Fullerenes, Nanotubes and Carbon Nanostructures

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Mass Spectrometric Transmutation of Fullerenes

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MS/MS studies of the higher fullerenes Cₙ⁺ (ₙ = 60, 70, all even from 76-94) revealed that certain product ions were especially stable, and that these matched closely to the fullerenes that are particularly abundant in synthetic mixtures. All fullerenes fragmented by loss of C₂ molecules.

Keywords Mass spectrometry, laser desorption, fragmentation, fullerenes

Introduction

In 2005, Cross and Saunders described the high temperature annealing of higher fullerenes (C₇₀, and various isomers of C₇₆, C₇₈, C₈₄) to form smaller fullerenes through loss of carbon atoms (1). C₆₀ survived the passage through the ~1000°C oven without decomposition. The authors memorably described this transformation as the equivalent of turning gold into lead, given the price differential between pure samples of the higher versus lower fullerenes. The annealing process occurred in the gas phase in an argon flow, and the fullerenes resided in the oven for about 40 seconds. C₇₀ decomposed to C₇₀ and small amounts of C₆₀, and larger fullerenes also lost carbon atoms to form smaller fullerenes.

A MALDI-TOF/TOF mass spectrometer offers the opportunity to study this process from a different angle, and the MS/MS capability allows a mixture of fullerenes to be investigated, rather than having to laboriously separate the higher fullerenes. We analysed a commercially available mixture of fullerenes by tandem mass spectrometry without a matrix using a MALDI-TOF/TOF instrument and gathered decomposition information on the fullerenes C₆₀⁺, C₇₀⁺, and all Cₙ⁺ (where n = even number) from C₇₆−₉₄⁺. All appear to decompose by sequential elimination of C₂ molecules, but certain fullerenes consistently dominate the suite of daughter ions. Experiments were run without a matrix, as we have found other inorganic cluster compounds to provide more intense spectra without a matrix (2).

The mass spectrometric study of fullerenes has a long and proud history (3), starting with the Nobel prize-winning discovery of C₆₀ from mass spectrometric experiments on the laser vaporization of graphite (4). Smalley reported the photodissociation of C₆₀⁺ in TOF/TOF experiments, he showed the primary fragmentation is C₂ loss and that the initial C₂ loss requires activation of 18 eV (5). High-energy collision-induced dissociation studies show a similar distribution of fragments, provided heavier target gases than He are used (e.g. O₂, N₂) (6). High-energy (150-1050 eV/molecule) surface impact fragmentation...
of C₆₀, C₇₀, C₇₆, C₈₄, and C₉₄ on graphite generated even-numbered Cₙ species with abundances similar to those observed in fullerene synthesis (7). Cordero, Cornish, and Cotter conducted a MALDI-TOF/TOF investigation of C₆₀⁺ and C₇₀⁺, including collisional activation with He, Ar, Xe, and SF₆(8). High-energy single collisions produced the best-resolved spectra, forming high mass C₂ₙ⁺ and low mass Cₙ⁺ ions. Our study used solely Ar as the collision gas, and we examined a range of higher fullerenes in addition to C₆₀⁺ and C₇₀⁺.

Results and Discussion

The LDI-TOF mass spectrum of a commercial sample of mixed fullerenes is shown in Figure 1. It consists primarily of C₆₀, C₇₀, C₇₆, C₇₈ and C₈₄ with smaller amounts of higher fullerenes, all with an even number of carbon atoms, up to about C₁₅₀ at which point the signal-to-noise ratio becomes very low. The intensity of the Cₙ⁺ radical cations was good, with sample preparation involving simply evaporating a CS₂ solution onto an AnchorChip™ plate. The spectrum resembles that obtained of crude fullerene soot produced by resistive heating of graphite under an inert atmosphere (9).

Each of these Cₙ⁺ ions may be selected for MS/MS analysis, fragmentation being caused primarily by increasing the intensity of UV laser used for desorption. The excess energy deposited into the ions causes them to fragment after acceleration, and fragment ions are separated by the reflectron TOF. Ions decomposing in the first field-free region of the reflectron will appear at an m/z value different from that of the ion entering the reflectron, and such post-source decay (PSD) peaks appear broadened and at lower m/z values. Data were collected at three values of fragmentation energy for all fullerenes studied: (a) threshold laser power, (b) high laser power, and (c) high laser power with CID gas (Ar) switched on. The Bruker LIFT experiment was used for all MS/MS studies (10). Precursor ions are selected and fragmented in TOF-1 (the first of two co-linear time-of-flight mass analyzers). Fragment ions are selected to proceed to the source of TOF-2, where they are again accelerated and analyzed. Both sources allow control over acceleration and focusing of ions (11). Sufficient intensity for MS/MS studies were obtained for the fullerenes C₆₀, C₇₀, C₇₆, C₇₈, C₈₀, C₈₂, C₈₄, C₈₆, C₈₈, C₉₀, C₉₂, and C₉₄. The higher fullerenes provided MS/MS spectra that were too noisy for successful analysis. Mass spectra of C₆₀, C₇₀, C₇₆, C₇₈, C₈₀, and C₈₂ are illustrated in Figure 2, while those for C₈₄, C₈₆, C₉₀, C₉₂, and C₉₄ are shown in Figure 3.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Positive-ion LDI-TOF mass spectrum of a commercial mixture of fullerenes.
Figure 2. Positive-ion LDI-TOF/TOF mass spectra of C\textsubscript{60}, C\textsubscript{70}, C\textsubscript{76}, C\textsubscript{78}, C\textsubscript{80}, and C\textsubscript{82}. For each fullerene: threshold laser power (bottom), high laser power (middle), and high laser power and CID gas (Ar) switched on (top).

