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Production, characterization and reactions of fullerenes

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Rice University, 1994
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PRODUCTION, CHARACTERIZATION AND REACTIONS OF FULLERENES

BY

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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The new third form of carbon, known collectively as fullerenes, is studied in several general aspects. Efficient production methods have been developed along with an increased understanding into the formation mechanisms. Several physical and chemical properties are investigated in attempts to characterize these unique molecules. An exciting feature of these all-carbon molecules is their ability to undergo chemical modification while maintaining their cage structure, unlike diamond or graphite. One of the fundamental alterations is the addition of oxygen atoms to the cage. Techniques to produce these derivatives and their characterization is also presented.
ACKNOWLEDGMENTS

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Introduction

Initial experiments on laser vaporization of graphite led to the discovery of a unique family of carbon cage molecules known collectively as fullerenes\textsuperscript{1,2}. Preliminary attempts to produce macroscopic quantities from these cluster beams did not produce visible amounts of fullerenes. It was not until the announcement by Huffman and Krätschmer\textsuperscript{3,4} that it was possible to generate and characterize the icosahedral molecule, C\textsubscript{60}, buckminsterfullerene and related larger fullerenes. The new allotropic form of carbon was obtained from soot produced from condensing carbon vapor under inert atmosphere.

In the short time that the fullerenes have been available an immense research effort has set forth to probe the uniqueness of these molecules. Almost every field of science has become involved, presenting that field's own special viewpoint. This unheralded interest in a single molecule, and now the many related cousins,(endohedral fullerenes, cage-doped, bucky onions, and buckytubes) makes ones own research interests seem meager by world standards, but it is hoped that the research set forth in this thesis will be both informative and thought-provoking.

The thesis will focus on the attempts to develop and understand techniques that efficiently produce fullerenes. Initial experiments regarding spectroscopy and thermal stability are shown followed by effective methods to purify each of the fullerene cages. Characterization of the pure material as well as the derivatives derived from ozonolysis exhibit the beginning of fullerene chemistry as we learn how to control the stereochemistry of these perfectly round, functionless molecules.
Chapter 2 - Macroscopic Synthesis

The first samples of fullerenes detected in 1985 by laser ablation of graphite contained only nanogram amounts. Beyond mass spectrometric techniques, chemical characterization and structural verification was not possible. Previous to the report of Huffman and Krätschmer, fullerenes remained a theoretical curiosity. After macroscopic synthesis, $C_{60}$ was quickly verified to possess the truncated icosahedron structure, the now famous soccer ball molecule. In our labs, we rapidly pursued several schemes based on the generation of carbon vapor with subsequent quenching in inert gas.

Resistive Heating

Based on what we believed to be the Huffman-Krätschmer technique, wherein a large current was passed through a graphite rod in a 50-100 Torr helium atmosphere, we achieved our first success in producing fullerenes. Figure 2.1 below depicts our source.

The alternating current source (100 A, 20 V, 60 Hz) was from a step-down transformer (10:1) working from a 220 V, 15 A house power line. The surface temperature of the graphite rod was measured as the current was varied using single-color optical pyrometry. At typical operating currents, the temperature would easily reach 2800 °C, where the dominant heat loss mechanisms were thermal conductance to the water-cooled electrodes and blackbody radiation. A small temperature dependence on gas pressure was observed, presumably due to increase heat loss to convection. At these temperatures the dominant gas phase species are not atomic, but rather dimers and particularly trimers, etc. At the sublimation point (4100 K) the relative abundances of C, C$_2$, C$_3$, C$_4$, and C$_5$ are 1, 2.8, 4.5, 0.35, 0.5 respectively.

For a 10-15 minute duration, a fine soot layer would coat the inside of the cross, totaling approximately 10-20 mg. The graphite rod which appeared intact, actually consisted of hardened amorphous carbon sheath surrounding a narrowed rod, with the
smaller diameter at the center corresponding to the hottest region, i.e. highest rate of evaporation. The soot did not contain macroscopic fullerene quantities (detected by dissolution in toluene producing a wine-red color, i.e. the "bucky test") until a water cooled heat shield was used. This suggests that the temperature profile across the vapor region plays a crucial role in the selective formation of fullerenes.

At times it was observed that the narrowing at the center of the rod would proceed to the point of breakage, whereupon rapid soot production would occur across the gap for 10-30 seconds. Essentially, an arc had formed and would consume the electrodes until the gap was too large to maintain the arc. It was at this serendipitous moment when it was realized that an arc could produce carbon vapor more efficiently than resistive heating.

![Diagram of resistive-heating source](image)

**Figure 2.1** Resistive-Heating Source for generating fullerenes. Other flanges contained vacuum, gas feed, and gauge connections.
Contact-Arc

A significant increase in the production of fullerenes resulted from the next generation of sources that utilized the contact-arc. Figure 2.2 presents a diagram of such a source.

![Diagram of a contact-arc source](image)

**Figure 2.2** Contact-Arc source installed in the six-way cross.

Contact between a 6 mm graphite rod and graphite disk is maintained by a small spring. The rod and disk were connected to copper clamps as part of two water-cooled vacuum feedthroughs. The same external power source used for resistive heating was connected to the feedthroughs. Surrounding the electrodes was a water-cooled copper shroud (8 cm inner diameter, 15 cm long) that facilitated collection and acted as a heat shield. The arc unit was mounted inside a standard 6" UHV six-way cross pumped to below $10^{-6}$ Torr with a 50 Ls$^{-1}$ turbopump. Helium pressure was controlled by a small inlet valve (feed at 1 sccm) and slow pumping was maintained with a small mechanical pump.

The 6 mm graphite rod was evaporated by passing a current of 100-200 A ($V_{rms} = 10-20$ V). The highest production rates occurred when the electrodes were barely touching such that the main power dissipation was in the arc proper and not in ohmic
heating. The spring depicted in Fig. 2.2 insured that the rod maintained contact throughout the run. After pumping down and purging several times with helium, a burn would last for approx. 1/2 hour in which 5 grams of black soot was collected on the surrounding cool surfaces. The soot production rate was increased by 250 times over that of resistive heating. The soot was solvent extracted using a Soxhlet apparatus, producing extractable yields of 10 ± 2 wt %.

It was readily observed that improvements were in order. The spring would often overheat and lose its tension, thereby terminating the run. A volcano-shaped, non-conducting deposit would quickly grow on the graphite disk minimizing further evaporation and had to be removed periodically. The confines of the small cross (i.d. 9.7 cm) made it difficult to implement larger designs and to collect soot. Also, the power source was not designed for maintaining arc plasmas; as the arc became hotter, the resistance across it decreased and current would continually increase, resulting in many blown fuses. Figure 2.3 illustrates a typical V-i curve for an arc, showing the falling dependence of voltage with current. With increased current, a greater degree of gas-phase ionization exists due to the higher plasma temperatures, thereby reducing the potential between the electrodes. By including a variable ballast resistor in the power supply (as in a commercial arc welder), a stable variable-current operating region is facilitated.
Figure 2.3 Typical V-i curve for an arc. For a constant power source will output greater current uncontrolled as the voltage decreased (a). In (b), a variable ballast resistor is added to balance this runaway effect.

