



# On an improved pyrolytic synthesis of [60]- and [70]-fullerene

N.R. Conley, J.J. Lagowski\*

*The University of Texas at Austin, Department of Chemistry and Biochemistry, Austin, TX 78712, USA*

## Abstract

The nickel-catalyzed pyrolysis of two fullerene precursors — (1) naphthalene and (2) 1-bromonaphthalene — at 1200°C in an argon atmosphere has been investigated. Fullerenes, polycyclic aromatic hydrocarbons (PAHs), and polycyclic aromatic brominated species (the latter obtained in pyrolysis of 1-bromonaphthalene only) were extracted from the pyrolysates by reflux in toluene. The toluene extracts were subjected to mass spectrometric analysis using the chemical ionization technique in the negative mode. Mass spectra are included with discussions on fullerene yields and on the mechanism by which fullerenes are formed in pyrolysis. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the toluene-insoluble material. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* A. Fullerene; Carbon nanotubes; B. Pyrolysis; Catalyst; C. Mass spectrometry

## 1. Introduction

Following the discovery of buckminsterfullerene in 1985 [1] and the subsequent publication of the Krätschmer–Huffmann fullerene synthesis [2] in 1990, the first macroscopic preparation of this novel molecule, an explosion of publications marked the advent of a new chemistry. Among these publications, several alternative methods of fullerene synthesis emerged. In 1991, Howard et al. identified fullerenes in the mass spectrum of toluene-extracted soot from hydrocarbon combustion, triggering several publications on optimization of fullerene yields in combustion [3] and on the mechanism by which fullerenes are formed in flames [4–6]. In 1993, Taylor et al. described the pyrolytic conditions in which [60]- and [70]-fullerene could be produced from naphthalene [7] and their results were soon confirmed by Zumwalt and Huffman [8]. This work led to the discovery that corannulene and benzo[k]fluoranthene can also serve as pyrolytic precursors to fullerenes [9]. Most recently, Osterodt et al. demonstrated that a large variety of hydrocarbons and cyclopentadienide–metal complexes produce very small amounts of fullerenes when subject to pyrolysis [10].

While few authors agree upon the details of pyrolytic fullerene formation from aromatic precursors, all realize

that at some point, carbon–hydrogen bonds of the hydrocarbon must be broken, new carbon–carbon bonds must form in their place, and removal of the peripheral hydrogens must ensue so that ring closure may occur. Substantial theoretical and experimental evidence implicates halonaphthalene derivatives as good pyrolytic precursors to fullerenes because of the tendency for homolytic cleavage of carbon–halogen bonds at high temperatures. The manner and ease of this cleavage provides several advantages. Firstly, the naphthalenyl radical may serve as a site for ring cyclization. Hagen et al. describe this phenomenon in the pyrolytic synthesis of bowl-shaped PAHs [11]. Next, the resulting halogen radical can serve as a hydrogen scavenger to expedite dehydrogenation of the naphthalene and larger fullerene intermediates, as observed in chlorinated flames [12]. Finally, the energy required to break a carbon–halogen bond homolytically, especially a carbon–bromine bond in 1-bromonaphthalene (69.2 kcal/mol) [13], is significantly less than the energy required to break a carbon–hydrogen bond in naphthalene (~109.5 kcal/mol) [14,15] in the same manner. (There is a slight discrepancy in the values reported for bond dissociation energy in the formation of a 1-naphthalenyl radical from naphthalene; to account for this, we use the average value for our arguments.) Thus, the activation barrier for formation of the 1-naphthalenyl radical is ~40.3 kcal/mol lower if a bromonaphthalene derivative is used in place of naphthalene. The pyrolysis of 1-chloro- and 1-bromonaphthalene has already been carried out by Crowley et al.

\*Corresponding author. Tel./fax: +1-512-471-3288.

E-mail addresses: lagarto2@aol.com (N.R. Conley), jjl@mail.cm.utexas.edu (J.J. Lagowski).

[9]. Based upon peak intensities in the mass spectrum, this group has estimated lower fullerene yields in the pyrolysis of these derivatives compared to naphthalene. We have chosen to investigate naphthalene and 1-bromonaphthalene as pyrolytic precursors to [60]- and [70]-fullerene under different conditions than previously reported [7–9].

