Fullerenes, Nanotubes and Carbon Nanostructures

Formation Mechanism of $C_{60}$ under Nonequilibrium and Irreversible Conditions — An Annotation

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Available online: 14 May 2012

To cite this article: Eiji Ōsawa (2012): Formation Mechanism of $C_{60}$ under Nonequilibrium and Irreversible Conditions — An Annotation, Fullerenes, Nanotubes and Carbon Nanostructures, 20:4-7, 299-309

To link to this article: http://dx.doi.org/10.1080/1536383X.2012.655104

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Formation Mechanism of C₆₀ under Nonequilibrium and Irreversible Conditions — An Annotation

EIJI ÖSAWA
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A few topics related with the latest mechanism of C₆₀ formation during condensation of carbon vapor proposed by computer simulation of Irle/Morokuma group are introduced in an invited lecture of CAN’2011. Mysterious failure of the shrinking hot giant road mechanism in the last step was rationalized by low yield (0.001%) obtained in independent discovery of C₆₀/C₇₀ formed under identical conditions in a planetary nebula. Better yields (1–14%) obtained in carbon vapor experiments on earth were rationalized by taking the collision effect of inert atmospheric gas into account. Much higher yields (20–100%) from combustion method should come from a more positive role of the atmosphere, in this case combustion exhausts in the inner flame, if SHGR mechanism applies as well. Formation mechanism of carbon nano-onions is discussed.

Keywords Shrinking hot giant road, Prigogine’s chaotic theory, white dwarf Tc 1, C₆₀/C₇₀, giant fullerenes, carbon nano-onion

Introduction

The mechanism of C₆₀ (I) formation has remained elusive for 25 years, ever since its serendipitous discovery, but recently Irle/Morokuma theoretical group almost solved the problem (1–4). Their QM/MD simulation of carbon vapor condensation process under irreversible and non-equilibrium conditions generated a highly plausible route wherein vapor of C₂ self-assembled into a series of dissipative structures, eventually overshooting to form giant fullerenes as distinct intermediates (Figure 1). However, as the giant fullerenes began to pop off C₂ species to shrink towards C₆₀, all the large fullerene intermediates seemed to decompose. This is a crucial point because if the yield is definitely zero, then the whole scheme could be wrong.

Fortunately, however, huge amounts of C₆₀/C₇₀ were found accumulating in space (5) under exactly the same conditions as in the Irle/Morokuma QM/MD simulation. Thus, the dynamic processes that came out of simulation turned out to have an open end, but they could not observe C₆₀ in the computer simply because the scale of simulation was too small to reproduce such phenomena.

One of the purposes of this review is to combine the results of computer simulation and the events occurring around the nebula Tc 1 in space to confirm the shrinking hot giant road of C₆₀ formation. Major purpose of this lecture is to extend the SHGR concept to the combustion method of synthesizing C₆₀, which consists of burning aromatic solvents.

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such as benzene with oxygen and proved an order of magnitude more efficient than the carbon vapor condensation methods but has been considered to involve different formation mechanism.

Background

When C₆₀ (I) was discovered (6,7), we were struck by the balanced beauty of its structure with perfect symmetry. Naturally many of us were interested in the way such a novel structure evolved. Organic chemists were particularly attracted by the formation mechanism of C₆₀, because the syntheses of highly symmetric polyhedral molecules such as pentagonal dodecahedral hydrocarbons (II) have been highly esteemed subjects. For these purposes, chemists always chose step-by-step total synthesis but never thought these polyhedral molecules to exist in nature (8). Hence we were genuinely surprised and excited to see the super-cage C₆₀ formed *spontaneously* by simply condensing hot carbon vapor, produced by laser ablation (5), resistive heating (6) or arc discharge. A great many mechanisms were presented for the formation of C₆₀ during 1988 and 2004. At first, the mechanistic researchers simply followed traditional deterministic methodology to study the reaction mechanism, postulating reversible elementary steps with one or a few transition states for each step and assuming all the intermediates are in equilibrium. If key intermediates could be isolated and characterized, or elaborate computational results including transition states gave a consistent picture, the mechanism was considered right.

