Anticorrelated formation of fullerenes and polyynes upon laser ablation of graphite under various concentrations of hydrogen sources

Abstract

Soluble fullerenes were produced with a somewhat unexpectedly high yield (10^{-2} wt% of the evaporated carbons) by laser ablation of graphite in a "room-temperature" argon gas flow. The high yield was likely due to the high temperature of the graphite after heating by the ablation laser. Laser ablation experiments using argon-diluted propane gas showed that fullerene formation was strongly inhibited by the addition of propane, while the formation of hydrogen-terminated, chain-form carbon molecules (polyynes) was enhanced. The reactivities of the fullerene precursors and chain-form carbon clusters are discussed based on the anticorrelation of the yields of fullerenes and polyynes.

Keywords: fullerenes, polyynes, laser ablation

1. Introduction

Just 25 years after the discovery of fullerene formation by the laser vaporization of graphite by Kroto et al. in 1985 [1], clear evidence showing the presence of these species in the universe was provided by the detection and identification of the vibrational modes of fullerene species in the *Spitzer Infrared Spectrograph* spectrum of the young planetary nebula Tc 1 [2]. According to recent research on C_{60} in astrophysical environments, C_{60} has been detected in over 20 different stars [3]. C_{60} is detected in places where hydrogen-attached carbonaceous materials, such as polycyclic aromatic hydrocarbons (PAHs), are also detected and an anticorrelation of the abundances of these species has been observed [4]. Although the presence of circumstellar [3] and interstellar [4] fullerenes is now firmly established, many questions about their formation processes remain. In fact, even on the laboratory scale, fullerene-forming reactions are still controversial [5].

To understand fullerene growth processes in laboratory experiments, the structure and reactivity of size-selected carbon clusters has been studied most extensively with the aid of mass spectrometric techniques. Many such experiments, including theoretical calculations, have indicated that the most stable structure varies from a linear form to fullerene with increasing cluster size, with monocyclic and polycyclic forms in between [6, 7]. Although the high sensitivity of mass spectrometry allows detecting even very small amounts of carbon

clusters, in most cases, it has been difficult to establish the geometrical and electronic structures of these carbon clusters. Thus, even for C_{60} , we had to wait until 1990 to confirm the presence of C_{60} with a truncated icosahedral structure (I_h-C_{60} or soluble C_{60}) using conventional experimental tools to identify the structure [8].

A key question that arises in fullerene studies in both the laboratory and astrophysical environment is how the circumstantial temperature drives the formation yield of these species. From an astrophysical point of view, this is fundamentally important, because it determines how the fullerene yield can be used to probe the physical conditions of the environment in which they are formed. As for C_{60} formed by the "room temperature" laser ablation of graphite, that is, without an extra heating device, the upper limit was estimated to be 0.1 % in molar ratio based on mass spectra obtained under various laser vaporization conditions [9]. The formation of "macroscopic" amounts of C_{60} by the laser ablation of graphite was first reported by Meijer and Bethune [10]. In those experiments, laser ablation (532 nm, 200 mJ, 6×10^3 shots) was performed in 500 Torr Ar as a means of preparing samples for laser *desorption* mass spectroscopy of as-deposited films of the ablation products. The evaluated lower limit for the surface density was 10^{14} molecules/cm² (120 ng/cm²). An Ar atmosphere was also found to be effective in generating macroscopic amounts of fullerenes by the laser ablation of graphite together with the use of a heating device to achieve higher temperature conditions around the ablation area.[11] Soon afterwards, the effects of temperature and pressure on fullerene formation were studied quantitatively, where the absolute yields of C_{60} were determined as a function of Ar atmospheric temperature by isolating C_{60} from the soot and measuring the optical absorption spectra.[12, 13, 14] The threshold temperature was around 500 °C and the maximum yield of C_{60} was 5 wt% at around 1000 °C. The co-existing solvent-insoluble residual carbonaceous materials were also studied by high-resolution transmission electron microscopy (HRTEM), in which the morphology of the insoluble carbon soot was found to be dependent on the temperature [15].

In the present study, laser vaporization (ablation) of graphite was performed in a flowing argon atmosphere without any external heating device. We found that a macroscopic amount of soluble fullerenes was formed, and that the yield was considerably higher than expected for low-temperature laser vaporization. To examine how the presence of hydrogen affects the formation of both the hydrogen-attached carbon clusters (polyynes in the present work) and fullerenes, propane was mixed as a hydrogen source in the ablation area, and the products, including those unstable in the solid phase, were analyzed.