## 2. Experimental

Details of the pyrolysis apparatus are reported elsewhere [9]. In a typical experiment, 0.5 g of nickel powder (2.2–3.0  $\mu\text{m}$ ) was first spread throughout the portion of the silica tube to be heated. The tube was placed inside a tube furnace (Thermolyne Type 21100, 40-cm heated zone) and declined at a 25° angle to prevent the fullerene precursor from condensing at the inlet of the tube. The precursor (0.5 g) was then introduced into the well via the inlet of the tube. A hose through which argon gas flowed was clamped onto the inlet of the pyrolysis tube and heating tape (Barnstead Thermolyne, 104 W, 61 cm in length) was wrapped around the well up to the entrance of the tube furnace. The hose also accessed a mercury bubbler, which prevented a significant build-up of pressure in instances when the tube became obstructed with pyrolysate. A glass coil, submerged in a dry ice/isopropanol slush, was connected to the tube and a toluene bubbler was placed at the end of the coil to prevent loss of the more volatile pyrolysate.

Prior to the start of an experiment, the apparatus was flushed with argon for 5 min. Once this was complete, the argon flow-rate was lowered to  $\sim 2$  ml/min and the tube furnace was activated. (This decreased flow-rate prevented premature pyrolysis of the precursor while maintaining positive argon pressure through the system until the tube furnace reached 1200°C.) After the tube furnace stabilized at 1200°C, as indicated by the built-in thermocouple, the flow-rate was increased to 15 ml/min and the variac controlling the heating tape was activated to deliver between 50 and 90 V. Pyrolysis occurred over  $\sim 15$  min and upon completion, the tube furnace was rapidly cooled to room temperature using compressed air. (By rapidly decreasing the temperature, potential thermal destruction of any fullerenes remaining in the silica tube was avoided.)

The pyrolysate was removed from the apparatus by sonication with toluene. The slurries from the tube and coil were combined and additional toluene was added to increase the volume to  $\sim 100$  ml. This mixture was subject to reflux for 30 min. After reflux, the hot mixture was gravity-filtered and the excess toluene of the filtrate was removed under vacuum to give a saturated solution. These extracts were subject to mass spectral analysis within 24 h of their preparation using a Finnigan Mat TSQ700 instrument; the source temperature was  $\sim 150^\circ\text{C}$  and the probe was ramped to  $\sim 1000^\circ\text{C}$  over 1 min;  $\text{CH}_4/3$  Torr; negative ions were detected with a chemical ionization technique. The toluene-insoluble material was characterized using a LEO 1530 scanning electron microscope and a Philips EM 208 transmission electron microscope.