To our embarrassment, no intermediate could be identified experimentally for the C₆₀ synthesis. Even elaborate experiments with mass spectrometers to control the flight time and paths for particles smaller than m/e 720 did not produce any useful information on the intermediates of direct and shortest path from carbon atoms to C₆₀. Monte Carlo (MC) and molecular dynamics (MD) simulations are left as the only viable methods to study

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**Figure 1.** Illustration of the MD snapshots for each clustering step in the size-up process of C₆₀ formation mechanism by Irle/Morokuma, obtained in one of the early computer simulations. Reproduced with permission from American Chemical Society (color figure available online).
the spontaneous formation mechanism of C\textsubscript{60}, but it took some time to find the right tools and conditions. The first full-scale unbiased simulation was carried out in the late 1990s by Maruyama and his group using Brenner potential (9,10). Although their primary target was the carbon nanotube, their work clearly demonstrated the necessity of using a quantum mechanical approach even though it will need several orders of magnitude longer computing time than empirical approaches.

Chaotic Mechanism of C\textsubscript{60} Formation

To our knowledge, the Irle/Morokuma group was the first to realize that “hot carbon vapor is a system far from thermodynamic equilibrium, and that such systems may give rise to autocatalysis and self-organization processes associated with irreversible process, as shown in the pioneering work Prigogine” (11). According to the chaos theory by Prigogine, when elements of such a system form self-assemblies by autocatalysis, their local interactions may cause unpredictable changes in their close environments, and sometimes these changes create a new order, which is called emergence. The order formed by emergence is called dissipative structure. Emergence occurs in bottom-up fashion, and undergoes dynamic changes; hence it is difficult to predict the direction of such changes in advance. Hence it is clear that MD or MC computer simulation should be performed while at the same time taking care of formation and cleavage of all the chemical bonds existing in the system by appropriate level of quantum or empirical theory.

Computational technique

The Irle/Morokuma group chose the quantum mechanical/molecular dynamics (QM/MD) combination, wherein QM portion consists of non-self-consistent charge/density functional theory with tight binding approximation (NCC/DFTB). No less important is the choice of computing conditions. The final set they decided is as follows:

Material: Only up to a few hundred C\textsubscript{2} molecules in random orientation were used as the starting material, and they were added in portions at certain time intervals. The reaction cells were expanded from time to time after a certain period of shaking to keep conditions non-equilibrium and irreversible.

Temperature: During the initial size-up period (see below), temperature was set to 2,000 K and during the final shrinking period increased to 3,000 K.
Periodic boundary condition: Applied during the size-up process but suppressed during the size-down process.

Experiments were carried out at least 25 times for each condition in a cubic box having 8 to 27 nm$^3$ in volume.

**Results**

An experiment was deemed success if the added C$_2$ molecules self-organized themselves into one giant cluster. The success rate was 5–30%. In all the successful cases, the clusters once grew to a giant fullerene (size-up process, Figure 1), then shrank towards C$_{60}$ by popping out C$_2$ fragments (size-down process). Further analysis revealed that all the successful experiments followed the same pattern as summarized in Table 1.

