

Selective and High-Yield Synthesis of Higher Fullerenes

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Fullerenes have been prepared by dc arc synthesis with graphite (anode) rods containing light elements such as B, Si, or Al in a series of concentrations. Furthermore, the influence of mixing N₂(g) with He(g) on the yield of higher fullerenes has been addressed. For each type of experiment, the relative fullerene yields are obtained from the relative peak areas in surface analysis by laser ionization–mass spectrometry (SALI–MS) spectra and the absolute yield of C₆₀ and C₇₀ from calibrated HPLC; the relative yields in SALI–MS represent closely the nascent distribution in the primary soots. We determine the approximate absolute yields of higher fullerenes, for which extinction coefficients are not yet available for HPLC analysis, by scaling the absolute C₆₀ and C₇₀ yields with the relative concentrations from SALI–MS. The most prominent increased higher fullerene yield was obtained with a 1% B-doped graphite rod with a 2:100 volume mixture of N₂(g):He(g); the absolute yield of C₆₀ was reduced from 8.85% to 2.75%, and the yield of higher fullerenes such as C₇₈ and C₈₄ was increased by a factor of 2 over the pure C, pure He(g) case. We conclude that using a B-doped graphite rod and mixing in small amounts of N₂(g) into He(g) enhances both the absolute and relative yields of higher fullerenes.

Introduction

Since the development of the synthesis of macroscopic quantities of fullerenes¹ and of the arc discharge method,² the concern and interest among researchers about the physical properties and the use of fullerenes as a new material has centered around C₆₀ due to its greater abundance relative to other fullerenes. Recently, research efforts have been extended to higher fullerenes such as C₇₆ and C₈₄.³ For typical production, the ratio of higher fullerenes larger than C₇₆ to that of C₆₀ and C₇₀ is less than 0.05; also the extraction efficiency of higher fullerenes from the soot by organic solvents is smaller than that of C₆₀ and C₇₀.^{4–8} Considerable effort has been made in the development of an apparatus for improving the production of fullerenes and also for their extraction from soot. Consideration of operating parameters such as discharge current, distance between electrodes, the type of inert gas, and the gas-flow rate have led to increases in the production efficiency of fullerenes in the soot, and yields of fullerenes above 20 wt % have been achieved.⁹ For fullerene extraction, solvents play an important role and the use of selected solvents has rapidly led to the effective extraction of higher fullerenes^{4–8} and their subsequent separation using HPLC methods.¹⁰ However at this time, obtaining acceptable quantities of higher fullerenes for research and development remains labor intensive. For further improvement of the separation of higher fullerenes, it would be important to suppress the production of C₆₀ and C₇₀ and at the same time selectively increase the content of higher fullerenes in the soot.

In this work, fullerenes have been prepared by dc arc synthesis with graphite (anode) rods containing light elements such as B, Si, or Al in a series of concentrations. Our original intent was to synthesize doped fullerenes, e.g., C₅₈B₂; observation of altered fullerene distributions led us to the study reported here. The influence of mixing N₂(g) with He(g) on the yield of higher fullerenes has also been addressed. For each type of experiment, the relative fullerene yields are obtained from SALI–MS spectra, and the absolute yields of C₆₀ and C₇₀ from calibrated

HPLC. Because the relative signal intensity in SALI–MS represent the nascent distribution in the primary soot, we determined the approximate absolute yields of higher fullerenes, for which extinction coefficients are not yet available for their analysis by HPLC, by scaling from the absolute C₆₀ and C₇₀ yields with the relative concentrations from SALI–MS.