**Controlled Arc**

A better design would involve two 6 mm rods symmetrically opposed provided with translational and rotational control. Greater arc gap control and deposit removal was now possible. The power source was replaced by a standard arc welder (Sears, Craftsman™ Infinite Amp 230/140 AC/DC). A 30 cm stainless steel cube replaced the confining cross which allowed greater flexibility in our designs. Figure 2.4 depicts a schematic of the opposing arc.

To insure that the rods were sufficiently outgassed, a current of 50 A was passed through contacted rods, where the surface temperature was measured to be ~ 700-800 °C. The chamber was pumped and purged with helium 2-3 times to a base pressure under 30 mTorr then brought to operating pressure, typically between 100 - 200 Torr. An arc was initiated by simply drawing back the rods after the arc welder had been turned on, thereby
producing a current around 150 A a.c., and $V_{\text{rms}} = 25\text{-}30$ V. The arc was so voracious that the rods could be turned in nearly an inch/minute, corresponding to a production rate of over 2 grams/minute.

The yield, taken as the mass of toluene extractables divided by the amount of soot, was investigated as a function of the gas pressure, type, arc gap and current. Initial yield measurements involved tedious extraction, filtering, solvent evaporation and drying of the fullerene solids. To simplify the analysis, a quick spectrophotometric routine was established in which a calibration curves were constructed from carefully prepared samples. Such a curve is illustrated in Figure 2.5 using a Beckman DU65 @ 340 nm and is based on Beer-Lambert's law that the absorbance of light is linearly proportional to the species concentration. In our case it was assumed that the ratio of $C_{60}/C_{70}$ did not vary. The most important factors affecting the yield were gas type and pressure as is evidenced in Figure 2.6. The maximum yields were always in helium, though it was interesting to
note that fullerenes could be generated in N₂. This variance reflects the ability of the gas to confine the arc, and hence the zones favoring fullerene formation. With Ar and N₂ the collision cross-sections are much greater producing a more restricted arc and in a much higher carbon density leading to rapid condensation. Likewise, the formed fullerenes would be spending a longer time near the arc due to the lower mean free path and suffering photoactivated degradation.

![Graph](image)

**Figure 2.5** Spectrophotometric Yield Calibration Curve at 340 nm.

The yield of fullerenes as a function of arc gap did not vary substantially from near contact to nearly 10 mm, although the greatest production rate was in the "contact" mode. The previous observation that a contact-arc was useful was verified, but was found not to be crucial to the production of fullerenes.

Reflecting economic law, increased production generated greater demand for fullerenes so our next design logically involved 1/2" rods with improved soot collection, in what was termed the "white glove" mode. Extending the opposing configuration, new electrodes were designed that would provide easy alignment and facile loading. Another
factor was to ensure the source current contact point was as close as possible to the arc proper so that less power would be lost in ohmic heating of the graphite electrode, thereby increasing the arc efficiency.

![Graph showing weight percent of soluble fullerenes as a function of buffer gas pressure.](image)

**Figure 2.6** Controlled Arc Fullerene Yield as a function of gas and pressure determined by spectrophotometry.

It had been previously observed that soot which remained in the line-of-sight of the arc during a run would generally give lower yields. It appeared that baking the soot was detrimental to the survival of fullerenes in the soot matrix although still under inert environment. Thus, the online removal of soot would be beneficial to maintaining high yields. The design illustrated in Figure 2.7a,b addressed these challenges. To efficiently evaporate four times the amount of graphite, three additional arc welders were connected in parallel, making sure that the electrical power supply for the welders was in phase. Using a standard vacuum cleaner motor (Sears, of course), recirculating gas was continuously filtered and soot collected in a baghouse using standard vacuum cleaner bags. Additional water cooling had to be utilized to cool the hot gases before filtering.
After several design improvements, it was possible to get about 80% of the soot nicely contained in the baghouse.

Typical operating parameters were 300-400 A (a.c.), with a potential around 27 V. Once again, a yield study was initiated using only helium and varying gas pressure and arc gap. The dependences were similar to the smaller electrode apparatus, but disturbingly the yield maximum was never more than 6% of the soot, which occurred at 150 Torr. Many variations in local temperature environments and aerodynamics were attempted to better understand and improve on the lower yield. A discussion concerning the mechanism of formation of fullerenes in the arc will be presented later in this chapter which will draw from these experiments.

An important experiment was performed which determined the affect of more reactive gases on the yield of fullerenes. Earlier, a water leak accounting for less than 0.1% of the background gas, greatly reduced the yield. Of particular technological concern is the affect of hydrogen gas, which is a byproduct of thermal decomposition of hydrocarbons as used in the production of carbon black. Also, in previous uses of carbon arcs for generating diamond thin films, hydrogen gas was usually an intimate player in good film formation.

Using the apparatus described in Fig. 2.7 modified to introduce hydrogen gas (Matheson, 99.99%) in the static mode, runs were performed with an increasing partial pressure of H₂ in He. The generation conditions were 300 A (ac), 20 V, 150 Torr (total pressure), and an arc gap of ~ 1 mm. For this experiment the runtime was kept under 5 minutes. It was noted that upon completion of each run and cooling to room temperature, the gas pressure would return to within 2% of the starting pressure verifying that little gas was consumed or generated. This assures that the partial pressure of H₂ did not vary significantly throughout the run. Using the much more versatile method of HPLC (High Performance Liquid Chromatography, consult Chapter 4 for further discussion), provided quantitative yield measurement as well as fullerene size distributions. Analysis was done by
Figure 2.7a  Large Fullerene Production Unit, utilizing on-axis electrodes, recirculating gas and 1/2" graphite rods.

Figure 2.7b  Overall View of Fullerene Production Unit showing recirculating system with baghouse filter.
sonicating equal soot masses in equal volumes of toluene, filtering and diluting to equal volumes of toluene. Equal injections into our HPLC (Reverse-phase, C18; toluene:MeOH, 50:50 at 2.0 ml/min) system facilitated direct comparison between experiments.

Table 2.1 presents the chromatographic results as a function of partial pressure of H₂ and actual chromatograms are shown in Figure 2.8. Yield was determined as the integrated area under the peaks identified as fullerenes. The lower fullerene yields are also readily seen in the lower intensity toluene solutions. The chromatograms also show increased non-fullerene toluene-soluble products, most likely polyaromatic hydrocarbons, that appear with the injection peak. The apparent yield decreased by more than a factor of 20 for only an addition of 4.9% H₂; the effect of hydrogen gas on fullerene yield is quite negative. The detrimental effect of hydrogen can be understood as simply the tying up of dangling bonds of fullerene precursors with terminal carbon atoms, unable to participate further in the growth formation. This may indeed be the case where the high temperature (> 2500 K, as exists on the periphery of our arcs) favors atomic hydrogen from H₂ which has a high propensity for carbon.

