### Abstract

The availability of macroscopic quantities of fullerenes has resulted in a vast number of physical and chemical studies of these new materials. However, the mechanisms that lead to the formation of these spherical carbon allotropes are not well understood. Mass spectral evidence has been obtained for the size-selective growth of fullerenes through the coalescence of cyclo[n]carbons, molecular carbon allotropes consisting of monocyclic rings with \(n\) carbon atoms. Whereas coalescence of cyclo[30]carbon (cyclo-C\(_{30}\)) produces predominantly buckminsterfullerene (C\(_{60}\)), the smaller rings cyclo-C\(_{18}\) and cyclo-C\(_{24}\) preferentially produce fullerene C\(_{70}\) through distinct intermediates. The present studies not only provide new insights into fullerene formation mechanisms but also raise the possibility of tailoring the size distributions of fullerenes by variation of the appropriate properties of the precursors.
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Cyclocarbon Coalescence: Mechanisms for Tailormade Fullerene Formation.

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The availability of macroscopic quantities of fullerenes has resulted in a vast number of physical and chemical studies of these new materials. However, the mechanisms that lead to the formation of these spherical carbon allotropes are not well understood. Mass spectral evidence has been obtained for the size-selective growth of fullerenes through the coalescence of cyclo[n]carbons, molecular carbon allotropes consisting of monocyclic rings with \( n \) carbon atoms. Whereas coalescence of cyclo[30]carbon (\( cyclo-C_{30} \)) produces predominantly buckminsterfullerene (\( C_{60} \)), the smaller rings \( cyclo-C_{18} \) and \( cyclo-C_{24} \) preferentially produce fullerene \( C_{70} \) through distinct intermediates. The present studies not only provide new insights into fullerene formation mechanisms but also raise the possibility of tailoring the size distributions of fullerenes by variation of the appropriate properties of the precursors.
One of the most ambitious as well as rewarding intellectual and experimental challenges in fullerene chemistry (1) and carbon chemistry in general is the elucidation of the mechanisms for fullerene formation (2). Understanding the mechanisms of fullerene synthesis may well lead to the discovery of other, from a classical synthesis viewpoint unconventional, preparative techniques and to the production of entire classes of new compounds. Isotopic scrambling observed in fullerenes generated by arc heating from mixtures of $^{12}$C- and $^{13}$C-graphite indicated that the reactant carbon source must undergo vaporization into atomic C or small carbon fragments, such as C$_2$ (3,4), which contradicts the originally proposed sequential graphitic shell closure mechanism (5-7). This evidence, along with the early observation that fullerenes fragment through loss of C$_2$ (8), has resulted in models (4,6) in which fullerene growth occurs upon assembly of small carbon species. More recently, fullerene growth has been modeled by sequential addition of larger polycyclic ring systems (C$_{10}$ to C$_{20}$) (9) and the implication of linear, monocyclic, and polycyclic carbon clusters in fullerene synthesis has been suggested (10-12).

As a part of our ongoing efforts to synthesize molecular forms of carbon from structurally and chemically well-defined precursors (13,14), we prepared the carbon oxides C$_n$(CO)$_{n/3}$ (1 to 3) with $n = 18$, 24, and 30, as precursors to the cyclocarbons cyclo-C$_{18}$, -C$_{24}$, and -C$_{30}$, respectively (15). Initial laser desorption mass spectrometry studies on the carbon oxides provided intriguing but ambiguous results (15). These experiments showed that the carbon oxides undergo loss of CO molecules to form the desired cyclocarbon ions. Large carbon cluster ions, C$_x^+$ ($x > 50$) were also observed for all even $x$ but with little or no dependence of the C$_x^+$ distribution on the size of the precursor molecule. The production of similarly wide C$_x^+$ (even $x > 50$) distributions by laser vaporization of various carbon-containing materials (such as polymers and polycyclic aromatic hydrocarbons) (16) suggests that the carbon oxides may undergo decomposition prior to forming large C$_x^+$. A possible requirement for such decomposition prior to the growth of large C$_x^+$ was not ruled out experimentally during these initial studies.
Compounds 1-3 and C_{18}, C_{24} and C_{30}

We conducted laser desorption Fourier transform mass spectrometry (FTMS) experiments (17) on 1 to 3 in which there is no evidence of laser-induced fragmentation of the cyclocarbon units in the neutral carbon oxide precursors. The negative ion mass spectra show the successive loss of CO molecules from the precursor anions to give the cyclocarbon ions \( \text{C}_{18}^- \), \( \text{C}_{24}^- \), and \( \text{C}_{30}^- \) as the final products. The positive ion mass spectra from laser desorption of 1 to 3 are shown in Fig. 1, A to C, respectively. The general pattern in these spectra includes loss of CO molecules to form the cyclocarbon cations \( \text{C}_{18}^+ \), \( \text{C}_{24}^+ \), and \( \text{C}_{30}^+ \), respectively, analogous to the negative ion results. Positive ions higher in mass than the precursors are also observed and correspond to successive addition of 18, 24, or 30 carbons, respectively (depending on the precursor), to form larger and larger carbon clusters. No peaks corresponding to carbon oxides of greater mass than the starting material were detected, which excludes reactions involving ions or neutrals that still contain oxygen.