**Size-up process**

This process consists of three consecutive steps. The first step begins with linear polymerization of C$_2$ molecules into linear polyyne chains up to C$_{10}$, which then undergo ring closure and cycloaddition to form mono- to tri-cyclic polyyne containing an average of 20 carbon atoms. These initial stages are already well known. Intertwining and cycloaddition within cyclic polyyne to fuse more than three 4- to 6-membered carbon rings produces polycyclic aromatic nuclei, capable of further growth into stable graphene patches (nucleation substep). It should be noted that at 2,000 K, aromatic stabilization acquired by forming graphitic clusters becomes the driving force for the cluster growth. At this temperature range, however, 5-membered rings appear to form in about the same probability as 6-membered rings; hence the aromatic patches will start to bend as they grow by adding C$_2$ and polyyne chains. Despite frequent bending, the whole system will acquire

<table>
<thead>
<tr>
<th>Time sequence</th>
<th>Heat of reaction</th>
<th>Size changes</th>
<th>Clustering steps</th>
<th>Clustering reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic</td>
<td>Exothermic</td>
<td>Size-up</td>
<td>Nucleation</td>
<td>Intertwining polyyne, cycloadditions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Growth</td>
<td>Expansion of aromatic conjugation, stabilize.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Slow curvature</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cage closure</td>
<td>Cross-linking across edges</td>
</tr>
<tr>
<td>Endothermic</td>
<td>Endothermic</td>
<td>Size-down</td>
<td>Falling-off branches</td>
<td>Relatively fast</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Popping-out of C$_2$</td>
<td>$6556 \rightarrow 565 + C_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$1C/1pc, 3000K$</td>
</tr>
</tbody>
</table>
Formation Mechanism of \( C_{60} \)

Large aromatic stabilization by delocalization of conjugated \( \pi \)-electron system (growth sub-step). In this way, a basket-shaped cluster is formed with its opening carrying short polyyne chains like antennae. When the basket cluster grew large enough and its opening bent deep enough, polyyne bridges will be spun across the opening. Thus, the basket is closed to a cage and gives a giant fullerene with a few antennae sticking out (cage closure) (Figure 1).

Throughout these steps (polyyne formation, nucleation, growth and cage closure), hybridization of carbon valence orbitals changes from \( sp \) to \( sp^2 \) and emits large amounts of heat (exothermic process, Table 1). The growth of carbon clusters by interaction of polyyne chains and polycondensed aromatic rings provides a good example of autocatalysis reaction in the irreversible non-equilibrating system.

Although the formation of countless isomeric giant fullerenes \( C_{200} \) to \( C_{500} \) in the initial stages of \( C_{60} \) synthesis by arc discharge had been noticed, their role as the crucial intermediate group has been recognized for the first time in this simulation. Compared with the direct transformation of small polycondensed aromatic intermediates to spherical \( C_{60} \), which involves high-energy barriers, the detour or overshooting routes through giant fullerenes having much smaller angle strain are energetically much more favorable. Large freedom to choose from a large number of giant fullerenes is an additional advantage (Figure 1). Recognition of this low-energy route highlights the Irle/Morokuma theory.

**Size-down process**

\( C_2 \) addition and boundary conditions were suppressed and the detached polyyne chains were driven out of the reaction chamber in order to start the size-down process. In contrast to the exothermic and fast size-up process, this final step is endothermic and slow. It consists of slow release of extra carbon atoms from giant fullerenes in thermally excited vibrational states. The most vulnerable sites for thermal expulsion are \( sp^3 \) carbon atoms at the point of attachment of polyyne side arms to the surface of giant fullerene. However, after all the side arms have been removed and the temperature increases to 3,000 K, and the \( C_2 \) popping-out process became the only event that occurs along the shrinking hot giant (SHG) road, crisis comes. If we assume that \( C_2 \) is released from precursor fullerenes only if an adjacent pentagons pair appear, the process must involve generalized Stone-Wales rearrangements twice before and after the expulsion reaction (Figure 2). As the size of fullerene shell decreases, skeletal strain increases sharply and at some point, the rate of the vibrational decomposition of cage skeleton overcomes that of shrinking. Even though Irle achieved down sizing to \( C_{64} \) at least in one experiment, \( C_2 \) expulsion under their conditions proved too slow and decomposition of large fullerenes prevailed.