Table 2.1

<table>
<thead>
<tr>
<th>Run#</th>
<th>% H₂</th>
<th>Area [AU/min]</th>
<th>Ratio to Run 1</th>
<th>Soln' Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.200</td>
<td>1.000</td>
<td>wine-red</td>
</tr>
<tr>
<td>2</td>
<td>1.3</td>
<td>0.0364</td>
<td>0.182</td>
<td>pinkish red</td>
</tr>
<tr>
<td>3</td>
<td>4.9</td>
<td>0.0100</td>
<td>0.050</td>
<td>pale yellow</td>
</tr>
</tbody>
</table>
Figure 2.8  Labeled Chromatograms indicating the effect of H₂ on the distribution of fullerenes. Note the increased signal near the injection peak.
To date, several other methods hold promise for producing fullerenes. Essentially any method that can produce carbon vapor in inert quenching gas can produce fullerenes. Techniques such as RF induction heating, ion sputtering and electron beam evaporation, and flame synthesis have already succeeded with very interesting results. Other methods that can use a cost-effective feedstock (graphite is an expensive end-product; rather oils and hydrocarbon gases as used in the carbon black industry) coupled with other techniques, such as plasma torch devices are certainly feasible within the next few years. The capability of making tons of fullerenes/day is certainly viable wherein the price should approach the cost of making carbon black. The thought of truckloads of fullerenes is inspiring from the present vantage point of only gram quantities.
The Golden Pentagon Road

The remarkable result that over ten percent of condensing carbon vapor, originating from the chaotic high temperature domain of a carbon arc can produce a single carbon species so efficiently requires consideration. It is known that in the laser vaporization of graphite it is possible to produce fullerenes \( > C_{300} \). Considering the number of even mass channels that carbon can access, and integrating over these, the amount of \( C_{60} \) is a negligible amount of the total, and early attempts to scale-up this process always failed in producing visible amounts of \( C_{60} \).

Graphite is a more stable (eV/atom) allotrope than fullerene due to the induced strain from curvature by incorporating pentagons, so overall thermodynamics is not revealing. A mechanism based on the growth kinetics has been proposed\(^\text{12}\). During growth, condensation into graphitic sheets with dangling bonds occurs rapidly. The energetically most favored form of any open sheet is one in which follows the criteria of the "pentagon rule", namely, 

a) the graphitic sheet is made up solely of hexagons and pentagons,

b) has as many pentagons as possible to tie up dangling bonds,

c) avoidance of adjacent pentagons.

A more illustrative view is seen in Figure 2.9 which depicts a growing sheet. A comparative plot of the number of dangling bonds for a growing open graphitic sheet is shown in Figure 2.10. The relation between hexagons only and the pentagon rule clearly suggests that during the growth process, pentagon incorporation lowers the energy for a given \( C_n \), even at the cost of the induced curvature strain. Interestingly, it also suggests that every even numbered fullerene about \( C_{70} \) are also stable cages with no dangling bonds and thus extractable from the soot matrix.
Figure 2.9 A growing open graphitic sheet; comparison of dangling bonds of hexagon only with pentagon rule.

Figure 2.10 Pentagon Rule versus Hexagons only (PR wins!)
Since the intermediate pentagon structure is more stable, it is simply a matter of allowing the growing sheet enough time and energy to sample parameter space, i.e. to anneal.

Apparently, with the arc and resistive heating methods, as the condensing carbon vapor is migrating away from the source, there is sufficient time and energy for the pentagon road to be followed. With the laser vaporization at room temperature, the rate of cooling of the high density plasma in the inert gas is very rapid and the clusters do not have time to anneal. Lowering the rate of cooling by heating the surrounding gas should facilitate annealing. To test the hypothesis a simple apparatus was constructed as in Figure 2.11.

![Laser vaporization in the furnace](image)

**Figure 2.11** Laser vaporization in an oven.

The apparatus consists of a graphite rod mounted on a rotatable shaft in a quartz tube that fits in a Lindbergh oven (max. temp. 1200 °C). A vaporization laser (pulsed, Nd:YAG, 300 mJ/pulse, focused to a 1 mm x 1 cm line) smoothly eroded the end of the rod and material was seen to sublime down the tube onto the cool regions with a small flow of carrier gas (Ar or He).
Remarkably, at temperatures above 1000 °C, substantial yields of fullerenes were seen. Annealing had occurred! This correlates well with the finding\textsuperscript{13} that 5 ↔ 6 ring interconversions in polycyclic aromatics proceed rapidly at temperatures above 1100 °C.

Likewise, in the arc, substantial annealing must be occurring. Knowing that fullerenes photofragment by the successive loss of C\textsubscript{2} suggests a temperature of approximately 3000 °C (the temperature necessary to allow easy carbon bond rearrangement), permits a mapping of the temperatures indicating the various zones of fullerene production; namely generation, nucleation, growth and annealing.

Such a mapping is illustrated in figure 2.12, for the known temperature profiles of a free standing arc. Knowledge of these zones is a powerful tool in understanding and controlling the production of fullerenes. A case in point is the pressure dependence of the background gas on the yield of fullerenes, at pressures below 25-50 Torr the yield drops off drastically. As the pressure decreases around an burning arc, a disparity in ion temperature and electron temperature (defined as 1/2mv\textsuperscript{2} = 3/2KT) is seen. At lower pressures, the electrons, energized by the electric field, experience much fewer collisions with background gas, and hence the energy is not partitioned across all species. Figure 2.13 depicts the characteristic positive ion, gas and electron temperature as a function of gas pressure. It is interesting to note that the crucial annealing zone for the positive species (i.e. growing graphitic sheets), 1200-2500 °C, occurs at precisely the same pressures in which fullerenes begin to form as shown by the laser-in-the-oven experiment above. At higher pressures, as mentioned previously, the arc is more confined, so that produced fullerenes in close proximity of the intense high temperature radiating source are destroyed by fragmentation or photo-activated reaction with other growing species.

It should then be possible in the near future to construct a device in which the spatial and temperature zones are so well controlled that one could simply "dial" in your desired fullerene and produce it - pure!
Figure 2.12 The Golden Pentagon Road for Fullerene Formation.
Figure 2.13 Ion Temperature dependence on background pressure characteristic of free standing arc.
Chapter 3 - Spectroscopy of $C_{60}$ and $C_{70}$

Apparatus

The study of carbon in the laser vaporization supersonic source was initially motivated by astronomical questions. Carbon is the most abundant self-assembling element in the cosmic medium and there is much interest in its involvement in some of the mysteries of the universe. Once it was seen that fullerenes were inherently stable and abundant in supersonic beams, could they exist in the interstellar medium and be responsible for many of the unassigned diffuse interstellar adsorption lines observed? With bulk amounts of $C_{60}$ and $C_{70}$, it was now possible to produce cold supersonic molecular beams by direct laser desorption of deposited films and measure their electronic features.