Experimental Section

Synthesis of Fullerenes by a dc Arc Discharge Method. The synthesis of fullerenes was carried out using the dc arc method. The cathode electrode was AC-8 type carbon rod of 12.7-mm diameter (Advanced Carbon) and for the anode either pure graphite rods or rods drilled out and packed with a mixture of light elements such as B, Si, or Al (as powders) with carbon (high-purity graphite powder), were used; composite rods containing B were also used, as described below. The anode was coupled to a stainless steel rod that is itself coupled to a translation stage. The feed rate of the anode was computer controlled. The anode was advanced until the arc was struck, and the electrode gap was maintained at a constant 2 mm. The arc was imaged by a simple lens onto a calibrated screen so that the gap between electrodes could be accurately determined. The current was held at 100 A and the voltage at about 25 V. The typical feed rate for the anode was 0.03 mm/s. The base pressure of the chamber prior to a run was 0.020 mbar, and the chamber was pressurized to 150 mbar with He. The He flowed in a horizontal collection tube at a rate of about 70 cm³/s; at this space velocity most of the soot was entrained and was collected directly in a Soxhlet thimble by dynamic pumping with a roughing mechanical pump.

Preparation of Carbon Electrodes. Packed Graphite Electrodes. The anode was prepared by packing a predrilled 3.2-mm diameter hole of 23-cm-depth with the mixture of light elements (as powders) and high purity graphite powder mixed to a specified ratio. The details of the manufactured rods are given in Table 1.

Boron Composite Graphite Electrode. The composite rod containing boron was manufactured by Toyo Tanso Ltd., Japan. A large composite block has been prepared by mixing boron carbide and high grade carbon using an advanced technology,

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TABLE 1: Composition of the Packed and Composite Rods

no.	type of rod	material added	atomic ratio (%)
1	pure C		
2	packed	B ₄ C	1.2
3	packed	B	1.5
4	packed	B	3.2
5	packed	B	6.0
6	packed	B, La ₂ O ₃	2.9B, 0.5La
7	packed	Al ₂ O ₃	0.72
8	packed	Al ₂ O ₃ , La ₂ O ₃	0.5Al ₂ , 0.2La
9	packed	Si	0.7
10	packed	Si	2.4
11	packed	Si	5.5
12	composite	B ₄ C	1.0
13	composite	B ₄ C	3.0
14	composite	B ₄ C	10.0

and then treating it at 2000 °C. Later, the large composite block was cut into the specified size of 8-mm square, 16-cm long. The properties of the composite rods are given in ref 11.

SALI-MS Measurements. For SALI-MS analysis the primary soot was pressed into an indium foil and introduced into the vacuum chamber (10⁻⁹ mbar) of the apparatus. A brief description of the SALI-MS technique^{12,13} is given below. Neutrals desorbed from a sample were photoionized by a laser beam passing 1 mm above and parallel to the sample surface. The ions were mass analyzed by a reflecting time-of-flight mass spectrometer and detected by a dual-microchannel plate assembly. Laser desorption with pulsed 532 nm light from a Nd:YAG laser was used to obtain the relative concentrations of different fullerenes in the primary soot. The desorption laser power was maintained at low enough levels so that no fullerene fragments or directly produced ions were detected. Photoionization was achieved with 118 nm light (the ninth harmonic of the Nd:YAG) by a single-photon process. The photoionization cross sections of the different fullerene molecules are assumed to be the same (based on observations of ionization efficiencies for other large molecules¹⁴). Therefore, observed intensities are expected to be fairly accurate representations of the actual concentrations of desorbing species.

High-Performance Liquid Chromatography (HPLC) Measurements. The absolute amount of fullerenes in the soot was determined by calibrated HPLC measurements. Approximately 100 mg of the soot and 50 mL of toluene were placed in a glass container with a Teflon-lined cap. This suspension was sonicated for 1 h, allowed to settle for about 2 h, and then filtered using a 0.45 μm pore membrane filter (Gelman Science Co. Ltd., FP-450). The accuracy of HPLC measurements at wavelengths of 330 and 405 nm was confirmed by measurements with standard solutions of C₆₀ and C₇₀.

Results and Discussion

Figure 1 shows the SALI-MS spectra of the primary soot produced using (a) a high-purity pure carbon electrode and (b) No. 12 composite carbon rod containing boron as shown in Table 1. The composite carbon rod No. 12 was selected because it had larger (higher fullerene)/C₆₀ ratio and because the good S/N (signal/noise) indicated a high absolute yield of higher fullerenes in comparison to the other rods of Table 1. If we compare the SALI-MS spectra (a) and (b) in Figure 1, it is clear that the primary soot produced using the composite boron rod has a higher production ratio of higher fullerenes than the run with the pure carbon rod. Furthermore, higher fullerenes such as C₁₀₈ and larger are clearly observed.