**Figure 2.** Illustration of elementary steps in the “shrink-wrap” transformation considered to play a key role in the popping-out step of \( C_{60} \) formation mechanism.
Despite unexpected difficulty in the last step, the shrinking hot giant road (SHGR) mechanism mentioned above represents a dramatic progress in the mechanistic study of C\textsubscript{60} formation. The most important is, as the discoverers noted, this work seems to prompt a paradigm shift away from deterministic anthropomorphic formation mechanism solely based on thermodynamic stability, to indeterminate and unpredictable systems. We anticipate that many other non-equilibrium and unstable phenomena can be studied by the methodology developed in this work.

Natural Proof of Chaotic Mechanism

Surprisingly, an independent piece of evidence that supports Irle/Morokuma’s original mechanism was recently discovered in space. In 2005, NASA’s Spitzer Space Telescope (Figure 3) had caught infrared radiation from the surface of planetary nebula Tc 1 (Figure 4). It took five years to analyze the data, but it turned out that the spectrum was surprisingly simple, containing almost exclusively absorptions of C\textsubscript{60} and C\textsubscript{70} (Table 2). Further analysis revealed the average combined yield of fullerenes based on the total emitted carbon vapor is 0.001% (see caption of Figure 4), with a C\textsubscript{60}/C\textsubscript{70} ratio of 55:45. Actually this low yield rationalizes the apparent failure in the very last step of SHGR. Under the present capability of a supercomputer, irreversible and too large computations cannot be run too frequently. Hence it is impossible to differentiate between very small and zero probabilities.

Role of Inert Gas

In laboratory experiments of carbon vapor condensation, use of inert gas, especially helium, is known to lead to the production of C\textsubscript{60}/C\textsubscript{70} in measurable amounts (1–14%). Inclusion of helium and its cooling effect by van der Waals collision with giant fullerene in the simulation (using QMMM/MD) did lead to the formation of C\textsubscript{60} and C\textsubscript{70} (12). The role of helium gas is clearly removing the heat from hot giant fullerenes to slow down the

Figure 3. Artist’s drawing of NASA’s Spitzer Space Telescope. Background is a view of milky way seen through a 100 µm infrared filter. Offered by courtesy of NASA/JPL-Caltech (color figure available online).
Planetary nebula Tc 1 used to be as large as the Sun but now it is aged and the outer portions have gone. The rest shrunk to a high-density white dwarf heating itself up to 30,000K. The young dwarf has been emitting $10^{-4} \, M_\odot$ carbon vapor per year from its inside at an initial speed of 20 km/s in the past 100 years. The emitted carbon forms thick nebula, which surrounds the dwarf and hinders its direct observation. Amounts of accumulated $C_{60}$ and $C_{70}$ in nebula are estimated to be $5.8 \times 10^{-8}$ and $4.7 \times 10^{-8} \, M_\odot$, respectively. Light gas like hydrogen had already been exhausted ($1M_\odot$[solar mass] = $1.99 \times 10^{27}$ ton) (color figure available online).

Table 2

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Laboratory$^b$</th>
<th>Tc 1$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_{1u}(1)$</td>
<td>528</td>
<td>529</td>
</tr>
<tr>
<td>$T_{1u}(2)$</td>
<td>577</td>
<td>575</td>
</tr>
<tr>
<td>$T_{1u}(3)$</td>
<td>1183</td>
<td>1177</td>
</tr>
<tr>
<td>$T_{1u}(4)$</td>
<td>1429</td>
<td>1423</td>
</tr>
<tr>
<td>$C_{70}^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_2'^{''}$</td>
<td>458</td>
<td>458</td>
</tr>
<tr>
<td>$E_1'$</td>
<td>642</td>
<td>642</td>
</tr>
<tr>
<td>$E_1^{''}$</td>
<td>674</td>
<td>676</td>
</tr>
<tr>
<td>$E_1'^{''}$</td>
<td>795</td>
<td>799</td>
</tr>
</tbody>
</table>

$^a$Excerpted from Supplementary Materials of Ref. 5.
$^b$Solid state, room temperature, literature values.
$^c$Wave numbers at the maximum peak position
$^d$According to literature, $C_{70}$ contains six absorptions at 534, 564, 578, 1133, 1414, 1430 cm$^{-1}$, in addition to the four peaks given in this table. However, these peaks are either overlapped with those of $C_{60}$ or too weak to observe.

