became fullerenes, while the rest apparently formed large soot particles. The party line scheme therefore offered an explanation of a rare but noticeable event. Most of the nucleating carbon would, in this scenario, create large spiraling particles where the "growth edge" overshot the op-

posite edge of the graphite cup, forming a new layer of graphite surrounding it.[3] Kroto and McKay extended this picture to account for the presence of polyhedral particles in soot, observed by transmission electron microscopy (TEM).[4] But this mechanism does not explain how soluble fullerenes like $C_{60}$ can form in macroscopic quantities, with yields of 20% and more.

In searching for a replacement to the party line, it is helpful to understand some general information about fullerene production. Bulk fullerenes form from graphite vapor, produced via either resistive heating or a carbon arc under helium atmosphere in a pressure range of 100−400 Torr.[5] Isotope studies involving vaporization of mixed samples of $^{12}$C- and $^{13}$C-graphite have shown that the reacting material first breaks down to atomic carbon or small fragments ($C_2$ or $C_3$) before recondensing into fullerenes.[6] In addition, production of fullerenes in an electric field leads to their isolation almost entirely from the cathode, rather than the anode, suggesting that cations are important to the reaction.[7] Although varying the conditions of bulk production can alter the ratio of isolated $C_{60}$ to $C_{70}$ considerably, generally $C_{60}$ is the dominant product, with fullerenes forming in up to 40% overall yield.[8] However, $C_{60}$ is less thermodynamically stable than the larger fullerenes, according to both theoretical[9] and experimental[10] evidence.



$C_{60}$        $C_{70}$
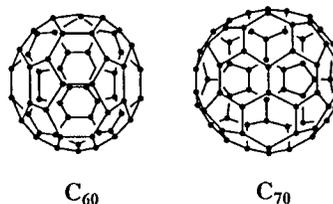
The prevalence of $C_{60}$ in fullerene samples indicates that kinetics rather than equilibrium processes govern

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162−164.

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(7) Bunshah, R. F.; Jou, S. K.; Prakash, G. K. S.; Doerr, H. J.; Isaacs, L.; Wehrsig, A.; Yeretzian, C.; Cynn, H.; Diederich, F. N. *J. Phys. Chem.* **1992**, *96*, 6866−6869.

(8) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. R.; Hunt, J. E.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499−7503.

(9) Cioslowski, J. *Chem. Phys. Lett.* **1993**, *216*, 389−393 and references cited therein.

Nancy S. Goroff was born in Chicago in 1968. After earning a B.A. in 1990 from Harvard University, where she worked with Joseph J. Grabowski, she attended UCLA, conducting research under the joint guidance of François Diederich and Orville L. Chapman. Since receiving her Ph.D. in organic chemistry in 1994, she has been a National Science Foundation postdoctoral fellow at Michigan State University, in the lab of James E. Jackson. Her research interests include all-carbon and carbon-rich molecules, unsaturated carbenes, and unusual organic π systems of all sorts.
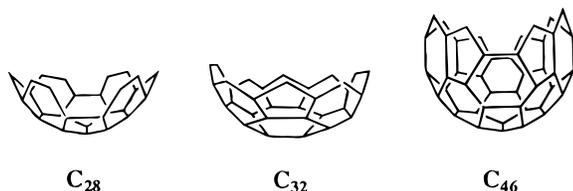
C₂₈            C₃₂            C₄₆

**Figure 1.**   Some hypothetical intermediates along the Pentagon Road to the fullerenes.

cluster growth. Early mass spectrometry experiments by Kroto et al. support this idea. They found that, at early reaction times, $C_{60}^+$ and $C_{70}^+$ do not dominate the mass spectrum, but with increasing length of reaction, the other even-*n* $C_n^+$ ions of similar size disappear.[1] Thus, whatever the mechanism of cluster growth, $C_{60}$ and $C_{70}$ seem less vulnerable to it.

This Account discusses several proposed mechanisms for fullerene formation and, in particular, how they fit the available experimental evidence with regard to the following key aspects of the reaction: (1) the intermediates involved in carbon cluster growth; (2) the "growth species" which react with the intermediates to increase their size, and the mechanisms of those interactions; (3) the mechanism for forming an isolated-pentagon fullerene structure; and (4) what makes $C_{60}$, and to a lesser extent $C_{70}$, special, i.e., what about the reaction sequence causes these two compounds to dominate the fullerene yield.
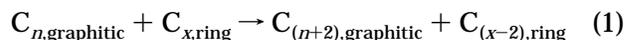
## The Pentagon Road