Previous efforts by using laser-vaporization of graphite was plagued by the necessity of high carrier gas pressures during the instant of vaporization to remove internal vibrational excitation incurred during fullerene growth and formation. Under these conditions, the plasma is confined leading to rapid condensation and resulting in very low abundance of $C_{60}$. Figure 3.1 illustrates a re-design to facilitate extreme cooling for laser-desorbed molecules.

![Vaporization Laser Diagram](image.png)

**Figure 3.1** Dueling Nozzle Molecular Beam Source
With this source, the plume is allowed to expand freely for a few microseconds into low pressure carrier gas, then extreme cooling is achieved by rapidly increasing the gas pressure in the "waiting room" just before supersonic expansion. Opposing fast pulsed valves insure symmetrical gas mixing over the plume as well as increasing overall gas pressure. The pulsed valves shown in Fig. 3.1 utilize the magnetic current loop design\textsuperscript{14} successfully implemented in supersonic beams\textsuperscript{15,16,17}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{magnetic_leaf_spring.png}
\caption{Magnetic Leaf Spring design used in fast pulsed valves.}
\end{figure}

These valves use a fast current pulse (3000-5000 A, 30 \(\mu\)s) to excite the fundamental vibration of a copper-beryllium leaf spring (4 kHz), induced by magnetic repulsion. In doing so, the top leaf lifts off the o-ring giving a very fast, reproducible gas pulse (10-20 \(\mu\)s, \(<3 \mu\)s jitter). The laser plume, which was initiated at the rise of the gas pulse, is then carried into the "waiting room", where the gas pressure quickly rises to over an atmosphere and the species are vibrationally cooled by collisions before exiting through the supersonic nozzle.

The improved sources were incorporated into a tandem time-of-flight mass spectrometer shown in Fig. 3.3.
Figure 3.3  Tandem Time-of-Flight Mass Spectrometer

The vaporization laser (Quanta Ray DRC-1, Nd:YAG, doubled to 532 nm, Q-switched), excitation laser (a Questek 2820 XeCl-excimer pumping a Lambda Physik FL3002 dye laser system) and ionization laser (Questek 2820 ArF excimer) are all coincident with the molecular beam axis which required careful attention to alignment procedure. Ions produced are pulsed-field extracted from the beam by a Wiley-McClaren repeller stack and isoenergetic ions separate in time (as a function of mass$^{1/2}$) down the flight tube. The time dependent signal as ions impinge on amplifying microchannel plates (Galileo) are digitized and recorded, producing time-of-flight mass spectra.

**Triplet Lifetime**

Arbogast et al.$^{18}$ discovered that the lowest triplet state for C$_{60}$ in benzene is detectable and has a lifetime of approximately 40 µs. Since C$_{60}$ possesses $l_H$ symmetry, the electronic levels are calculated as
Electronic States of $C_{60}$

**Figure 3.4** Electronic levels for $I_{h} - C_{60}$

The ionization potential for gas phase $C_{60}$ and $C_{70}$ is $7.62 \pm 0.02$ eV$^{19}$.

Our experimental method is resonant two-photon ionization (R2PI), wherein an initial photon excites a valence electron into the singlet manifold above $t_{1g}$ which intersystem crosses into the triplet manifold within nanoseconds. The electron quickly relaxes to a relatively long-lived triplet (1.7 eV above the ground state), which is then subsequently ionized by a 6.4 eV ArF excimer photon. With the much more intense and stable fullerene molecular beams it was possible to observe true two-color R2PI signals. The triplet lifetime of cold $C_{60}$ and $C_{70}$ in the gas phase was measured by such a technique, and the probe method is schematically represented in Figure 3.5.
Figure 3.5 Experimental Methology to measure Triplet State.

The sample target was prepared by evaporating a fullerene toluene solution onto a roughened graphite rod. The vaporization laser (Nd:YAG, 0.1 mJ/pulse) was focused to 1 mm at the target and molecular fullerenes thermally desorb. The fullerenes were excited into their triplet state by a XeCl excimer (4.0 eV, 5 mJ/cm² pulse), and after certain time delay, \( t \) (microseconds), the resulting triplet is ionized by an ArF excimer (6.4 eV, 0.1 mJ/cm²). The entire beam of the ArF laser was kept within the XeCl beam to insure that only initially excited ions would be ionized. Also, to minimize the contribution of ArF two-photon ionization the fluence was adjusted to just below the threshold of detecting ions from ArF laser alone. The ion signal intensity was solely dependent on the number of ions that remained in the triplet state. Because of non-radiative decay mechanisms there was a finite lifetime that the ion remained in the triplet state which could be probed varying \( t \), the time between initial excitation and subsequent ionization laser pulses. Five hundred scans were done of each time dependence to improve the signal-to-noise. Results are depicted in Figure 3.6, and the measured lifetimes (1/e time) were 42 ± 4 \( \mu \)s for \( C_{60} \) and 41 ± 7 \( \mu \)s for \( C_{70} \) which is remarkably close to the measured lifetime in room temperature solution. Similarly, the excitation energy was lowered to 2.3 eV and lifetimes
measured for C$_{60}$ and C$_{70}$ as 150 µs and 225 µs, respectively (see decay curves Figure 3.7). It is expected and observed$^{20,21,22}$ that with less excess energy in the triplet state, there is less coupling to nonradiative mechanisms and hence lifetimes are expected to be longer, as is verified in Figure 3.6 for the fullerenes.
Figure 3.7 Triplet decay curves for C₆₀ and C₇₀ with 2.3 eV excitation.
Electronic Spectroscopy

Interest in the diffuse interstellar lines (DIL) and the interesting structure of the fullerenes stimulated the measurement of the visible adsorption spectrum of C\textsubscript{60} and C\textsubscript{70}. Previously, a molecular beam depletion experiment\textsuperscript{23} (photofragmentation of a benzene-C\textsubscript{60}-van der Waals complex) identified a electronic spectral feature at 386 nm, tentatively assigned as the first allowed transition. With bulk amounts of C60 and C70, it was now possible to produce cold supersonic molecular beams. Using the resonant two-photon ionization (R2PI) technique on our tandem time-of-flight apparatus, the electronic spectra were measured from 370-640 nm. Instead of varying the time delay as in the triplet lifetime experiments above, the photon energy (at fixed delay, \( t = 5 \) μs) of the excitation dye laser was varied. When a resonance absorption into the singlet manifold occurred, an ion signal would be recorded due to the subsequent ionization of the long-lived triplet. The relative absorption cross-section as a function of wavelength revealed the visible absorption spectra.