Table 2 shows the production ratio of fullerenes C₆₀, C₇₀, C₇₆, C₇₈, C₈₂, and C₈₄ calculated against the production of C₆₀ in the soot produced using the rod listed in Table 1. The right

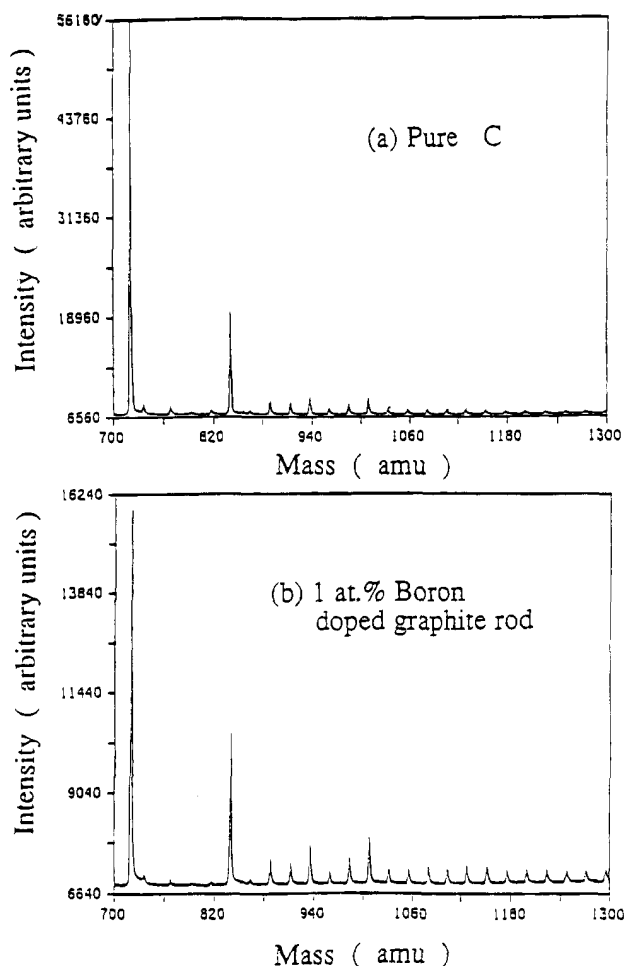


Figure 1. SALI mass spectra of soots from a pure carbon rod and B-doped rod.

TABLE 2: Relative Yield of Fullerenes Obtained from SALI-MS

no.	C ₆₀	C ₇₀	C ₇₆	C ₇₈	C ₈₂	C ₈₄	mg/100 mg of SOOT	
							C ₆₀ yield	C ₈₄ yield
1	1	0.18	0.012	0.023	0.012	0.019	8.85	0.168
2	1	0.6					<0.01	
3	1	0.31	0.07	0.08	0.06	0.104	1.03	0.107
4	1	0.39	0.10	0.139	0.10	0.180	0.23	0.041
5	1	0.33	0.09	0.135	0.09	0.128	0.02	0.003
6	1	0.25	0.03	0.038	0.027	0.058	6.31	0.356
7	1	0.25	0.03	0.038	0.026	0.038	<0.01	
8	1	0.34	0.064	0.12	0.064	0.12	<0.01	
9	1	0.23	0.02	0.04	0.022	0.029	11.25	0.326
10	1	0.24	0.022	0.043	0.022	0.024	7.5	0.217
11	1	0.23	0.023	0.046	0.028	0.032	4.38	0.140
12	1	0.27	0.041	0.063	0.045	0.068	5.2	0.354
13	1	0.28	0.038	0.061	0.047	0.08	1.55	0.124
14	1	0.26	0.035	0.035	0.027	0.027	0.04	0.002