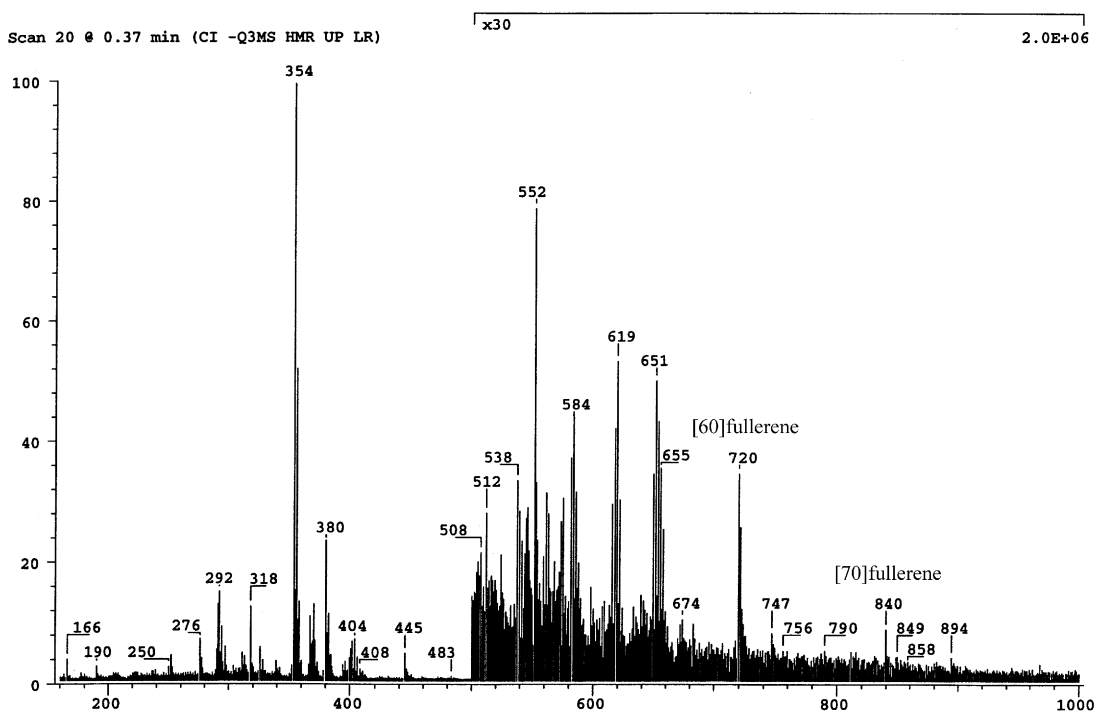


Fig. 1. Mass spectrum of toluene extract from soot obtained in the nickel-catalyzed pyrolysis of naphthalene at  $\sim 1200^\circ\text{C}$ .

### 3. Results and discussion

Mass spectrometric analysis of the toluene extract from soot obtained in the pyrolysis of naphthalene (Fig. 1) suggests the presence of [60]- and [70]-fullerene,  $m/z = 720$  and  $840$ , respectively. The observed isotopic distributions of these species are consistent with those previously reported [16]. Under these conditions however, fullerenes seem to comprise only a small portion of the product. The mass spectrum in Fig. 2, analysis of the toluene extract from soot produced in the pyrolysis of 1-bromonaphthalene, also contains signals with  $m/z$  ratios and isotopic distributions indicative of [60]- and [70]-fullerene; compared to Fig. 1, these peaks appear at more than 10 times the intensity of their respective counterparts. Also predominant in Fig. 2 is a species with  $m/z = 447$ . Based on the isotopic distribution ( $M+2$ ), it appears to be a monobrominated species. We believe it may play a significant role in the pyrolytic formation of [60]- and [70]-fullerene and are pursuing further work in its separation and characterization.

Throughout numerous trials, it became evident that successful fullerene formation using either precursor relied heavily upon its rate of feed into the pyrolysis zone. If the feedstock was heated too quickly, resulting in a high concentration of naphthalenyl radicals, extensive polymerization occurred. In this case, large PAHs, consisting of  $nC_{10}$  units (where  $n=2-11$ ) plus peripheral hydrogens were observed in the mass spectrum of the toluene extract (Fig. 3) but it is not clear whether any fullerenes were formed. Following intramolecular dehydrogenation, Taylor

and Langley believe that the species for which  $n=6$  and  $n=7$  are precursors to [60]- and [70]-fullerene, respectively [17]; our experimental data match well with this proposal. Although intramolecular dehydrogenation occurs most readily at higher temperatures and slower feed rates, we found that such conditions led to a significant decrease in the percentage of toluene-soluble material and a shift in its composition to smaller PAHs; both are undesirable trends. Changes in any of the experimental conditions generally compromised either the polymerization or dehydrogenation processes, and our average fullerene yield when naphthalene was used as a precursor approximated the previously reported value of 0.05% by weight [8]. Mass spectrometric peak intensities, although not necessarily proportional to yield, suggest that when 1-bromonaphthalene is used as a precursor, total fullerene yields may be as high as 0.5% by weight.

Carbon nanotubes were characterized using the SEM and TEM techniques. Although most of the toluene-insoluble material appeared as bead-like structures, probably due to the less-than-optimal conditions for nanotube growth, some nanotubes were observed. The bead-like structures have been suggested as being involved in the first steps of nanotube growth [18] and indeed our results would seem to support this. Fig. 4 shows several of these beads bound together to form tube-like structures that have approximately the same diameter as the tubules shown in Fig. 5. Using a backscattered electron detector, we observed nickel as a significant component of the beads and tubules; this was confirmed by energy dispersive X-ray analysis (EDX). TEM revealed that the nanotubes are coated with