The adsorption spectrum of chromatographically pure C\textsubscript{60} in a methylcyclohexane/isopentane glassy solid matrix at 77 K was obtained by another research group at Rice. Comparison of the spectra is presented in Table 3.1. The shift due to solvent effects is about 5.5 nm to the red, indicating the coupling of electronic states to the solvent shell.
Table 3.1

<table>
<thead>
<tr>
<th></th>
<th>77 K Solution</th>
<th></th>
<th>R2PI</th>
<th></th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>(nm)</td>
<td>(cm^{-1})</td>
<td>(nm)</td>
<td>(cm^{-1})</td>
<td></td>
<td>(cm^{-1})</td>
</tr>
<tr>
<td>408.2</td>
<td>24 491</td>
<td>402.4</td>
<td>24 842</td>
<td>-351</td>
<td></td>
</tr>
<tr>
<td>4.308</td>
<td>24 758</td>
<td>398.0</td>
<td>25 116</td>
<td>-358</td>
<td></td>
</tr>
<tr>
<td>396.8</td>
<td>25 194</td>
<td>361.6</td>
<td>25 527</td>
<td>-333</td>
<td></td>
</tr>
<tr>
<td>391.2</td>
<td>25 555</td>
<td>385.7</td>
<td>25 917</td>
<td>-362</td>
<td></td>
</tr>
<tr>
<td>387.4</td>
<td>25 806</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>384.6</td>
<td>25 994</td>
<td></td>
<td></td>
<td></td>
<td>ave = -351</td>
</tr>
<tr>
<td>380.2</td>
<td>26 294</td>
<td></td>
<td></td>
<td></td>
<td>s.d. = 13</td>
</tr>
</tbody>
</table>
Figure 3.8 Cold Gas-Phase Absorption Spectrum of C$_{60}$ compared with solid solution at 77 K in the region of the first allowed transition.
Figure 3.9  R2PI spectrum of C60 (a) and C70 (b) in the 595 to 640 region.
It is interesting to note that the cold electronic spectrum of C_{60} resembles the diffuse interstellar lines in respect to the linewdths and density of lines. Though the spectrum does not account for the DILs, it is gratifying to see linewdths generally increase with energy, as is observed for the DILs. It should also be noted that if C_{60} were in the interstellar medium, it would most likely be ionized suggesting the need to measure the cold electronic spectra of the ionic species.
Chapter 4 - Purification and Characterization

Background

In every production technique discussed in Chapter 2, inherently a distribution of fullerenes is produced usually with C_{60} being the most abundant (75-90%), though there are methods which did produce C_{70} dominantly. The remaining extractables consist of higher fullerenes in the range of C_{76} to C_{96}. There has been much evidence^{24} that, depending on the solvent, a substantial portion of the soot is extractable, yielding C_{2n}, n>50 over a broad distribution up to C_{300}.

In any case, there does not exist any method which produces a single pure fullerene. To obtain pure fullerenes, the method of choice is chromatography, although some evidence suggests sublimation over a temperature gradient holds some promise^{25}. Purified fullerenes interestingly exhibit distinct colors in solution; C_{60} - magenta, C_{70} - red, C_{76} - yellow, C_{78} - brownish, and C_{84} - green. Their respective color is evident in the UV/Vis spectra obtained for each of these species as seen in Figure 4.1.

Taylor et al^{26} were the first to separate C_{60} and C_{70} using hexane/toluene on activated alumina and other laboratories soon had equal success^{27,28,29}. The use of carbon-based materials as the stationary phase provided for some degree of separation^{30,31,32}. A facile route to purifying gram quantities of C_{60}, involves selective, near irreversible adsorption of higher fullerenes on an activated charcoal/silica.

As well, several novel variations of classical column chromatography have been implemented. Khemani et al^{33} used a modified Soxhlet apparatus; Chatterjee et al used a Kauffman apparatus to separate directly from soot^{34}. In our laboratory, significant success has been achieved using what we term "trough 'n' brew" purification of the fullerenes and herein is described below.
Figure 4.1 HPLC trace showing separation of fullerenes and their corresponding UV/Vis absorption spectra.

Trough 'n' Brew Purification

We have reported the production capability of 10 grams/day of fullerene toluene extract (approx. 80% C_{60}, 17% C_{70}, 3% larger fullerenes)\textsuperscript{35}. The chromatographic system of choice utilizes neutral activated aluminum oxide as the stationary phase with toluene in hexane (0-100 \%v/v) as the eluant. Classical gravity column chromatography proved undesirable as a means of maintaining pure fullerene production. The inadequacies arose from; (1) each fullerene was distributed in large volumes of mobile phase - 1 g of extract generated 30-40 liters C_{60} fraction; (2) large volumes of mixed solvents requiring subsequent distillation, (3) difficulty in obtaining expected yields, typically obtaining 45% C_{60} per gram extract, (4) larger fullerenes appeared to degrade on the column, discoloring the alumina to light-brown with increased time, rendering the column non-recyclable, as
well as lose of product, (5) using optimal flow rates, a large column took 24-48 hours to complete. Herein is described a modification of the above process which has resolved many of the difficulties.

Experimental

In 1903, Mikhail Tswett, a Russian botanist studying plant pigments pioneered what is now column liquid chromatography. In one method, he would remove resolved bands of highly colored chlorophylls, then rinse the adsorbent free of the isolated pigments. Nowadays, column liquid chromatography customarily involves collection of mobile phase fractions that flowed through a adsorbent bed, individual fraction analysis, and subsequent evaporation of similar fractions. Like Tswett's pigments, the fullerenes exhibit disparate colors in solution (C_{60} -magenta, C_{70} -red, higher -yellow to brown). This allows for their straightforward identification. Utilizing this property, progress of the column is readily monitored (C_{60} leading band, then C_{70}, etc.). Once the fullerenes are resolved on the column, the mobile phase is drained and the stationary phase is physically removed according to color. The coated alumina is air dried, then placed into an elution column and the isolated fullerenes washed off with toluene.

The Column

The column proper was designed to facilitate packing and removal of alumina. The column developed is shown in Figure 4.2a,b.
A 95 cm X 30 cm x 45 cm (height) trough, consisting of 1/4" aluminum plate sides fixed to 1/2" aluminum plate bottom, and fitted with 1/2" plexiglas end-windows that could slide vertically along a compressible seal. The flat bottom plate was fitted with a single 3/8" swage-lock-to-1/2" NPT for drainage. A 0.035" thick stainless steel 304 perforated plate, on which 250 mesh SS304 wirecloth was spot welded, rested upon 3/4" aluminum stand-offs on the bottom. This bottom support screen was dimensioned to fit
snugly inside the trough. The whole apparatus sat on four leveling feet and equipped with a close-fitting lid to minimize solvent exposure and evaporation.

Of the column packing materials investigated (activated alumina, silica gel, sized graphite), alumina proved amenable for large scale application. It provided excellent selectivity (10 times greater than normal phase silica), adequate loading capacity, and reproducibility. To avoid the use of gradient elution, pure hexane was chosen as the mobile phase.