extreme column in Table 2 gives the amount of C₆₀ in 100 mg of soot determined from the HPLC measurement. Comparison of the production ratio of C₇₀:C₆₀ for the soot produced using the pure carbon rod versus the composite rods listed in Table 1 shows this ratio to be 0.18 for the pure carbon rod compared to ratios of between 0.23 and 0.39 for the composite rods, indicating an increase in the relative production of C₇₀. For rod 2 the ratio C₇₀:C₆₀ was 0.6, but the total yield is extremely low. The production of the higher fullerenes C₇₆ to C₈₄ has been found to vary from rod to rod. The higher fullerenes were not observed at all in rod 2. In the case of rods 3–5, which contain metallic boron, the ratio of higher fullerenes to C₆₀ was

several times that of the pure carbon rod. However, the production ratio of higher fullerenes is not strongly dependent on the concentration of boron in the carbon rod. In the case of rod 6 irrespective of the fact that it contains boron, the production ratio of higher fullerene was almost equal to that of high purity carbon rod 1.

The absolute amount of C_{60} in the soot produced with different rods was determined from the HPLC data and is shown in Table 2. The C_{60} yield from rods 1–6 was 8.85, 0.01, 1.03, 0.23, 0.02, and 6.31% by weight C_{60} and for other rods the yield of C_{60} as well as higher fullerenes was extremely small. For the rods containing aluminum (rods 7 and 8), the production of C_{60} was less than 0.01 mg/100 mg of soot and higher fullerene content was extremely small. The production ratio of higher fullerenes (higher fullerene: C_{60}) for rods containing silicon (rods 9–11) was about 1.7 times that of the pure carbon rod. Also, the absolute amount of C_{60} in the above rods (rods 9–11) per 100 mg was 11.3, 7.5, and 4.3 mg. Surprisingly the rod containing 0.7 at. % Si in C gave a C_{60} yield higher than the rod with pure carbon (rod 1), but the higher fullerenes were not enhanced. For the composite rod containing 1% boron (rod 12), the production ratio of higher fullerenes was three, and the absolute amount of C_{60} per 100 mg of soot was 5.2 mg. When the boron concentration increased to 3% and 10% as indicated for rods 13 and 14 of Table 2, fullerenes production decreased.

A summary of the results is given below:

(1) In packed carbon rods containing boron powder, the selectivity increases but the production efficiency is poor.

(2) In packed carbon rods containing aluminum powder, the selectivity and the production efficiency are poor.

(3) In packed carbon rods containing silicon powder at 0.7 at. %, a small increase in higher fullerene production efficiency is observed.

(4) In composite rods containing 1 at. % B, the selectivity as well as the production efficiency of higher fullerene increases.

In conclusion, the carbon rod containing 1 at. % B in C is found to have high selectivity as well as high yields of higher fullerenes.

Influence of Mixing $N_2(g)$ with $He(g)$ on the Yield of Higher Fullerenes

It is already known that the nature of the inert gas and the pressure influences production efficiency of fullerenes.¹⁵ However, the inert gases He and Ar do not strongly influence the selectivity. Here we examine the influence of nitrogen gas on the production of higher fullerenes. In this study the anode was a carbon rod containing 1 at. % boron, which gave selective production and high yields of higher fullerenes as noted above. The soots produced in the arc-discharge chamber when filled with a mixture of gases at volume percent of $N_2(g)$ in $He(g)$ of 0, 1, 2, 5, 10, and 20 vol % were analyzed using SALI-MS, and the results of this analysis are given in Figure 2.