With the discovery of a bulk method for production of fullerenes, Smalley and co-workers modified their original party line scheme, proposing an appealing mechanism which they dubbed the "Pentagon Road."[11,12] This view of carbon nucleation assumes that the lowest-energy form of any small graphitic fragment has the following properties: (1) it is made up only of hexagons and pentagons, (2) it includes as many pentagons as possible, and (3) none of the pentagons are adjacent (Figure 1). In addition, according to the Pentagon Road, for carbon clusters that have more than 20–30 atoms but are too small to make a closed fullerene with isolated pentagons, such open graphitic cups are lower in energy than any other structure. Furthermore, in the slow-cooling environment of bulk fullerene production, annealing allows the carbon clusters to find the energy minimum among structures. Thus, thermochemical stability dictates the formation of these graphitic cups in preference to other possible structures, and kinetic reactivity determines that they continue to grow toward fullerenes.

The main mechanism for this growth, according to the original Pentagon Road scheme, is addition of $C_2$ and other small carbon particles to the reactive edges of the developing graphitic network. The closed fullerenes, once formed, have no open edges and, therefore, generally do not grow any further. Thus, any nucleation path that leads to $C_{60}$, as many would

according to the annealing described above, is ultimately a dead end in cluster growth.

There is no experimental evidence to support the presence, in the later stages of fullerene formation, of the abundant supply of small carbon particles necessary for this scheme. However, Curl has proposed[5] a modification to the Pentagon Road, in which the growing graphitic cups react with intermediate-sized rings, according to eq 1, thus forming a larger graphitic cup and a smaller ring. Such reactions would obviate the need for a constant supply of $C_2$ and $C_3$. In addition, neither reactant would need to rearrange significantly, and therefore these reactions should occur with relatively low energy barriers.

$$C_{n,\text{graphitic}} + C_{x,\text{ring}} \rightarrow C_{(n+2),\text{graphitic}} + C_{(x-2),\text{ring}} \quad (1)$$

Theoretical consideration of the proposed Pentagon Road intermediates and other possible medium-sized carbon cluster isomers has led to mixed results. Density functional theory calculations have predicted that, among graphitic fragments, those including pentagons will have higher energy than those with planar structures.[13] However, recent coupled-cluster calculations on $C_{20}$ by Taylor et al.[14] found the bowl-shaped graphitic cup containing a central pentagon to be nearly degenerate in energy to the fullerene isomer, and both to be lower in energy that the monocyclic ring. The authors did not consider a planar graphitic sheet or other isomers in their study.

The Pentagon Road offered an attractive explanation of the observed preferential formation of $C_{60}$ from graphite vaporization, but experiments conducted since its proposal have cast doubt on its validity. Although a large body of information is now available on the isomer distributions of carbon cluster ions,[15–21] there is no evidence for the existence of curved graphitic structures, such as those which are predicted to act as the key intermediates in fullerene formation. The groups of Bowers[15,16] and Jarrold[17–21] have examined the isomer populations of carbon cluster cations from laser vaporization of graphite by drift-tube ion-mobility experiments. These studies separate different species with the same *m/z* ratio according to their cross-sectional area, averaged over molecular rotations. By comparing the experimental data with calculated average cross sections for different hypothetical carbon cluster structures, the groups of both Bowers and Jarrold have probed the isomer distribu-

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(14) Taylor, P. R.; Bylaska, E.; Weare, J. H.; Kawai, R. *Chem. Phys. Lett.* **1995**, *235*, 558–563.

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(21) Hunter, J. M.; Shelimov, K. B.; Jarrold, M. F. To be published.

tion for $C_n^+$, $n < 100$.[22] Bowers and co-workers[15] found that linear structures dominate the smallest carbon clusters but that, at $C_{10}^+$, the linear isomer disappears, and cluster cations with $n = 10-20$ appear as only one isomer, the monocyclic ring. Bicyclic ring structures come in around $C_{20}^+$, and other ring "families" containing three or more large rings become significant above $C_{30}^+$. The first fullerene cations also appear at $C_{30}^+$, and fullerenes become dominant around $C_{50}^+$. Jarrold's group has observed similar isomer distributions for carbon cluster ions in the 10–70-atom size range.[17−19] Scuseria et al. have calculated ion mobilities for a variety of possible carbon cluster isomers and have pointed out[23] that some of the isomers identified as tricyclic structures may actually be the three-dimensional products of 4 + 2 addition reactions and have only two large rings.