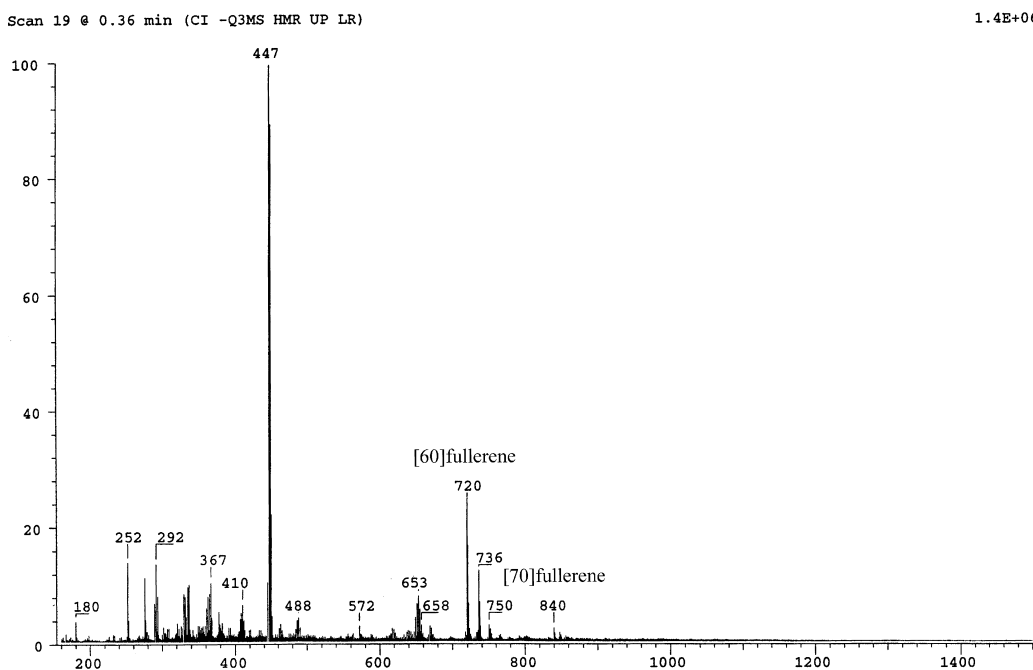


Fig. 2. Mass spectrum of toluene extract from soot obtained in the nickel-catalyzed pyrolysis of 1-bromonaphthalene at  $\sim 1200^{\circ}\text{C}$ .

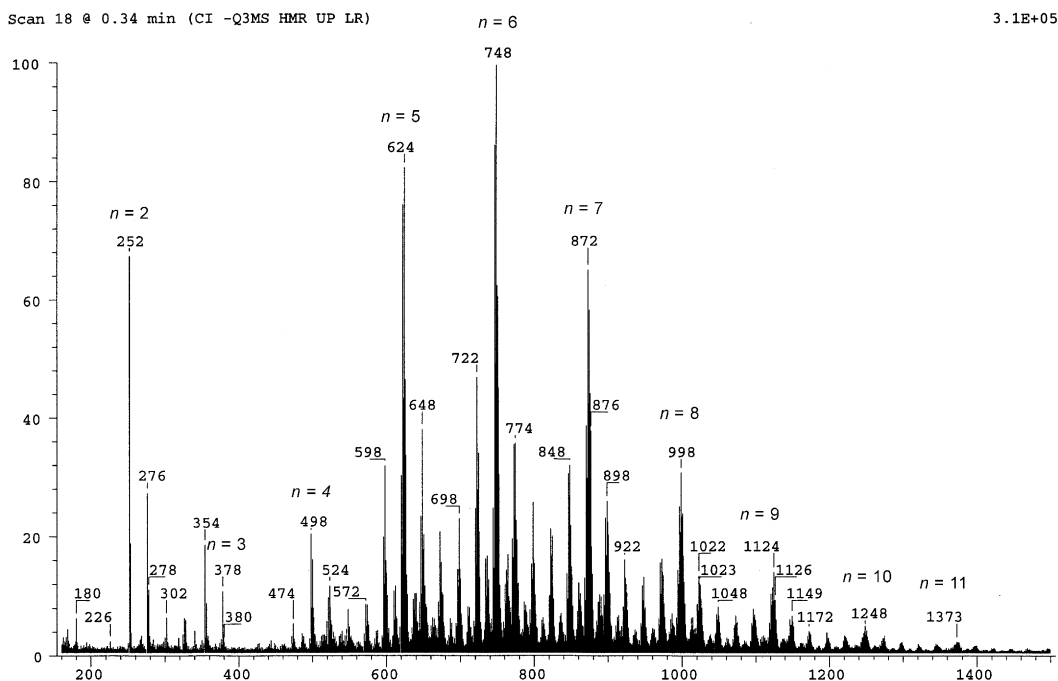


Fig. 3. Mass spectrum of toluene extract from soot obtained in the nickel-catalyzed pyrolysis of naphthalene (introduced into the tube quickly) at  $\sim 1000^\circ\text{C}$ .

an amorphous carbon sheath (Fig. 6) and resemble those reported by Müller et al. [18].