It is clear that when N_2 is mixed in, the production ratio of higher fullerene increases compared to when there is no N_2 . The amount of C_{60} contained in the soot calculated using the HPLC data was 5.23, 3.03, 2.75, 2.45, 1.82, and 0.75 mg of C_{60} /100 mg of soot and was less than the yield obtained in the situation where there was no N_2 . Using the relative concentration of fullerenes obtained from SALI-MS and the absolute yield of C_{60} obtained from HPLC data, the absolute values of all the fullerenes were calculated and are given in Table 3. The results indicate that for nitrogen concentration at 1 and 2 vol %, the yield of higher fullerenes is almost the same as for the cases where there is no N_2 . But the yields of C_{60} and C_{70} are reduced when N_2 is mixed with He and the yield of all the

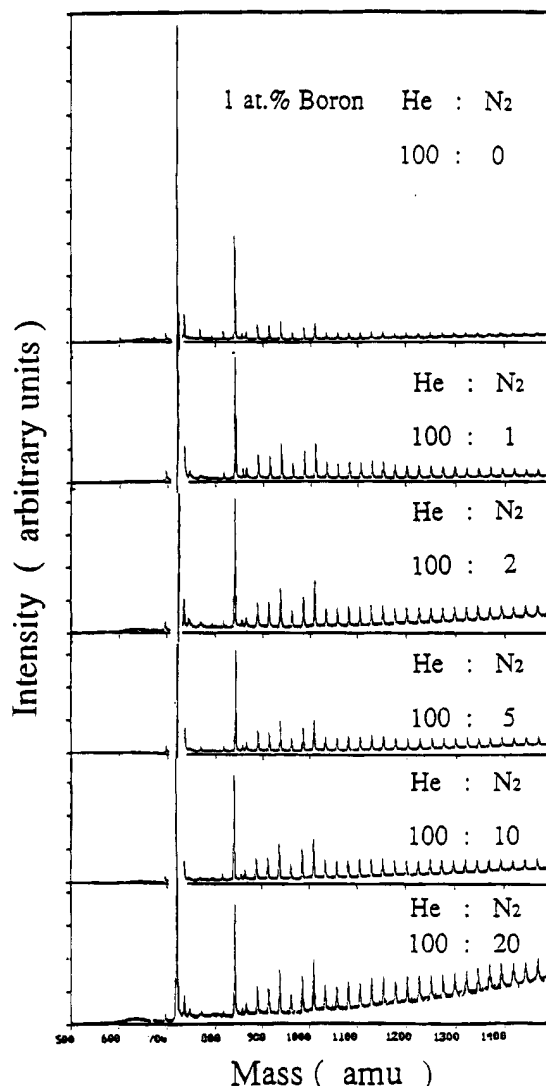


Figure 2. SALI mass spectra of soot from 1% B doped rod with various concentrations of N_2 .

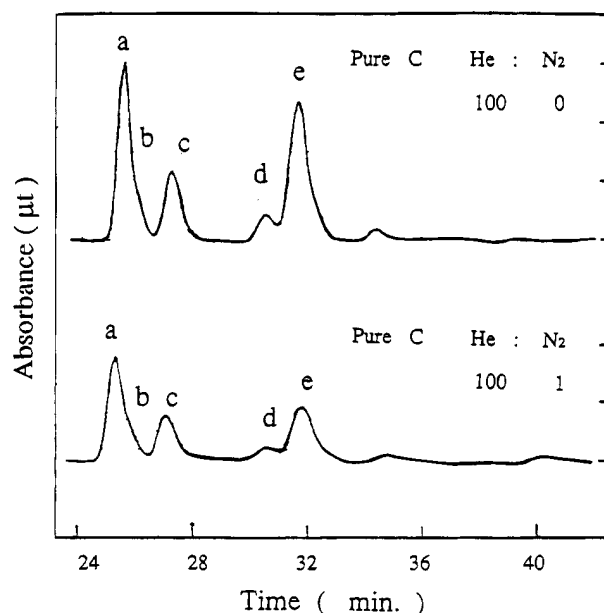
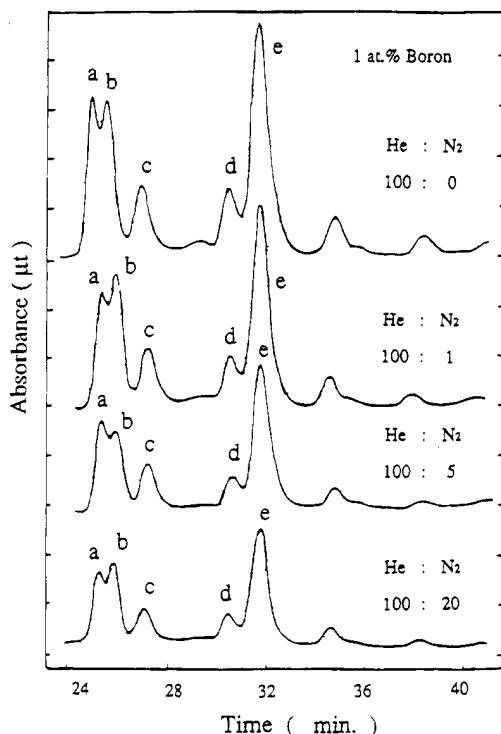