Preparation

The column was prepared by slurry packing which would insure more uniform packing and minimize trapped air. Aluminum oxide, (Brockmann Activity I, 150 mesh, 60 Å), was stirred in hexane (reagent grade), and the resulting slurry slowly poured into a reservoir of hexane (15-20 cm height) As the alumina settled, maximum flow of hexane was maintained along with occasional tapping of the walls. The process was continued until a bed of only 10-12 cm was obtained. The solvent head was brought to within 1 cm of the alumina bed and an adjustable scraper, which rode above the sides of the column, was used to level the column within +/- 1 mm. This is vital to insuring an even starting band.

The saturated toluene solution of carbon arc soot was dried unto previously used alumina (4 g/ 2 kg alumina), giving an uniformly coated, light brown solid The reduced activity of this alumina due to exposure to moisture assures less retention in the starting band. Similarly, silica gel sufficed for this purpose (using approx. 1/2 the mass due to greater surface area/gram).

Development

With the solvent head 1 cm above the column bed, the extract/alumina was poured onto the column and leveled with the scraper in the same manner as above. Another
perforated plate/wirecloth section was placed over the starting band to prevent its disturbance as solvent was added. Again, this is crucial for uniform loading. At this point, a reservoir of 40-60 liters of hexane is added and the flow rate set. The flow rate had been previously investigated for this system and found optimal at about 500 ml/min corresponding to a flow velocity of 1.8 mm/min. The same hexane containers were adapted as catch reservoirs. Once these were full, the hexane was simply recycled back into the column reservoir. This is an unique feature of this system, in that with an appropriate pump system, the separation of the fullerenes is easily automated, requiring no detection of the eluant and constant observation.

As mentioned previously, because of the associated colors of the fullerenes, the separation was readily identifiable. It was observed that within 1 cm of the column head a purple band was seen to form, and that this purple band, C_{60}, after migrating down 5 cm (8-10 hrs), would be resolved from the reddish band, C_{70}, with a 0.5 cm white band between them. Directly behind the C_{70} red band, a light brown-yellow tail to the baseline was observed. The original baseline band remained slightly discolored. At this point, it was concluded that the column had achieved adequate resolution, and the hexane was drained, aided by water-aspirator suction. Between 85-90% (70 liters) of the all the original hexane was recovered and immediately ready for another column, the remaining presumably wetting the alumina or lost via evaporation.

*Participation Chromatography*

With C_{60} and C_{70} resolved, the pure fullerene/alumina was removed, and grouped according to color. It is important to note that the yellow-brown higher fullerenes are the first recovered, minimizing needless migration through a long column. With this short a column, it was not expected to resolve them, but this provided a much higher relative concentration for later separation. As the layers were scraped away, the "mixed" fractions appeared marbled, and it was rather facile to determine when one was in a "pure" layer.
This continued down to the purple layer, in which the red C70 was very readily discernible, and it made it possible to obtain high purity C60 since it was the frontal band.

Once the separate layers were dried (natural convection, in darkness), the coated alumina was placed into a smaller cylindrical column and toluene rinsed through the column. The resulting saturated fullerene solution (2.5 liters for C60 band), was then rotovapped to dryness, followed by several ethyl ether rinses to remove trace toluene. Bulk pure C60 appeared deep-brown in color, with yellow-brown powder film on the flask walls. Pure C70 was a lustrous black powder. The used alumina can then be dried by conventional methods, with a final reactivation step of heating at 250 °C, for 48 hrs, and storing in airtight containers to prevent deactivation with water. The reused alumina has about 90% of its original activity. The toluene used throughout these experiments is recycled, retaining approx. 75% of the solvent, the main loss due to retention on the final alumina rinsing.

Results and Column Evaluation

Purification results are listed below, in which purity was verified by HPLC.

Actual yields: Starting 4.80 g extract

2.89 g C60, +99.95 %, purity, 60.2% recovered

0.775g C70, 93% purity (with C60).

The tailing bands behind C70 were found to contain the larger fullerenes, C76, C78, C84 (most abundant), C90, with C70 from the previous band

Although the standard techniques of evaluating column performance based on retention times and peak shapes are not possible here, measurements based on distance that bands traveled in a given time and corresponding band widths do provide some indication. The plate height was determined to be H=0.034 cm, which is typical for a "good" column. The capacity factor, k', (ratio of concentration of solute in stationary phase to mobile phase) was measured for C60: k'=17, and C70: k'=27. A value of k', such
that $2 < k' < 10$ is considered optimal, in terms of resolution and analytical time. The $k'$ factor is easily modified by addition of other solvents, but this optimization is not worth the subsequent time-consuming distillation. The resolution and selectivity between $C_{60}$ and $C_{70}$ were excellent, although there is significant band tailing ($C_{60}$ into $C_{70}$), as evidenced by the purity analysis. The tailing is the result of a combination of column loading and heterogeneous retention sites. In adsorption chromatography, the partitioning between stationary and mobile phases is not linear, but rather is much like an adsorption isotherm, fairly linear at low concentrations, then rapidly leveling off at higher concentrations. The distribution of heterogeneous retention sites accounts for the phenomena. Thus, at low mobile phase concentrations, species are more strongly retained resulting in tailing.

In the above system, it was only attempted to resolve the fullerenes. However, if the maximum yield of $C_{60}$ per column area is desired, it is possible to overload the column significantly and settle for low purity $C_{70}$, yet generate 4-fold quantity of $C_{60}$ for the same column system. Such experiments are in progress.

In conclusion, the trough 'n' brew method of fullerene purification has immediate ramifications in the straightforward and efficient (both in man-hours and cost) production of high purity fullerenes, especially $C_{60}$.

It should be noted that to date, this technique has been the only non-HPLC method successful in obtaining large quantities of mixed higher fullerenes as they are the first removed from the column. To separate fullerenes higher than $C_{70}$ much more efficient systems are required to achieve the necessary resolution. Preparative HPLC has been successful used to purify $C_{60}$ and $C_{70}$ and in isolating milligram quantities of $C_{84}$ implementing various systems. Initially reverse-phase columns with hexane/methanol were used but loading capacity was limited. Similarly, phenylglycine and dinitroaniline-propylene (DNAP) bonded-phase columns provided adequate separation with meager loading. Gel columns made from polystyrene cross-linked with divinylbenzene could be
used with higher proportion of toluene but resolution was poor. In our laboratory, we tested the commercially available Buckyclutcher column (Regis Chemical Co.) incorporating a novel tripodal π-acidic tri-(dinitrophenol) bonded to silica. The packing material (see Figure 4.3) was specifically designed to maximize interaction between fullerenes and the electron-withdrawing aromatic character of the di-nitrophenol. The capacity factor and selectivity are greatly increased such that even pure toluene could be used as the mobile phase. It has proven superior to all other columns for separating not only C₆₀ and C₇₀, but the higher fullerenes as well.