All data are summarized in Table 1. All fullerenes decompose by loss of even numbers of carbon atoms (2, 4, 6, \ldots 16). No low-mass C\textsubscript{n}\textsuperscript{+} fragments were observed in our product ion spectra.
Figure 3. Positive-ion LDI-TOF/TOF mass spectra of C₈₄, C₈₆, C₈₈, C₉₀, C₉₂, and C₉₄. For each fullerene: threshold laser power (bottom), high laser power (middle), high laser power and CID gas (Ar) switched on (top). The effect of introducing Ar (under computer control, increasing the pressure to approximately $6 \times 10^{-6}$ mbar) to act as a CID gas was minimal in these experiments, there was slightly more fragmentation for C₆₀⁺, but for the higher fullerenes the effect was barely discernible.
Table 1
Peak intensities of fragment ions in the LDI-TOF/TOF of C\textsubscript{n}\textsuperscript{+}.*

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*Under the harshest conditions attainable in the mass spectrometer, that is, 100% laser power, CID gas (Ar) switched on.

C\textsubscript{60}\textsuperscript{+} itself seems particularly resistant to fragmentation, the most abundant fragment ion, C\textsubscript{56}\textsuperscript{+}, represents the loss of only four carbon atoms (probably as 2 C\textsubscript{2} molecules). This observation is in stark contrast to the behaviour of the higher fullerenes under the same conditions, for which the most abundant daughter ions involve loss of between 6 (for C\textsubscript{76}\textsuperscript{+} → C\textsubscript{70}\textsuperscript{+}) and 16 (for C\textsubscript{94}\textsuperscript{+} → C\textsubscript{78}\textsuperscript{+}) carbon atoms in total. Particular product ions were especially prominent regardless of the precursor. C\textsubscript{70}\textsuperscript{+} readily lost five pairs of carbon atoms to form C\textsubscript{60}\textsuperscript{+}, much in preference to loss of 1, 2, 3, 4, or 6. Similarly, C\textsubscript{70}\textsuperscript{+} itself was the most abundant product ion in the MS/MS spectra of C\textsubscript{76}\textsuperscript{+}, C\textsubscript{78}\textsuperscript{+}, C\textsubscript{80}\textsuperscript{+}, C\textsubscript{82}\textsuperscript{+}, and C\textsubscript{84}\textsuperscript{+}. C\textsubscript{76}\textsuperscript{+} was also especially prominent, appearing as the most common fragment from C\textsubscript{86}\textsuperscript{+} and C\textsubscript{88}\textsuperscript{+}. C\textsubscript{78}\textsuperscript{+} is also especially prominent, appearing as the most common fragment from C\textsubscript{88}\textsuperscript{+}, C\textsubscript{90}\textsuperscript{+}, C\textsubscript{92}\textsuperscript{+}, and C\textsubscript{94}\textsuperscript{+} precursor ions. Notably, these ions — C\textsubscript{60}\textsuperscript{+}, C\textsubscript{70}\textsuperscript{+}, C\textsubscript{76}\textsuperscript{+}, and C\textsubscript{78}\textsuperscript{+} — are also those most abundant in the original mass spectrum of the mixture of higher fullerenes (Figure 1). There are also similarities with the high temperature annealing experiment of Cross and Saunders, in which C\textsubscript{76} formed C\textsubscript{70} and C\textsubscript{60}, C\textsubscript{78}A formed C\textsubscript{78}B, C\textsubscript{76}, C\textsubscript{70} and C\textsubscript{60}, and C\textsubscript{78}B formed C\textsubscript{78}A, C\textsubscript{76}, C\textsubscript{70} and C\textsubscript{60}. Of course, our experiment is over much more quickly and thus captures many of the kinetic products of C\textsubscript{2} loss rather than the thermodynamic products accessed by the high temperature oven and extended exposure (~40 seconds). Hence we see all the same products—and they are generally the most abundant—but we also observe all the intermediate species as well. Kroto came up with a simple set of rules that predicted certain fullerenes should display special stability, including C\textsubscript{60} and C\textsubscript{70} (12).
Early theoretical studies of $C_{20}$ through $C_{100}$ found $C_{60}$, $C_{70}$ and $C_{84}$ to be energetically more stable than their neighbors (13), and simple Hückel MO computations favoured $n = 60, 70, 76, 78, 84$, and $90$ (14).

**Experimental**

Mass spectrometric data were collected on a Bruker AutoflexII MALDI-TOF/TOF instrument. The fullerene mixture ("fullerite") was purchased from Aldrich and used without further purification. A saturated CS$_2$ solution of the fullerenes was prepared and single drops allowed to evaporate on an AnchorChip$^\text{TM}$ target (15). New spots were used for each experiment. MS/MS was performed using the LIFT experiment. The three spectra collected for each $C_n^{+*}$ were recorded under conditions of (a) threshold laser power, (b) moderate laser power, and (c) high laser power with the introduction of argon gas for CID. These parameters allowed representative coverage of the fragmentation processes. Each LDI mass spectrum represents the accumulation of between 50 and 500 laser shots on the target, the stage was moved over the course of each experiment to expose fresh sample. Data were not processed (subtraction, smoothing, etc.) in any way. Table 1 was generated by integrating peak areas for each fullerene fragment ion and expressing the intensity as a percentage of the total ion current. This method is likely to slightly overestimate the intensity of the less abundant ions due to contributions from noise.

**Conclusions**

LDI-TOF/TOF mass spectrometry has been found to be a simple yet informative technique for probing the fragmentation pathways of higher fullerenes, without the necessity for tedious separations of the individual fullerene components. This methodology should be applicable for the investigation of other polyhedral inorganic clusters.

**Acknowledgments**

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**References**