Figure 3. HPLC of the higher fullerenes from pure carbon rods. a–e are assigned to C_{76} , C_{78} (C_{27}), C_{78} (C_{27}), C_{82} , and C_{84} , respectively.

fullerenes are reduced when N_2 content is 5, 10, or 20 vol %. From these results, it could be said that selective production of

TABLE 3: Absolute Yields of All the Fullerenes Obtained from SALI-MS and HPLC

type of rod	material added	atomic ratio (%)	gas He:N ₂	C ₆₀	C ₇₀	C ₇₆	C ₇₈	C ₈₂	C ₈₄
pure C			100:0	8.85	1.59	0.108	0.204	0.106	0.168
composite	B ₄ C	1	100:0	5.20	1.40	0.213	0.328	0.234	0.354
composite	B ₄ C	1	100:1	3.03	1.12	0.212	0.327	0.245	0.330
composite	B ₄ C	1	100:2	2.75	1.14	0.237	0.366	0.259	0.400
composite	B ₄ C	1	100:5	2.45	0.902	0.162	0.270	0.215	0.215
composite	B ₄ C	1	100:10	1.82	0.597	0.114	0.198	0.171	0.220
composite	B ₄ C	1	100:20	0.75	0.246	0.059	0.103	0.088	0.129

**Figure 4.** HPLC of the higher fullerenes from 1% B doped rod with various N₂ concentrations.

higher fullerenes can be achieved by conducting arc-discharge in the presence of a mixture of He:N₂ of 50:1.

Figures 3 and 4 show the higher fullerene peaks in the HPLC chromatograms. From the left the peaks corresponding to a–e are assigned to C₇₆, C₇₈ (C_{2v}'), C₇₈ (C_{2v}'), C₈₂, and C₈₄, respectively. As shown in Figure 3 the HPLC profile for the soot produced by arc-discharge of pure carbon rod in 1 at. % N₂ in He shows a reduction in the yield of all the fullerenes with no selectivity for higher fullerenes. In contrast, as can be seen from Figure 4, the carbon rod containing 1 at. % boron produced C₇₈ (C_{2v}') and C₈₄ selectively and the amount was 3-fold larger than that of the soot produced from the pure carbon rod. Furthermore, the production rate of fullerenes higher than C₈₄ was also increased. This trend can also be seen in the case of He and N₂ gas mixtures. However, it is clear that the reduction in the yield of all fullerenes occurs with an increase in N₂(g) concentration. It appears that the relative production ratio of higher fullerenes remains unchanged.

Therefore, it can be concluded that boron acts as a catalyst and assists the production of higher fullerenes, whereas N₂ gas lowers the production of C₆₀ and C₇₀. We note the recent work by Zhou et al., who have found ordered carbon cages which encapsulate boron carbide B₄C in the soot; this material was produced by carbon arc using a B-doped carbon composite anode.¹⁶ Normally, the carbon in soot appears largely amorphous when examined by TEM, for soots prepared with a variety

of composite rods containing elements other than B. The authors suggested that the tendency for B to play a role in ordering carbon in the soot was in agreement with the role of B in catalyzing graphitization of pyrolytic carbon.¹⁷ The results of our study show that B catalyzes the growth of more stable forms of carbon even in the fullerene size range, as it is well-known that the energy of carbon fullerenes decreases as the fullerene size increases.¹⁸

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