Arc discharge and other carbon vapor condensation synthesis of $C_{60}$ usually does not report the yield, but it is estimated to be 1–14% (13), which means 1,000 to 10,000 times increase from vacuum reaction. Clearly, the use of He gas is effective but not enough for large-scale production.
It would be ideal to increase the rate of C₂ popping-out reaction without increasing temperature to 3,000 K in order to suppress thermal decomposition of fullerene cages. This point is discussed in the next section.

### Extension to Combustion Method

Combustion method is by far the more important than carbon vapor condensation method (14), giving C₆₀/C₇₀ yields of 20% and higher based on the weight of extractable and solid products. Mechanism of C₆₀/C₇₀ formation in combustion has long been considered to be different from that of the carbon vapor method because the combustion method involves hydrogen atoms in addition to carbon and leads to polyaromatic hydrocarbon (PAHs) (or nanographenes) as the major products, with C₆₀/C₇₀ as very minor by-products. This view was held by Homann who constructed his own formation mechanism for C₆₀ based on the intermediacy of PAHs (15).

However, the situation changed when Howard used benzene premixed with oxygen flame. Although he never clearly described flame temperature, once he mentioned about 1,800 K (16), which is close to 2,000 K used in the size-up stage by Irle/Morokuma. Howard initially achieved only 0.003–9.0% yields (16), but they increased to 20% and, shortly before his untimely death in 2007, to quantitative yield (14). Although his latest flaming conditions were never disclosed, we can guess if the combustion method follows the SHG road. This last assumption is likely in view of the following reasons:

1. Combustion methods give soot as the major by-product, which is an aggregate of defective multishell fullerenes (17). In the case of the carbon vapor method, the major by-product is carbon nano-onions (synonym to multishell fullerenes). By-products are essentially the same.

2. In high-temperature flames, most of the bonded H atoms on the surface of feedstock molecules will be preferentially burnt to water. H atoms and H-containing intermediates will also burn out quickly in the early stage of combustion. In the inner region of the flame, some of the H atoms might remain on the edges of small PAH. However, these flat molecules tend to move slower than C₂, small polyynes and other typical dissipative structures in the stream of flame; therefore, they tend to transfer themselves from the inner to outer flame zone and burn out.

As long as the flame of combustion method is made long enough and in sufficiently high temperature, the composition of downstream inner flame will be the same carbon “soup” as in the carbon vapor method, but medium gas is different, consisting of H₂O, CO₂ and CO. Among these, only CO is reactive. One likely phenomenon that would happen in the size-down process of abstraction of C₂ from the abutting pentagon unit (III, see Figure 2) in giant fullerene by carbon mono-oxide (IV) from the gas by way of stable cyclopropenone intermediate (V):

$$\text{III} + \text{CO} \rightarrow \text{IV} + \text{V}$$  \hspace{1cm} (1)
The well-known aromaticity in V would contribute to reduce the transition state of C_2 popping-out reaction from III. Once the abstract reaction is complete, V will be quickly decomposed to give back carbon-monoxide IV; hence, equation (1) represents an ideal autocatalysis reaction that reduces the barrier of C_2-popping reaction, promotes the shrink step and increases the yields of C_{60}/C_{70}.

A definite advantage of the combustion method is the possibility to adjust the conditions to optimize flame structure, temperature distribution, flow rates of feedstock and air in order to maximize the yield of C_{60} and combustive removal of by-products. By all accounts, combustion method is the best candidate for quantitative production of C_{60}/C_{70}.