Another minor isomer first appears at around $C_{30}^+$, with an ion mobility intermediate between that of the fullerene isomer and the planar ring isomers. Bowers has attributed this small feature in the arrival time distribution to a "3-dimensional ring" isomer of indeterminate structure.[15] In contrast, Jarrold et al.[17] have argued that the mobility of this isomer agrees well with the calculated average cross-sectional area of a roughly planar graphitic sheet for carbon clusters over a large size range. Scuseria et al.[23] report similarly that graphite fragments with no pentagons or with pentagons only on the periphery (where they affect the curvature of the cluster only minimally) could account for the experimental results. However, graphitic cups including interior pentagons would have mobilities inconsistent with the observed ions.[23]

Jarrold's group has also conducted annealing studies, in which the ions are injected into the drift tube at variable energies, and then collisions with the buffer gas convert their kinetic energy to internal energy.[17−19] Measuring the mobilities provides the isomer distribution at a given energy, allowing an understanding of the relative energies and activation barriers for interconversion of different isomers. In these annealing experiments, Jarrold and co-workers have found that most of the non-fullerene cluster ions convert to two isomers, the fullerene and monocyclic ring, with the percentage attributable to the graphitic fragment increasing slightly. For $n = 30-50$, most of the planar polycyclic isomers anneal to the monocyclic ring,[18] but above $n = 50$, the non-fullerene isomers rearrange almost entirely to the fullerene, with only a small fraction converting to the monocyclic ring.[18,19] $C_{60}^+$ behaves essentially the same as other clusters near it in size, even though the others cannot form isolated-pentagon structures. (Bowers and co-workers have conducted similar annealing experiments on $C_n^+$, $n = 30-40$, with qualitatively similar results.[16]).

In more recent, particularly elegant studies, Jarrold and co-workers have used pulsed laser annealing in the middle of a longer drift tube to examine the rearrangements of specific carbon cluster ion isomers.[20,21] By timing the laser pulse to correspond with
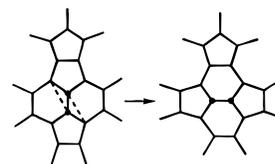


**Figure 2.** The Stone−Wales rearrangement, predicted to allow fullerenes to isomerize to the structure with the most isolated pentagons.

the drift time of a particular isomer, the researchers can target that isomer and separate its reactions from those of the others. From these experiments, they have determined that the more rings the initial structure contains, the smaller the barrier is to rearrangement to a fullerene. Tricyclic or tetracyclic isomers rearrange readily to form fullerenes, while bicyclic ions are significantly slower, and monocyclic rings appear to fragment rather than to rearrange.[20,21]

In the many drift-tube ion-mobility studies performed in the Jarrold and Bowers labs, neither group has observed any all-carbon ions that resemble the expected open partial fullerenes predicted by the Pentagon Road mechanism. As Curl has pointed out,[5] this fact in itself does not prove that the graphitic cups do not exist and act as the key intermediates in fullerene formation. The Pentagon Road structures could be present in very small concentrations, reacting away as quickly as they are formed. Bowers's and Jarrold's experiments might observe only the relatively unreactive $C_n$ isomers, those "left behind" as a high flux of material passes through the reactive open partial fullerene isomers. But even annealing experiments, which should produce the thermodynamically, rather than kinetically, favored species, do not provide evidence for the structures predicted in the Pentagon Road scenario. Thus, the basic assumption of the Pentagon Road mechanism, that the lowest-energy structures for all-carbon molecules in the 25−50-atom range are open graphitic cups, seems unlikely.

## The Fullerene Road

Heath[24] has suggested another mechanism, which agrees better with the drift-tube ion-mobility data. His "Fullerene Road" scheme involves a growth mechanism similar to the Pentagon Road (addition of small carbon fragments), but the intermediate all-carbon molecules with 30−58 atoms are, like the larger products, closed fullerene cages. Because these small fullerenes cannot obey the isolated pentagon rule, they are more reactive than the larger ones, with the 5−5 ring junctures serving as activated sites for addition of $C_2$. Thus, $C_{60}$ and $C_{70}$, if formed as the isolated pentagon isomers, act as end points of cluster growth. Heath also invokes the Stone−Wales rearrangement,[25] shown in Figure 2, as a method for producing the fullerene isomer with the fewest adjacent pentagons.

As with the Pentagon Road mechanism, the Fullerene Road as stated requires a large concentration of $C_2$ and $C_3$, even at the later stages of cluster growth. However, Curl's modification applies equally well to both mechanisms.[5] The advantage of Heath's mechanism is that it is based on the most abundant, and thermodynamically most stable,[14−17] species in the 50−60-atom size range.

(22) Note that the ion drift-tube method cannot distinguish between closely related structures, such as a monocyclic carbon ring $C_{20}$ and an 18-carbon ring with a 2-carbon branch. Such linear branches have only a very minor effect on ion mobility.