2. Experiments

An apparatus for laser ablation, comprising a gas preparation line with flow meters, a glass cell for laser irradiation with a cone-shaped throat at the exit, and a cooled organic solvent at the bottom, is shown schematically in Figure 1. A Q-switched Nd:YAG (10 Hz, 532 nm) laser was loosely focused on an area

Figure 1: Schematic drawing of the laser ablation set-up. A: argon gas cylinder, P: propane (or argon-diluted propane) gas cylinder, F: flow meter (KOFLOC 3810DSII), G: graphite, S: solvent (decalin), C: coolant (methanol, -40 °C), L: lens

of 20 mm² with an average power of 3.0 W, resulting in an adopted fluence of 15 mJ/mm², which was similar to that usually employed in laser ablation mass spectrometry. The irradiation time was 30 min. For effective ablation, the irradiation spot was moved about 1.5 mm every 3 min. The graphite surface was set parallel to the gas flow.

The collection efficiency of the energetic products, which were mainly directed at the glass wall, was considered to be low. That is, products with low initial velocities were collected preferentially in the solvent. Some of the products were attached to the wall as a soot-like material. The flow rate of the carrier gas (Ar with 99.9999 % purity) was fixed at 100 mL/min. This is high enough to prevent contamination of vaporized solvent molecules into the irradiation cell. The exit of the gases was open to the atmosphere; thus, the internal pressure was near atmospheric. Cooled decalin (cis/trans-mix, -40 °C, 5 mL) was used as the solvent because of its good solubility of fullerenes and polyynes.[18, 19]

To examine the reactivity of C₆₀ precursors, propane gas with 99 % purity or Ar-diluted 5 % propane gas was mixed with the pure Ar gas by varying the propane gas ratio, denoted as $R = f_p / (f_a + f_p)$, where f_a and f_p stand for the flow rates of Ar and propane, respectively. The total flow rate was kept constant, $f_a + f_p = 100$ mL/min.

After irradiation, the solution was filtered and analyzed by UV-vis absorption spectroscopy (Shimadzu UV-3600). An analytical HPLC with a COSMOSIL Buckyprep column was used for the analysis of fullerenes. The eluent was toluene, the injected sample volume was 1 mL, and the detection wavelength was 340 nm. The soot attached to the wall was collected by washing with decalin

solvent and the solution was filtered and analyzed. The amounts of fullerenes and polyynes were obtained from the HPLC and UV data, respectively.

The weight of vaporized carbon was measured in order to determine the yield of fullerenes (wt%). First, the graphite target was heated in a 400 °C quartz tube and weighed with an electronic balance. After 30 min laser irradiation, the target disk was reweighed and the decreases in mass were determined for three independent runs.

The ablation laser itself may heat the target and surroundings to a high enough temperature. Indeed, irradiation with much stronger lasers, a long-pulse (500 ms, 1 Hz) CO₂ laser of 20 kW/cm² and a 4.5-kW CW CO₂ laser, succeeded in forming fullerenes. In these cases, the laser heating of the reaction field was considered to be essential [16, 17]. Although the laser power used in the present study was much lower, surface temperature was an important factor. Thus, we measured the temperature changes of the graphite target under irradiation with two devices: a K-type thermocouple pasted on the graphite surface and an infrared pyrometer (KTL-P1).

3. Formation of C₆₀ by "room temperature" laser ablation

A typical UV absorption spectrum of the dissolved products, produced by laser ablation in pure argon, without propane, and transferred to the solvent by the gas flow, is shown in Figure 2a. The UV absorption bands were assigned to C₆₀ and C₇₀, as indicated in the figure, while there appeared to be essentially no polyyne peaks. An HPLC chromatogram of this solution is shown in Figure 2b. The peak positions in the HPLC chromatogram agree with the known retention times of C₆₀ and C₇₀. Thus, we conclude that fullerenes were formed by the laser vaporization source. The ratio of C₇₀ to C₆₀ was nearly the same as that known for fullerenes produced with a high-temperature laser ablation source [13]. The absolute yield of C₆₀ was evaluated from the areal intensity of the HPLC peak, calibrated against a pure C₆₀ solution of known concentration. Higher fullerenes, for example C₈₄, and other carbon-rich compounds were not identified in the HPLC chromatogram.

Temperature changes in the graphite surface under irradiation, measured with the thermocouple, are shown in Figure 3. The temperature went up quickly with laser heating and became saturated at around 210 °C. The time-averaged temperature would be somewhat lower, about 200 °C. The surface temperature measured with the pyrometer was consistent, around 210 °C. These temperatures are far below the reported lower limit for detectable fullerene formation by laser ablation.

The amount of C₆₀ carried by the argon gas was about 0.4 μg. It follows that C₆₀ in an order of magnitude of 10¹⁰ was contained in the carrier gas for a single laser shot, on average. The average value for the decrease in target weight for three independent runs was about 13 mg and the total amount of C₆₀, including that attached to the wall of the irradiation cell, was about 1.4 μg, resulting in a 1.1 × 10⁻² wt% yield of C₆₀.