**Perspectives**

We mentioned that carbon nano-onion is the major by-product in the synthesis of C_{60}/C_{70}. Actually, carbon nano-onion should be regarded as the most stable and abundant product of fullerenes formation reaction unless the conditions are fine-tuned to make C_{60} the dominant product. C_{60} (but not C_{70}) is the first member of the Goldberg series (60n^2, n = 1, 2, ...) of fullerenes, and concentric nesting of the series members one outside the other gives nano-onion series (VI), reminiscent of ivory Chinese ball (16).

\[
C_{60}@C_{240}@C_{340}@C_{900}@\cdots C_{60n^2}\cdots
\]

An interesting issue here is the mechanism of nano-onion formation. We have previously proposed a spiral growth mechanism, but 3D spirals involve discontinuous points, making them unsuitable in real systems (17). If the CO-assisted shrinking hot giant road (COASHGR) mechanism introduced in the section on the combustion method proved correct, it is quite attractive to think of the COASHGR mechanism working repeatedly for each new shell. The formation of each shell will become faster as the onion becomes larger because of decreasing angle strain. Even in thin onions, the overshoooting of a new shell will be modest because the freedom in carbon deposition in the nucleation and growth steps is limited to within a spherical isopotential surface covering the new nano-onion surface at the van der Waals distance. Therefore, it is not surprising to see very fast formation of soot in any incomplete combustion.

Attempts are being made to synthesize carbon nano-onions from nanodiamonds by irradiation of high-energy beam. The reaction will be clean but costly. Perhaps the best strategy would be to modify the existing combustion cylinders used to manufacture carbon blacks. Carbon blacks (or industrial soot) are complex and random aggregates of highly defective carbon nano-onions with low crystallinity. Dispersed and defect-free particles of nano-onions will be highly useful substitutes of carbon blacks, which are the single and largest carbon product in the current industrial carbon market.

How do the properties and behaviors of a carbon nano-onion change with its size? Smaller onions will resemble smaller fullerenes; hence, smaller onions should behave as “stuffed” fullerenes. These are good substitutes of still completely unknown larger or giant fullerenes. On the other hand, larger onions should resemble graphenes. Therefore, a giant onion may be regarded as a stuffed spherical graphene analog with well-defined rigid geometry. In view of the recent research on graphene, extensive applications will be explored for graphenes, and some of them can be extended directly to large carbon...
nano-onions. Carbon nano-onion should be one of the most interesting targets of research in nanoscience and nanotechnology.

Conclusions

1. The shrinking hot giant road mechanism of $C_{60}/C_{70}$ formation by the carbon vapor condensation method proved correct by independent evidence obtained from the carbon star Tc 1 and demonstrated the power of indeterministic Prigogine approach to mechanistic studies.

2. The poor yield (0.001%) of $C_{60}/C_{70}$ by the carbon vapor method in vacuum (in space) can be improved to 1–14% by judicious use of inert gas as the heat remover.

3. Combustion method is considered to involve essentially the same formation mechanism as carbon vapor condensation method but gives at least one order of magnitude higher yields of $C_{60}/C_{70}$. A possible role of autocatalysis by a reactive combustion gas component (CO) is suggested. This method will achieve quantitative conversion of aromatic solvents such as benzene or toluene into $C_{60}/C_{70}$ after optimization of combustion conditions.

4. If the SHGR mechanism can be extended to carbon nano-onions, as suggested, then the scope of fullerene science will be greatly expanded. The importance of continuing mechanistic studies on the formation of $C_{60}$ and related nanocarbons cannot be overemphasized.

Acknowledgments

We thank Professor A. Vul’ for his untiring encouragements given during writing this review, Professor S. Irle for supplying the latest progress and useful suggestions and Professor X. Zhao for helpful discussion. We are grateful to NASA for free downloading and reproduction of their superb artworks of space.

References