Figure 4.3 The bonded phase used in the BuckyClutcher.
Chapter 5  Chemistry in the Round

Background

The chemistry of fullerenes has somewhat lagged behind the intense interest in their unique physical and superconductive properties. Basic reactions such as hydrogenation, fluorination, alkylation, etc. yield an uncontrolled broad range of products. The greatest difficulty is determining the product stereochemistry as species dot the fullerene surface or become incorporated into the cage framework itself. A new age in nomenclature must now be invoked has chemists begin to design precise fullerene adducts. The path to rich fullerene chemistry has already begun in which the entire palettes of organic/inorganic reactions are being applied. At Rice University, soon after the availability of fullerenes, the first fullerene chemistry was reported\(^{36}\) as the Birch reduction (partial hydrogenation) of C\(_{60}\) including a intriguing proposed structure, where an unconjugated double bound was left on each pentagon.

Thermal Decomposition

To study fullerene stability in ambient conditions the rate of decomposition in heated air was performed\(^ {37}\). Such studies may lead to a better understanding of the processes of degradation of fullerenes in air and the results could also have important implications for the long-term storage of fullerenes as well as their lifetimes in natural environments. In these studies, mixed fullerenes and pure C\(_{60}\) solids were heated, separately in air at different temperatures for differing time exposures in darkness (ambient conditions). The solids were then tested by; a) solvent extractability in toluene, b) spectrophotometry, c) Raman, Infrared, and UV/Vis spectroscopy, d) mass spectrometry, e) X-ray diffraction, and f) electron microprobe analysis.
A spectrophotometric calibration curve based on known concentrations was used to determine weights. In Figure 5.1, the absorbance as a function of heating time at 210 °C clearly indicates the loss of toluene recoverable material. After only 5 hours, half of the initial material is no longer soluble in toluene. The decay curve based on weight of fullerene recovered by toluene is shown in Figure 5.2 and it is seen that the rate of decay is temperature dependent, increasing at higher temperatures. Furthermore, the material that is soluble, takes longer to redissolve. It is generally known that fullerenes do exhibit a time dependence in their dissolution, but here the decomposition products are further impeding the dissolution (see Figure 5.3) with increased effect at longer heating exposure.

The material remaining after toluene extraction was also characterized. Some portion did dissolve in water (colored yellow, pH 3.85), methanol, and acetone, but did not indicate the presence of derivatized fullerenes (via mass spectrometry and UV/Vis). The IR spectrum taken of the acetone soluble fraction is shown in Figure 5.4. It shows five significant absorption features. They are consistent with the occurrence of ketones, carboxylic acids, esters, or aldehydes, correlating with finding of acidity in the water soluble portion. The B feature suggests that the sample contains aromatic bonds. Furthermore, the acetone-soluble fraction indicated (see Figure 5.5) by electron microprobe contained a fair amount of oxygen incorporation with a little nitrogen as well.
Figure 5.1 Spectrophotometric spectra in toluene of mixed fullerenes as a function of heat exposure. Since all samples had same initial weight, the decrease in absorbance directly relates the degree of decomposition.
Figure 5.2 Recovery of fullerenes decomposed at 230° and 250 °C, defined as weight of material solvent extracted normalized to the weight of the untreated sample and given in percent.
Figure 5.3 Rate of dissolution of recoverable fullerenes normalized to the final recovered weight, as a function of increased heat exposure. Large graph is at 250 °C; untreated, 2 hours and 4 hours. The inset at 230 °C for untreated and 2 hours.
Figure 5.4 FT-IR spectrum of acetone soluble fraction of decomposition product mixed fullerenes at 200 °C, exposed for 234 minutes.
Figure 5.5 Electron microprobe X-ray analysis of sample studied in FT-IR in above figure. The inset shows an enlarged view of the nitrogen region.
The evidence is clear that the fullerenes decompose fairly rapidly when heated in air (150-250 °C) and that the rate of decomposition is temperature dependent. The decomposition appears to follow exponential decay;

\[ dN = -kN \, dt \]

where \( N \) is the weight of fullerenes and \( k \) is the rate constant. Following this approximation, the rate constants can be derived from decay curves like in Figure 5.2 for all runs. Then using the Arrhenius relation,

\[ \ln k = -\frac{E_a}{R} \frac{1}{T} \]

the logarithm of the rate constants as a function of \( 1/T \) (see Figure 5.6) can be extrapolated to room temperature. Since the decomposition was assumed first order, the deduced rate constants can be converted to half-lives. Clearly, the mixed fullerenes (F1) decompose faster. See Table 5.1.

**Table 5.1** Extrapolated half-lives of heated decomposition of fullerenes in air

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Extrapolated half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure C(_{60})</td>
<td>25</td>
<td>400 yr.</td>
</tr>
<tr>
<td>Pure C(_{60})</td>
<td>100</td>
<td>0.88 yr.</td>
</tr>
<tr>
<td>Mixed</td>
<td>25</td>
<td>88 yr.</td>
</tr>
<tr>
<td>Mixed</td>
<td>100</td>
<td>0.16 yr. (∼60 days)</td>
</tr>
</tbody>
</table>

The data suggests that the presence of C\(_{70}\) catalyzes the degradation of fullerenes. Experiments with pure C\(_{70}\) are addressing this issue.
Figure 5.6 Arrhenius plot of the decomposition rates deduced from the various heating experiments. Least squares fit were obtained to obtain the extrapolated value in Table 5.1.
Ozone

Fullerene stability in air is believed to be dominated by its reactivity with oxygen (and perhaps water). Numerous photochemical studies\textsuperscript{38,39,40,41} have clearly indicated that oxygenated adducts are made, but also irreversible degradation of the carbon cage occurs. In the course of the study of the stability of fullerenes in air\textsuperscript{42}, the possibility was considered that the transformation of C\textsubscript{60} and C\textsubscript{70} to substances insoluble in toluene was due to the reaction of fullerene with ozone, not molecular oxygen.

The reaction of ozone with C\textsubscript{60} has been investigated, and suggested as an intermediate in the oxidation of C\textsubscript{60} with oxygen. Interestingly, it was observed in thin films\textsuperscript{4} the co-presence of photons with oxygen was necessary for chemical change to occur, resulting in carbonyl-type products. Without the light flux, the adsorbed layer of oxygen did not cause a change in carbon environment throughout the temperature range studied.

In our experiment C\textsubscript{60} was obtained by standard methods. Fullerene rich soot was generated by the contact-arc method, and mixed fullerenes extracted under sonication with toluene followed by filtration (.22 micron). Purification by chromatography using alumina/hexane utilizing the trough 'n' brew technique provided high purity C\textsubscript{60} (>99.9\% by HPLC). Further purification of the C\textsubscript{70} provided +98 \% quantities for comparative studies. Stock solutions in toluene and cyclohexane were prepared.

Ozone was generated in O\textsubscript{2} (Welsbach, determined to be 2.6 vol \% by iodometry) and bubbled through 5 ml aliquots of several stock solutions. A rapid change in color was observed. For C\textsubscript{60} the intense magenta, to pinkish, red, light orange-brown and eventually pale yellow at the longer exposure. Quantitative HPLC analysis of the careful ozonation of C\textsubscript{60} in toluene is illustrated in Figure 5.7. In Figure 5.8, the loss of C\textsubscript{60} as a function of ozone exposure is plotted. The loss mechanism appears as pseudo-first order, but the extraction of kinetic data is not feasible as the reaction is essentially diffusion-
limited by the gas bubble mixing in with solution. Indeed, the reaction may be occurring right at the gas/solvent interface.