Figure 2: (a) UV absorption spectrum and (b) HPLC chromatogram of the decalin solution of the pure-argon-carried laser ablation products. The peaks assigned to C_{60} and C_{70} are indicated by ∇ and $\blacktriangledown$, respectively.

Figure 3: Temperature evolution of the irradiated surface, monitored with a K-type thermocouple.

Figure 4: C₆₀ yield as a function of temperature. The value obtained in the current study is indicated by the red triangle. The high-temperature data, indicated by the open circles in black and blue, are those obtained at 200 and 500 Torr, respectively [12, 13, 14]. Because the temperatures of the cited data are those of the irradiation cell, those of the irradiated surface could be higher.

Laser ablation experiments with graphite targets at higher gas temperatures were reported previously, in which an electric furnace heated the ablation cell together with the graphite target and the ambient argon gas, and the yield of soluble fullerenes was measured at various temperatures and gas pressures. [12, 13, 14] At 200 Torr, yields were reported from 500 to 1500 °C, while yields at temperatures lower than 500 °C were too small to be evaluated. [14] The temperature dependence at 500 Torr was reported only for the range of 600-1200 °C. [12] Pressure dependencies at given temperatures were reported from 850-1200 °C. [13] At 850 and 1000 °C, the optimum pressure was about 200 Torr, and yields were one order of magnitude lower under atmospheric pressure. Despite the differences in pressure, it is worthwhile to compare the C₆₀ yields obtained in the present study at 210 °C under atmospheric pressure with those obtained at high temperatures. Temperature-dependent C₆₀ yields are shown in Figure 4. With simple extrapolation from the yields at high temperature, which show an exponential decrease with decreasing temperature (Fig. 4), the efficiency at 210 °C seems to be relatively high. Indeed, it seems to agree with an extrapolation of the yields at 200 Torr, rather than those at 500 Torr. Phenomenologically, the present results indicate that the exponential relationship does not hold at low temperatures, while the underlying mechanism of this behavior remains an open question.

4. Anticorrelation of fullerene and polyyne yields

Typical UV absorption spectra obtained at a propane ratios of $R = 5 \times 10^{-4}$ and 0.1 are shown in Figures 5(a) and (b), respectively, where the characteristic peaks of fullerenes and polyynes are observed [20]. The ratio of the C₇₀ yield to that of C₆₀ was about 0.2-0.3, and systematic variation with respect to R was not apparent. The R dependence of the fullerenes and polyynes is shown in Figure 6, where fullerene yields decreased and polyyne yields increased with increasing R . The anticorrelation between polyyne and fullerene yields provides information on the reactivities of the precursors. Precursors of fullerenes have not been identified and could be both larger and smaller carbon clusters [5]. For polyynes, however, it seems reasonable to consider that they were formed by hydrogen attachment to chain-form carbon clusters. [21, 22, 23] As seen in Figure 6(b), the yields of polyynes increased monotonically with R in the range of 0-0.1. The unsaturated behavior of the yields demonstrates that the chain-form clusters are still in the gas flow at $R = 0.1$ while fullerene formation is almost suppressed. This indicates that the reactivity of the fullerene precursors is much higher than that of chain-form carbon clusters.

5. Conclusions

We have shown the utility of laser ablation in a gas flow-cell, combining analyses of (macroscopic amounts of) products stabilized by organic solvents, as a tool for the study of fullerene formation reactions. The yields of fullerenes and

Figure 5: UV absorption spectra of the products in an Ar-diluted propane gas flow with propane ratios of (a) 0.05% and (b) 10%. The peaks assigned to C_{60} are indicated by ∇ and those to polyynes are indicated by the numbers n for $H(C_2)_nH$.

polyynes showed a clear anticorrelation, depending on hydrogen-rich and -poor conditions. Although this tendency is not surprising, and has already been revealed by mass spectrometric studies, this is the first report of measurements in which the anticorrelation was analyzed by conventional wet chemistry, allowing a quantitative discussion. Considering that a similar anticorrelation between fullerenes and hydrocarbons was found in space, the quantitative information on the branching between them will affect the interstellar fullerene formation model.

Finally, the possibility of identifying unresolved hydrocarbons should be mentioned. The ablation products obtained under coexistence conditions of fullerenes and polyynes are especially important because there might be hydrogen-terminated fullerene precursors and less reactive ring-form carbon clusters in solution, or at least in the gas flow [24]. To separate such unidentified hydrocarbons, a larger scale of cluster production is planned.

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Figure 6: (a) Plots of the yield of fullerenes as a function of the mixing ratio of propane. Yields were determined by HPLC analysis. (b) Those for polyynes, C_8H_2 and $C_{14}H_2$, were determined from UV absorption spectra. The scale for $C_{14}H_2$ is two orders of magnitude smaller than that for C_8H_2 . To convert absorbance to concentration, the molar absorption coefficient in hexane solution was used, ignoring solvent effects.

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