(23) Strout, D. L.; Book, L. D.; Millam, J. M.; Xu, C.; Scuseria, G. E. *J. Phys. Chem.* **1994**, *98*, 8622−8626.

(24) Heath, J. R. *ACS Symp. Ser.* **1991**, *481*, 1−23.

(25) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501−503.

Creasy has modeled the kinetics required for a fullerene ion formation mechanism that involves growth in small steps, such as the two described above.[26] He based his model on eqs 2 and 3 for cluster growth, where $x = 1, 2$, or 3. Estimating the rate of reaction ($k_1$) for all even $C_n^+$ to be identical, with the exception of $C_{60}^+$ and $C_{70}^+$, Creasy found appropriate $k_1$ values which reproduced the general character of a typical mass spectrum from laser vaporization of graphite, demonstrating that a mechanism involving addition of small particles could explain the observed cluster distributions.

$$C_n + C_x \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_{n+x}^* \qquad (2)$$

$$C_{n+x}^* + M \overset{k_2}{\longrightarrow} C_{n+x} \qquad (3)$$
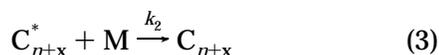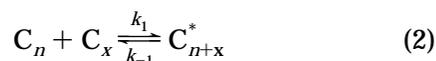
## Ring Coalescence and Annealing

Growing experimental evidence, however, indicates that carbon nucleation can occur through coalescence of medium-sized carbon clusters, rather than gradual addition of $C_2$ and $C_3$ particles. In Fourier-transform mass-spectrometry (FTMS) experiments on the carbon oxides **1**–**3**, McElvany et al.[27] have studied the formation and reaction of the cyclic all-carbon molecules $C_{18}$, $C_{24}$, and $C_{30}$. Following laser desorption of **3**, a monocyclic $C_{30}$ ring coalesces with a $C_{30}^+$ ion to form a fullerene ion $C_{60}^+$ (Figure 3C). Similarly, coalescence of four monocyclic 18-carbon rings or three 24-carbon rings, from laser desorption of **1** or **2**, respectively, leads to $C_{70}^+$, via $C_{72}^+$ (Figure 3, panels A and B, respectively). Significantly, in each of these experiments, $C_{60}^+$ or $C_{70}^+$ is the dominant product, under conditions which show no evidence for growth by $C_2$ addition.
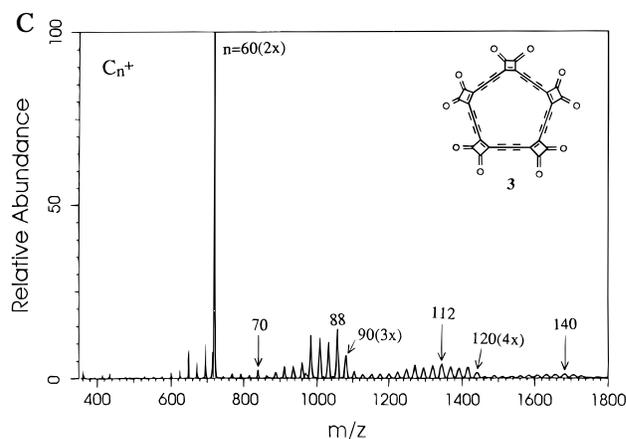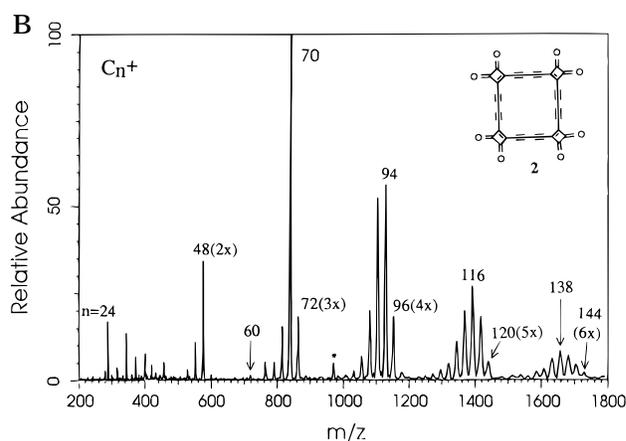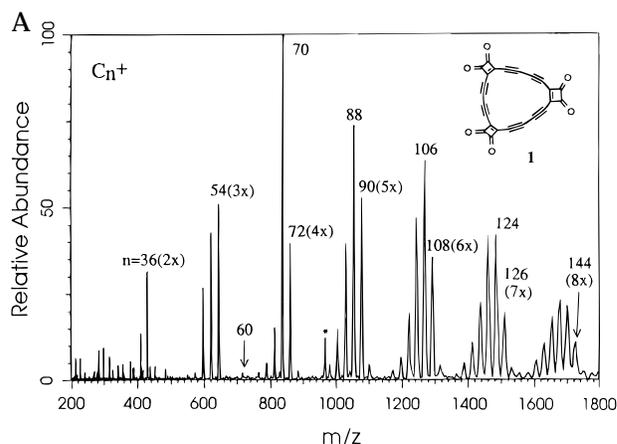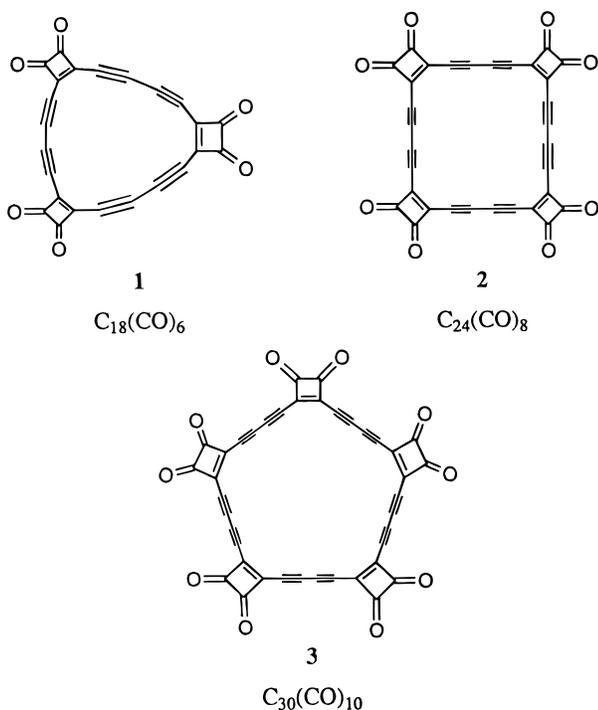
**1**