Figure 5.7 HPLC chromatograms of solutions with increasing ozone exposure. The assignments of peaks are discussed in text.

The peak assignment proved a difficult task. Attempts to characterize the ozonated toluene solutions by laser desorption mass spectrometry proved meaningless.

As part of the HPLC detection system, a photodiode array could obtain complete UV/Vis spectra across the entire chromatogram. The C₆₀O peak was assigned by comparison with the previously isolated and characterized data by Creegan et al.⁴¹ They
were able to characterize the oxide as an epoxide, where an oxygen atom bridged pentagons. The cage structure of the fullerene remained intact, as evidenced by the similar UV/Vis spectrum, suggesting that the electronic structure has not been drastically altered. The earlier peaks, based on their characteristic UV/Vis spectra, were believed to essentially be fullerene derivatives, that were becoming increasingly polar. An overlay of the UV/Vis spectra, illustrated in Figure 5.9.

By utilizing an HPLC system interfaced to a quadrupole mass spectrometer, it was possible to separate each peak, and determine it's mass. The interface, depicted Figure 5.10, generates a fine mist in a heated zone called a thermospray, in which the solvent

![Graph showing the decay of Parent C60 as a function of ozone exposure.](image)

**Figure 5.8** Decay of Parent C60 as a function of ozone exposure.
Figure 5.9 Overlay of UV-Vis spectra collected at maximum of chromatography peak as labeled in Figure 12. The similarity of the spectra along with the increasing UV shift supports that the electronic structure has not been significantly altered and hence the cage has remained intact.
quickly evaporates, leaving behind gas phase solute molecules that drift into the ionization and extraction zone, where they are detected by quadrupole mass spectrometry.

![Thermospray interface diagram](image)

**Figure 5.10** Thermospray© interface

Figures 5.11 a,b are a compilation of the results obtained. Mass spectra corresponding to the chromatography peaks indicated only presence of C$_{60}$ or oxygen adducts. The mass spectra obtained at each peak, did correspond to sequential addition of oxygen atoms as evidenced by signal appearing sequentially at $m= 736, 752, 768, 784, 800$, and $816$. This corresponds to a limit of C$_{60}$O$_6$. Also, the appearance of isomers is readily observed. Several resolved HPLC peaks possess the same parent mass (higher oxides, heated by the interface, readily lose oxygen atoms, as is seen in Fig. 11). Therefore, we are able to confidently assign to a well-resolved chromatogram the identity of each fullerene oxide as done in Fig. 12.
Figure 5.11a Respective mass ion signal as a function of elution time from HPLC column corresponding to sample in Figure 12. Peaks are due to presence of parent $C_60$, $C_60O$, $C_60O_2$, and $C_60O_3$ successively.
Figure 5.11b Respective mass ion signal as a function of elution time from HPLC column corresponding to sample in Figure 12. Peaks are due to presence of $C_{60}O_3$, $C_{60}O_4$, $C_{60}O_5$, and $C_{60}O_6$ successively.
Figure 5.12  HPLC Chromatogram of resolved fullerene oxide peaks labeled accordingly. Note the presence of isomers of \( C_{60}O_n \) which are resolved and hence isolable.
If indeed higher oxides are being formed, their geometrical structure would be most interesting, especially in the instances of isomers. The presence of functionality in predictable locations would serve as an important intermediate for a host of organic and inorganic reactions that, at this moment, has not been produced in literature.

Present research has led to the isolation of milligram quantities which are now awaiting characterization. It is possible to make some predictions on possible isomers. Since each HPLC peak corresponds to a single species (as verified by a uniform UV/Vis spectrum across each peak), then only select multiple oxides are being formed. For instance, if one follows that further epoxides will form across the shorter 6-6 bond (bridging two pentagons), then in adding two epoxides there are 9 isomers possible. Fig. 13 illustrates most of the possible arrangements, where "0" denotes the first epoxide bridge, and the set of single digits indicates the position of the next epoxide with equivalent isomers sharing the same digit.

![Diagram of epoxide isomers of C_{60}](image)

**Figure 13** Epoxide isomers of C_{60}.

Furthermore, it is likely that the addition of another oxygen atom will be directed by the activation of a nearest neighbor carbon by the previous parent epoxide.
The reaction of ozone with organic species is usually used to determine the substitution across carbon-carbon double bonds by oxidative cleavage to produce carboxylic acids. Usually an unstable primary ozonide is formed before the presence of acid or base will catalyze the cleavage process. The mechanism is a $S_N2$ type, requiring backside attack to open the double bond. In the case of fullerenes this is not possible. Based on preliminary temperature variant ozonations, an extremely small activation barrier to the formation of epoxides was observed. This suggests that the intermediate of an $O_3$ molecule bonding to $C_{60}$ with subsequent rearrangement to leave an oxygen atom and $O_2$, must occur in a facile concerted manner with the least amount of atomic rearrangement. The formation of a peroxy-epoxide intermediate is a likely candidate which meets the criteria set above.

Further experiments are now in progress to understand the differences between ozonolysis and photoactivated oxidation (which apparently due not form higher oxides). As well, progress on the ozonation of higher fullerenes as has revealed interesting reaction differences.

The importance of the well-characterized functionality of these epoxides has already been illustrated in what is believed to the methoxidation of the epoxide by simply warming a toluene solution in the presence of methanol. As well, cyclic voltammetry should shed light on the electronic structure of these species.
Future Research

It is quite clear that much has been learned about the third allotropic form of carbon as outlined in part in this thesis. Of more significance is the interest that fullerenes have exhibited in fields as diverse as semiconductors, medicine, electrochemistry, polymers, metallurgy, nuclear energy, for example, and has developed into a new branch of organic/inorganic chemistry. The evident versatility of these pure carbon molecules insure interest for decades to come. No other material ever produced has resulted in such explosive fundamental research to exploit its commercial potential.

However, several crucial developments must take place. First, the ability to produce fullerenes industrially must occur to bring the cost to perhaps that of graphite. For fullerenes to be of value commercially and used in whatever capacity as a new material, it must be cheap and not at the present value of $100,000 per kilogram. Only at realistic prices will fullerenes and their derivatives succeed as a technological alternative to either pre-existing markets or new advanced ones. Secondly, the most likely applications will arise as a result of our ability to control the chemistry of fullerenes, meaning that we will have to create well-defined stereoanalogs of fullerenes. Though the ozonation experiments presented here are the first steps in derivatizing and isolating functionalized fullerene isomers, much has yet to be accomplished.

As President Theodore Roosevelt said, "If you aim at nothing ... you will hit it every time!". I aim to continue to solve these issues.
References