#### 4. Conclusion

In contrast to results reported by Crowley et al. [9], our work indicates that 1-bromonaphthalene is a more suitable pyrolytic fullerene precursor than naphthalene. Although

yields are not yet high enough to be commercially viable, we are optimistic that further work in this area will lead to significant improvements. The formation of nanotubes and bead-like structures warrants further investigation. We are currently investigating the effect on fullerene yield of (1) directly introducing a halogen into the system to serve as a hydrogen scavenger and (2) using perhaloarenes as fullerene precursors.

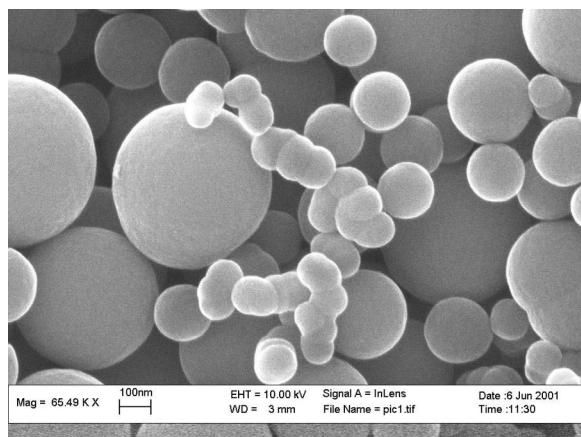


Fig. 4. SEM image of toluene-insoluble bead-like structures obtained in the nickel-catalyzed pyrolysis of 1-bromonaphthalene at  $\sim 1200^\circ\text{C}$ .

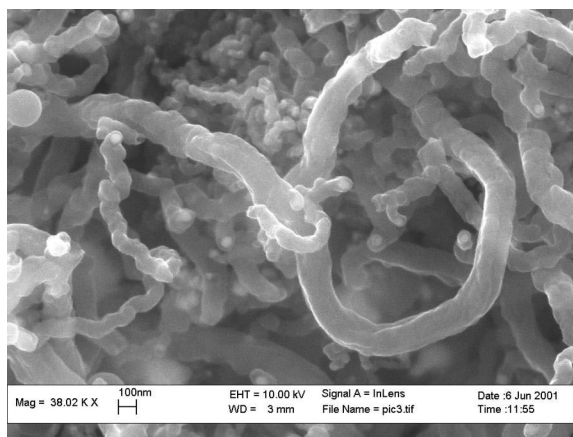


Fig. 5. SEM image of various toluene-insoluble tubular carbon structures obtained in the nickel-catalyzed pyrolysis of 1-bromonaphthalene at  $\sim 1200^\circ\text{C}$ .

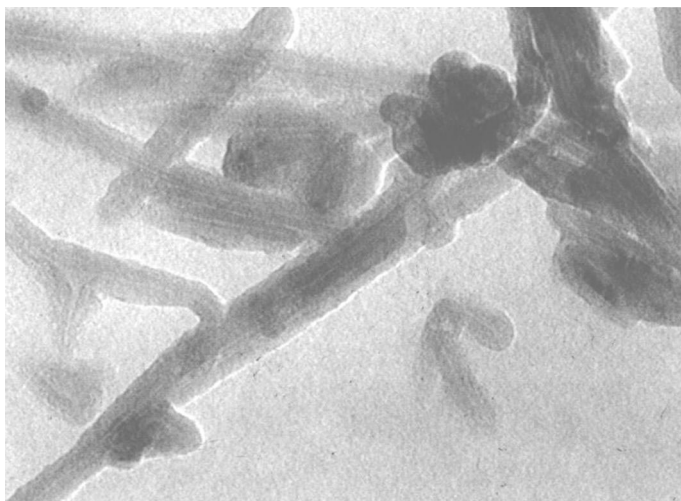


Fig. 6. TEM image (1 cm=52.9 nm) of toluene-insoluble tubular carbon structures obtained in the nickel-catalyzed pyrolysis of 1-bromonaphthalene at  $\sim 1200^{\circ}\text{C}$ . Note the nanotube core sheathed in a bundle of amorphous carbon.

### Acknowledgements

We owe special thanks to Bob Lewandowski for his masterful quartz and glassblowing. Also, we appreciate the assistance of Jeff Cook from the Texas Materials Institute at UT Austin for obtaining the SEM images and John Mendenhall at the Microscopy Facility of the Institute for Cellular and Molecular Biology at UT Austin for obtaining the TEM images. Finally, we gratefully acknowledge the support of this research by the Robert A. Welch Foundation.

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