$C_{18}(CO)_6$

**2**

$C_{24}(CO)_8$

**3**

$C_{30}(CO)_{10}$

(26) Creasy, W. R. *J. Chem. Phys.* **1990**, *92*, 7223–7233.
(27) McElvany, S. W.; Ross, M. M.; Goroff, N. S.; Diederich, F. *Science* **1993** *259*, 1594–1596.

**Figure 3.** Positive-ion laser-desorption mass spectra of **1**–**3**. The high-mass ions ($m/z > 500$) correspond to $C_n^+$ (even $n$) with several reference values shown. Also indicated are the oligomers of the parent cyclocarbons, $C_{18}^+$, $C_{24}^+$, and $C_{30}^+$, ($2x$, $3x$, etc.) Peaks denoted by an asterisk (*) are due to a noise artifact.

Initial studies on **1**–**3** by Rubin et al.[28] led Kroto and Walton to propose that a 60-carbon polyyne ring might rearrange to buckminsterfullerene.[29] In fact, Jarrold's and Bowers's annealing studies, described earlier, have since shown that all-carbon ions $C_n^+$ rearrange readily.[16–21] Hunter et al.[19] estimate that the activation energy for conversion of polycyclic rings in the size range 50–70 atoms to the fullerene isomer is less than the energy of a typical C–C $\sigma$ bond. In

(28) Rubin, Y.; Kahr, M.; Knobler, C. B.; Diederich, F.; Wilkins, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 495–500.
(29) Kroto, H. W.; Walton, D. R. M. In *Carbocyclic Cage Compounds: Chemistry and Applications*; Osawa, E., Yonemitsu, O., Eds.; VCH Publishers: New York, 1992; Chapter 3, pp 91–100.
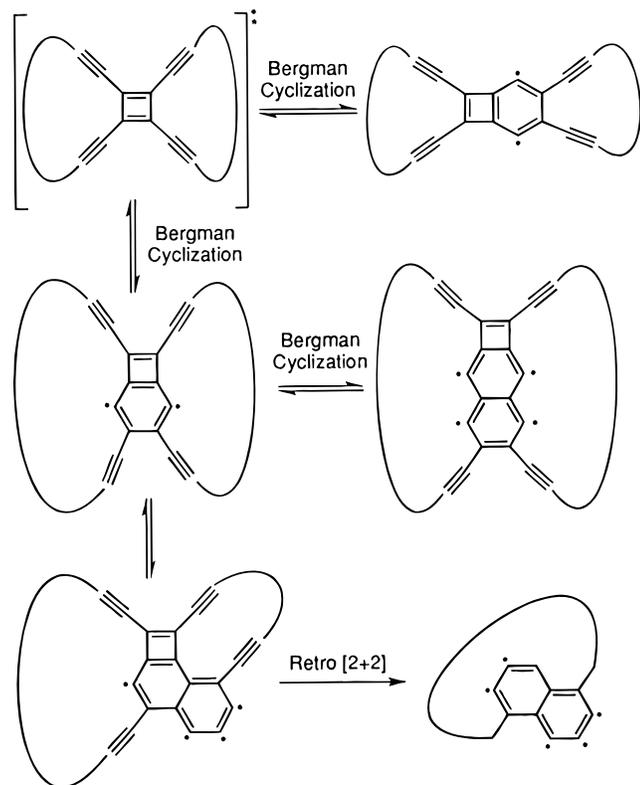
**Figure 4.** Mechanism proposed by Hunter et al. in ref 19 to initiate the annealing of bicyclic polyyne rings into fullerenes. The rearrangement pathway includes Bergman cyclizations, radical additions, and retro-[2 + 2] reactions.
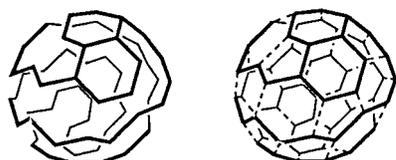