Figures 1A-C

Further experiments on 1 and 2 showed that the relative abundance of lower mass carbon oxide ions and higher mass carbon cluster ions depends upon the number of laser shots and the spot size. Relatively large but size-specific \( \text{C}_x^+ \) distributions are detected on the first laser pulse (see Fig. 1). However, the relative abundance of the higher mass \( \text{C}_x^+ \) distributions decreases with subsequent laser pulses until only the precursor molecular ion, fragment ions resulting from partial CO-loss, and the corresponding cyclocarbon ions (such as \( \text{C}_{18}^+ \) or \( \text{C}_{24}^+ \)) are formed. Similarly, desorption of smaller sample areas (see Fig. 2) mainly produced smaller carbon cluster and CO-containing precursor ions, indicating that the particle density in the laser desorption plume governs
the extent of clustering of the cyclocarbons. These results strongly suggest that the coalescence reactions leading to the higher-mass C\textsubscript{x+} distributions are occurring in the gas phase between carbon cluster ions and neutrals.

Figure 2

The major product ion in the laser desorption of 1 and 2 appears at mass-to-charge ratio (m/z) 840, presumably corresponding to C\textsubscript{70+}. Remarkably, the C\textsubscript{x+} distributions from 1 and 2 include little or no C\textsubscript{60+}. In the case of 3, the major product ion is C\textsubscript{60+} at m/z 720. The 24 amu (C\textsubscript{2}) separation between these ions and the accompanying carbon clusters at lower m/z values (such as C\textsubscript{58+}, C\textsubscript{56+}, and C\textsubscript{54+} ions are observed together with C\textsubscript{60+}) suggests that C\textsubscript{60+} and C\textsubscript{70+} have fullerene structures. To confirm that C\textsubscript{60+} and C\textsubscript{70+} are in fact fullerene ions, their gas-phase properties were characterized by additional tandem mass spectrometry experiments. No collision-induced dissociation could be observed in these FTMS experiments for either these ions or fullerene cations produced by laser desorption or electron ionization of pure fullerenes. Although the resistance to fragmentation does not provide convincing evidence for fullerene structures, it does rule out the possibility of simple adducts such as (C\textsubscript{30})\textsubscript{2+}. A more sensitive probe into the nature of these ions is the determination of the ionization energies (IEs) of the corresponding neutrals by charge-transfer bracketing in the FTMS (18). The IEs of both C\textsubscript{60} (from 3) and C\textsubscript{70} (from 1 and 2) were bracketed to be 7.6 ± 0.1 eV, whereas the IE of C\textsubscript{72} (from 1 and 2) was found to be significantly lower (7.0 ± 0.1 eV). These values are identical to those obtained with ions generated by laser vaporization (18) or electron ionization of sublimed fullerenes, thus providing convincing evidence for the C\textsubscript{60+} and C\textsubscript{70+} ions in Fig. 1 having fullerene structures.

The formation of fullerene ions in these laser desorption experiments is rather remarkable, considering the extensive structural rearrangements necessary in the assembly of several two-
dimensional large carbon rings into three-dimensional cages with five- and six-membered rings. The fullerene ions \( \text{C}_{60}^+ \) and \( \text{C}_{70}^+ \) can apparently form through coalescence of relatively large molecular precursors, not merely from addition of \( \text{C}_2 \) and \( \text{C}_3 \) units (10,12). These observations do not necessarily contradict the isotopic labeling studies (3,4). The small carbon species (\( \text{C}_1 \), \( \text{C}_2 \), and \( \text{C}_3 \)) formed in the vaporization of graphite may react to form larger cyclic species that then coalesce to yield fullerenes. This scenario is consistent with the low-mass \( \text{C}_x^+ \)-distributions (\( 3 < x < 30 \)) generated by laser vaporization of graphite that contain both linear (\( x < 10 \)) and cyclic (\( x \geq 10 \)) structures (19,20). The negative ion spectra of the cyclocarbons do not show the peaks at \( m/z \) 720 and 840, or at any of the higher masses, implying that carbocation rearrangements during or following coalescence may be necessary for their formation. Similarly, coalescence reactions of fullerenes can also be observed only in the positive ion mode (21).

Further insights into mechanisms for fullerene formation can be deduced by detailed examination of the relative \( \text{C}_x^+ \) abundances in the spectra. It is evident in Fig. 1A that \( \text{C}_2 \) losses occur concurrently with the addition of the 18-carbon unit, as has been suggested for \( \text{C}_{60} \) and \( \text{C}_{70} \) coalescence (21). This can account for the enhanced abundance of \( \text{C}_{70}^+ \) following the addition of \( \text{C}_{18} \) to \( \text{C}_{54}^+ \). For each successive cyclocarbon addition above \( m/z \) 840, the ions in Fig. 1A show increasing but not extensive \( \text{C}_2 \) loss. However, the major peaks above \( \text{C}_{70}^+ \) follow a pattern of \( \text{C}_{(70 + 18n)}^+ \), increasing by 18 carbons at a time instead of 16, indicating that loss of a \( \text{C}_2 \) fragment is not a necessary step in the coalescence reaction. It is more likely a channel for release of excess energy from apparently thermodynamically favorable reactions.