**Figure 5.** One possible route for a spiraling polyyne chain to "zip up" to form buckminsterfullerene $C_{60}$. The dashed lines represent new bonds to be formed.

addition, the authors find that $C_{60}^+$ is only slightly more likely to rearrange to a fullerene than is $C_{58}^+$. These results, combined with the evidence of polyyne ring coalescence in the studies on **1**–**3**, strongly indicate that the intermediates in fullerene formation need not look like fullerenes or fullerene fragments. In addition, mid-sized carbon rings can act as the growth species.

Jarrold and co-workers have developed further Kroto and Walton's mechanistic scheme based on this new experimental evidence.[19,20] They propose that the main mechanism for growth among all-carbon molecules is reaction with mid-sized rings and that the planar polycyclic and monocyclic ring compounds which they observe react much faster than the fullerene isomers. Reactions between the planar ring species create new planar polycyclic compounds, which can either grow further through ring coalescence or anneal to give a fullerene or monocyclic ring. They hypothesize that the coalescence to the fullerene begins with a Bergman enediyne cyclization, followed by a "zipping up" of the spiraling polyyne chain (Figures 4 and 5). The monocyclic ring, if formed, will continue to grow via coalescence with other planar ring species. Fullerenes grow by addition of small carbon particles.

According to Jarrold's picture, as in Heath's Fullerene Road scenario, $C_{60}$ and $C_{70}$ form preferentially because they are the first fullerenes with no adjacent pentagons and, therefore, are less susceptible to addition of $C_2$ and other small particles. In addition, as the molecules grow larger, the monocyclic ring isomer becomes relatively less and less stable, as the fullerene increases in stability. Thus, in the size range around 60–70 atoms, rearrangement to the fullerene, instead of the monocyclic ring, becomes much more likely, increasing the yield of $C_{60}$ and $C_{70}$. However, in Jarrold's experiments, $C_{60}$ and $C_{70}$, once formed, were no more likely than other clusters in their size regime to rearrange to a fullerene structure.

Initially, Jarrold and co-workers postulated[19] that the fullerenes, unlike the ring species, do not react with ring compounds and that they only add small carbon fragments, as in Heath's mechanism. However, in further studies on larger carbon cluster ions ($C_n$, $n = 100$–$320$), Jarrold et al. have found evidence for isomers which have the structure of a ring attached to a fullerene.[20,30] These isomers rearrange to fullerenes readily. Jarrold's latest experiments and the cyclocarbon coalescence studies of McElvany et al. suggest that fullerenes can also grow by addition of mid-sized rings.

Nonetheless, Jarrold's mechanism fits nicely with much of the observed data. Although it invokes $C_2$ addition for the last steps of fullerene formation, mid-sized rings provide most of the carbon for growth of the intermediates. The annealing and coalescence experiments described above demonstrate that, despite the previous assumptions to the contrary, addition of mid-sized rings to larger all-carbon molecules does not require a prohibitive amount of reorganization. The scenario presented by Jarrold and co-workers therefore contains all the advantages of the Fullerene Road (i.e., a reasonable explanation for the preferential formation of $C_{60}$ and $C_{70}$ which involves the thermodynamically favored and experimentally observed intermediates), but does not require a constant large supply of small carbon fragments.

Further support for a mechanism involving coalescence of ring species come from a study of the structure of the soot produced during bulk fullerene formation.[31] Schlögl and co-workers recently compared the TEM images of fullerene black to those from conventional carbon black and found considerable differences. The fullerene black images show evidence for large cyclic species cross-linked together, in addition to planar graphite-like layers, and the researchers propose that fullerenes form via rearrangement of similar large carbon rings which have not yet polymerized.[31]

Unfortunately, this mechanism still has one major weakness: although it invokes addition of mid-sized ring species as the major growth pattern of carbon clusters toward fullerenes, it assumes that $C_{60}$ and $C_{70}$ form preferentially because of their resistance to addition of $C_2$. There is no evidence for fullerene growth by addition of small carbon particles, and such an explanation is not necessary. In the experiments

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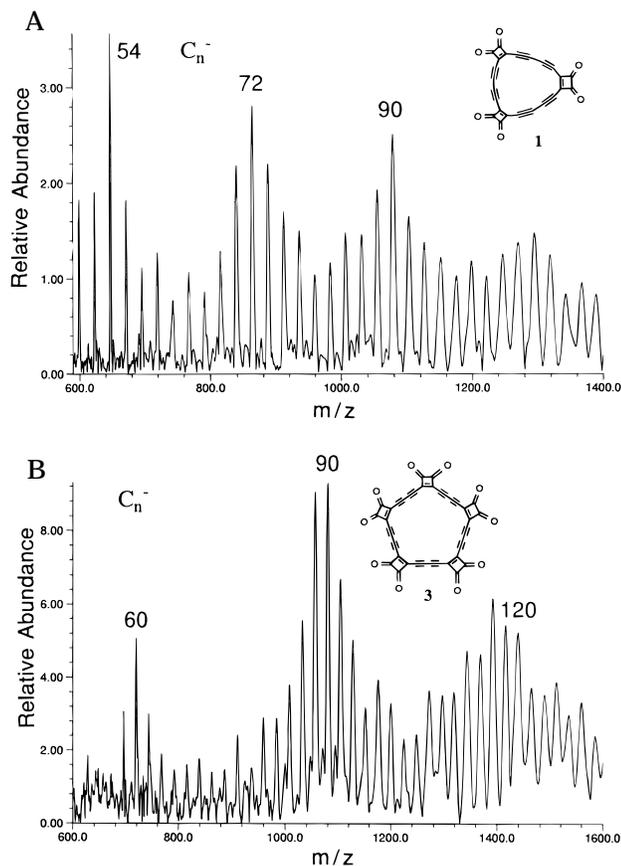
A



B



**Figure 6.** Negative-ion laser-desorption mass spectra of **1** and **3**. Only the high-mass ions are shown, corresponding to $C_n^-$ (even *n*) with several reference values shown. Note that $C_{60}^-$ and $C_{70}^-$ do not dominate these spectra, in contrast to Figure 3.

of McElvany et al.,[27] coalescence of the cyclocarbons leads preferentially to $C_{60}$ and $C_{70}$ and does not give any fragments corresponding to addition of $C_2$ or $C_3$. In Figure 3, the $C_{60}^+$ and $C_{70}^+$ ions are much more abundant than the other fullerene ions. Yet the only growth process observed in those experiments is addition of mid-sized rings. In these experiments, at least, $C_2$ addition is not the process which leads to preferential formation of $C_{60}$ and $C_{70}$. Although presumably some neutral $C_2$ fragments are present, resulting from the fragmentation of fullerene ions, they do not appear to add to the fullerene ions.

In fact, the *negative* ion spectra from laser desorption of **1** and **3** demonstrate that neutral $C_2$ fragments are available, although they do not react with the fullerene cations.[32] The negative carbon cluster ions formed from laser desorption of **1** and **3** clearly show evidence of both $C_2$ addition and loss (Figure 6). But in these spectra, $C_{60}^-$ and $C_{70}^-$ are *not* especially abundant, relative to the other carbon cluster ions, and there is no evidence that they have fullerene structure. These results suggest that cationic intermediates may play an important role in the formation of fullerenes, in agreement with the findings of Bunshah et al. regarding production of fullerenes in an electric field.[7]

## Resistance to Loss of $C_2$ or Addition of Rings

Thus, the available experimental evidence requires an explanation slightly different from the mechanism discussed above. As in Jarrold's scheme, the all-carbon molecules build up by coalescence of monocyclic rings and rearrange to fullerenes as suggested by Kroto and Walton. However, in keeping with Jarrold's more recent results and other studies, the fullerenes and other isomers are all susceptible to the addition reactions. (Fullerenes may also coalesce with other fullerenes, as has been observed experimentally.[33,34]) When a carbon cluster rearranges to a fullerene, it is likely to lose one or more $C_2$ units because of the exothermicity of the reaction. These are the only processes occurring in significant amounts which affect the size of the product all-carbon molecule. Bowers and co-workers have suggested a similar scenario.[16]