These results also suggest that formation of the higher fullerene ions from cyclo[18]carbon is surprisingly efficient. The pathway to these ions evidently includes \( \text{C}_{70}^+ \) (but not \( \text{C}_{60}^+ \)), because the major peaks have the formula \( \text{C}_{(70 + 18n)}^+ \), rather than simply \( \text{C}_{18n}^+ \) as do those below \( m/z \) 840. Thus the larger fullerene ions appear to form through sequential ion/molecule (\( \text{C}_x^+ / \text{C}_{18} \))
reactions. Surprisingly, C$_{70}^+$ appears to undergo addition of a C$_{18}$ unit as readily as the higher fullerenes from the observation of similar ratios of C$_{70}^+ / $C$_{88}^+$ and C$_{88}^+ / $C$_{106}^+$.

Laser desorption of 2 (Fig. 1B) yields very similar results to that of 1. Again, C$_{70}^+$ is the major product with further addition of C$_{24}$ units leading to higher fullerene ions. However, more C$_2$ loss accompanies these coalescence reactions than in the case of 1. This result is consistent with the expected higher exothermicity of incorporating an additional six carbon atoms into the fullerene for C$_{24}$ versus C$_{18}$ addition.

A laser desorption mass spectrum of 3 is shown in Fig. 1C. In this case, no C$_{30}^+$ is observed and C$_{60}^+$ is the major product ion. The extensive amount of C$_2$ loss observed in this spectrum confirms the expectation that the coalescence of C$_{30}^+$ with a neutral C$_{30}$ to form a C$_{60}^-$ ion is likely to be very exothermic. Further addition of C$_{30}$ units to C$_{60}^+$, C$_{58}^+$ etc. yields higher fullerene ions through both coalescence with C$_{30}$ and loss of C$_2$. However, although C$_{60}^+$ is by far the most abundant ion, C$_{90}^+$ is less abundant than C$_{88}^+$, C$_{86}^+$, and so forth. Thus, in contrast to the reaction of C$_{70}^+$ with C$_{18}$ and C$_{24}$ discussed above, it appears that C$_{60}^+$ reacts by addition of C$_{30}$ much more slowly than do the fragmentation products (C$_{58}^+$, C$_{56}^+$, etc.) which can account for its high relative abundance.

These results conclusively demonstrate that one reaction pathway to the formation of fullerenes is the coalescence of large cyclocarbon species. These studies with molecular precursors also show that the distribution of fullerenes can be directly affected by the properties, such as size, of these precursors. Insight into formation mechanisms as described and the use of molecular precursors (in contrast to graphite) should ultimately lead to the ability to control the size distribution of both fullerenes and fullerene derivatives, such as metallofullerenes, that are formed in growth processes.
REFERENCES AND NOTES

17. Experiments were performed on the Fourier transform ion cyclotron resonance mass spectrometer (FTMS) located at the Naval Research Laboratory as described in (20). Laser desorption was performed with the focussed output (10^7 to 10^8 W/cm^2) of a pulsed CO2 laser operating at 10.6 μm. Laser spot sizes were estimated to be 100 to 500 μm^2. Solutions of the carbon oxides in dichloromethane were deposited onto stainless steel probe tips which, following evaporation of the solvent, were inserted into the vacuum system.


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Captions to Figures:

**Fig. 1.** Positive ion laser desorption mass spectrum of (A) the carbon oxide precursor $C_{18}(CO)_6$ (1) to cyclo[18]carbon, (B) the carbon oxide precursor $C_{24}(CO)_8$ (2) to cyclo[24]carbon, and (C) the carbon oxide precursor $C_{30}(CO)_{10}$ (3) to cyclo[30]carbon. The high mass ions ($m/z>500$) correspond to $C_x^+$ (even $x$) with several reference values shown. Also indicated are peaks that correspond to the oligomers (that is, no fragmentation) of the cyclo[$n$]carbon precursor, such as $2n$ and $3n$. The dependence of the $C_x^+$ distributions on the size of the cyclo[$n$]carbon precursor is clearly shown, including the absence of $C_{60}^+$ in the spectra from the $n = 18$ and $n = 24$ species. All spectra were obtained by one laser pulse on a new sample spot. (Peaks denoted with an * are noise artifacts).

**Fig. 2.** Positive ion laser desorption mass spectrum of the carbon oxide precursor $C_{18}(CO)_6$ (1) as in Fig. 1A with the exception that the laser spot size (desorption area) was reduced by a factor of four. The extent of clustering reactions to yield high-mass $C_x^+$ is directly related to the density of the laser desorption plume indicating that these ions are formed by sequential gas-phase reactions of $C_x^+$ with $C_{18}$.
C_{18}(CO)_6

0  100  200  300  400  500  600  700  800  900  1000  1100  1200  1300  1400  1500  1600  1700  1800
m/z

Relative Abundance

C_x

+  

x=36(2n)  60

54(3n)  106  90(5n)  108(6n)

72(4n)  124

144(8n)
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