Thus $C_{60}$ and $C_{70}$ must be unusually stable either to the addition of mid-sized rings or to the elimination of $C_2$, or both. The only information available about relative reactivity to coalescence with rings comes from the results of McElvany et al., shown in Figure 3. Among the positive ions formed from the cyclo[30]-carbon precursor **3**, experiments indicate that $C_{60}^+$ is the most stable to both addition of $C_{30}$ and loss of $C_2$. In contrast, $C_{70}^+$ appears to add $C_{18}$ or $C_{24}$ as readily as the other fullerene ions present, but eliminates $C_2$ much less than the other fullerenes. Yet there is no evidence that the carbon cluster ions which add to the cyclocarbon rings have the same structure as those which are left behind (and observed) after reaction. Therefore, these studies are not sufficient to determine which process is responsible for the great abundance of $C_{60}$ and $C_{70}$.

Many experiments, however, have addressed the issue of fullerene ions' relative stability to loss of $C_2$.[35-38] Radi et al.[36] and Klots[37] have analyzed the metastable fractions from dissociation of $C_{62}^+$, $C_{60}^+$, and $C_{58}^+$; both studies found that the activation barrier for fragmentation of $C_{62}^+$ is about half that for $C_{60}^+$ or $C_{58}^+$. (According to these studies, $C_{60}^+$ has a slightly higher activation barrier for loss of $C_2$ than does $C_{58}^+$.) Lifshitz and Laskin have compared Klots's data with both a "magic number" model, in which $C_{60}^+$ is much more stable than its neighbors $C_{58}^+$, $C_{62}^+$, and $C_{64}^+$, and a "magic shell" model, in which $C_{60}^+$ and $C_{58}^+$ each are more stable than the clusters immediately larger, $C_{62}^+$ and $C_{64}^+$.[38] They found that either relationship could explain the observed ion ratios, but that the magic shell model fit the data better. On the other hand, Jarrold and co-workers observed that, in the dissociation of $C_{64}^+$, $C_{60}^+$ is only slightly favored.[19] Thus, it is still unclear whether the difference in dissociation energies between $C_{62}^+$ and $C_{60}^+$ can account for the preferential formation of $C_{60}$.

(32) Joint work with S. W. McElvany, M. M. Ross, and F. Diederich, published in the following: Goroff, N. S. Cyclocarbons, Fullerenes, and Polyyne Rods: An Investigation of the Chemistry of All-Carbon and Carbon-Rich Molecules, Dissertation, UCLA, 1994.

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## Attempting to Trap Intermediates

I have thus far omitted discussion of several experiments in which researchers have attempted to trap the intermediates in fullerene formation. These experiments, which involve the addition of new reactants to the helium buffer gas during graphite vaporization, are very interesting and informative, but cannot tell us the structure of the intermediates which exist in the absence of trapping agents. Addition of cyanogen, NCCN, to the reaction leads to isolation of polyyne rods, capped by cyano groups.[39] In contrast, perchlorinated polycyclic aromatic hydrocarbons (PAH) form in the presence of a partial pressure of $Cl_2$.[39] Including propene or methanol in the reaction atmosphere produces PAHs reminiscent of the proposed Pentagon Road intermediates, in addition to fullerenes.[40] In all of these studies, however, the presence of trapping agents may change the relative thermodynamic and kinetic stability of potential growth intermediates considerably. At the least, each trapping agent may preferentially deplete the supply of specific intermediates, giving the impression that these species are the major components of the reaction mixture in the absence of trapping agents. Schwartz[41] and Jarrold[17] have already noted the tenuous relationship between such trapped compounds and the intermediates in fullerene formation.

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## Concluding Remarks

A great deal of evidence regarding carbon cluster structures and reactions has developed in the past several years. This new information allows us to make sense of the reactions which lead from carbon vapor to fullerenes. There is no need to invoke unobserved cup-shaped graphitic intermediates in the process of fullerene formation, since reorganization from planar medium-ring species occurs readily. The Pentagon Road therefore seems unlikely as the primary path to the fullerenes. In addition, coalescence of monocyclic rings appears sufficiently facile to account for most, if not all, of the carbon molecules' growth. Thus, the Fullerene Road, relying on addition of small carbon particles for growth of the intermediates, does not fit the experimental evidence well, either. Resistance to either $C_2$ loss or addition of mid-sized rings, rather than to $C_2$ addition, should account for the large relative abundances of $C_{60}$ and $C_{70}$. Fullerenes, it turns out, form with unexpected ease.