

Soot-free synthesis of C<sub>60</sub><sup>☆</sup>Ryan P. Rodgers<sup>a,\*</sup>, Peter T.A. Reilly<sup>b</sup>, William B. Whitten<sup>b</sup>, J. Michael Ramsey<sup>b</sup><sup>a</sup>National High Magnet Field Laboratory, Ion Cyclotron Resonance Program, Florida State University, 1800 E. Paul Dirac Drive, Tallahassee, FL 32310, USA<sup>b</sup>Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6142, Oak Ridge, TN 37831-6142, USA

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**Abstract**

A new synthetic medium for the production of C<sub>60</sub> has been found that does not produce soot. C<sub>60</sub> was produced in the liquid phase of an aerosol of precursor soot at 700 °C. The precursor soot aerosol, a high temperature stable form of hydrocarbon, was produced by pyrolysis of acetylene at atmospheric pressure in a flow tube reactor. At 700 °C, the effluent particles were found to contain PAHs, small hydrocarbons and fullerenes but no observable black material. However, when the reactor temperature was changed to 800 °C, soot was also produced in the effluent particles along with PAHs and other small hydrocarbons, and the fullerene product disappeared. These results show a clear competition between the production of fullerenes and other forms of carbon. The filter-collected effluent was shown to be completely soluble in conventional solvents suggesting the possibility of an efficient cyclic synthetic process. Fullerenes were only found in the particle phase implying the first observed liquid phase synthesis of C<sub>60</sub>.

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**Keywords:** A. Soot; Fullerene; B. Pyrolysis; Carbonization; C. Mass spectrometry**1. Introduction**

Since their discovery in 1985 [1], fullerenes have been the focus of a vast amount of research. One of the fundamental problems with the synthesis of fullerenes is the co-production of soot (i.e. mature soot and/or amorphous carbon) requiring tedious, expensive and wasteful procedures for purification. Much has been done to alleviate this problem for catalytically produced carbon nanotubes. For example, Smalley's group used disproportionation of high-pressure carbon monoxide over narrowly dispersed catalyst particles to produce reasonably pure nanotubes [2]. More recently, Schlittler et al. [3] used thermolysis of nano-patterned layers of C<sub>60</sub> and Ni to produce single crystals of nanotubes with identical diameters and lengths. Given the quantity of research on

buckminsterfullerene, it is lamentable that little progress has been made to advance the production of C<sub>60</sub> without the production of soot and amorphous carbon. The lack of an economic method for producing C<sub>60</sub> is especially regrettable in light of Schlittler et al.'s [3] new method for producing single crystals of nanotubes from C<sub>60</sub>. Arguably, it should be possible to produce C<sub>60</sub> without soot. After all, fullerenes (i.e. nanotubes, C<sub>60</sub>, etc.) are more thermodynamically stable than soot because of the lack of what Smalley calls 'dangling bonds' [4] that are inherent in soot. Moreover, the same process creates both soot and fullerenes, namely rearrangement of the carbon bond structure with concurrent loss of the non-carbon species that make up the reactant. The real difference in the processes for producing soot and fullerenes is the time period where carbon rearrangement is energetically feasible. In other words, fullerenes are produced when the carbon bonds have enough time to rearrange themselves into the higher order yet thermodynamically lower energy state. Lack of sufficient time for rearrangement leaves the carbon structure in a state of much more random order and higher thermodynamic energy, hence the production of soot. The annealing behavior of mature soot at the same temperatures where the fullerenes are produced supports this

<sup>☆</sup>The publisher regrets to announce that Figs. 1, 2 and 3 in this paper were previously published incorrectly in [Carbon 41(4), 687–692, 2003]. It has been decided that the article is to be reprinted in this issue. The publisher wishes to apologise to the authors and subscribers for any inconvenience caused.

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thinking. Because fullerenes are more thermodynamically stable than soot, there must be a reason that soot does not immediately convert to fullerenes upon annealing at these temperatures. Rearrangement of the soot structure requires a huge energy investment to create Smalley's 'dangling bonds' (broken C–C bonds) [4]. This does not happen below 1000 °C. In the case of low temperature (<1000 °C) production of fullerenes during hydrocarbon pyrolysis, the same type of carbon rearrangement occurs but the energy costs are vastly mitigated by the presence of a leaving group that greatly reduces the number of 'dangling bonds' needed for rearrangement. The presence of hydrogen permits the creation of free radicals. Two free radicals are created whenever a hydrogen atom hops from one carbon site to another. This can happen in a concerted reaction whereby the large energy cost of breaking a C–H bond is offset by the energy gained in making another C–H bond, thereby mitigating the total energy cost and creating two radicals. Free radicals rapidly rearrange the carbon skeletal structure and just as rapidly are eliminated by recombination. Therefore, the presence of hydrogen acts as a sort of a facilitator or catalyst continually supplying free radicals that drive the rearrangement process.

The same hydrogen exchange process that creates the free radicals also produces molecular hydrogen inside the precursor soot matrix that can diffuse out and eventually deplete the particle matrix of hydrogen. This process is called dehydrogenation. When depletion of the leaving group (hydrogen) during the carbonization process (defined as the sum of the carbon rearrangement and dehydrogenation processes) is too rapid, the carbon structure becomes frozen in local potential energy minima (i.e. in the form of mature soot or amorphous carbon). Consequently, if a system can be found where carbon rearrangement occurs and the concentration of leaving group species can be intimately controlled, then it should be possible to bypass the local energy minima to produce a global minimum energy structure thereby producing fullerenes without producing soot and/or amorphous carbon.

Here, we report the soot-free production of C<sub>60</sub> in the liquid phase of an aerosol of precursor soot and demonstrate the aforementioned principles for controlling the carbon rearrangement process. Furthermore, analysis of the effluent medium shows that it is made up of readily soluble liquid hydrocarbon species that can be recycled back into the production of precursor soot. This finding suggests the possibility of producing fullerenes in a cyclic process that reuses the hydrocarbon products and thereby improves the efficiency of the overall process. Just as importantly, the product fullerenes are produced in a liquid medium so that the product is easily manipulated and purified.

Precursor soot as its name implies is an integral step in the production of mature soot. Conversion of precursor soot into mature soot occurs by rapid loss of hydrogen with concurrent rearrangement of the carbon skeletal structure (the carbonization process). Precursor soot can be formed during the pyrolysis of *any* hydrocarbon species.

Firstly, the hydrocarbon fuel species pyrolyze to form gas phase polycyclic aromatic hydrocarbons (PAHs) through the stepwise addition of two and three carbon-containing species [5]. Under the right conditions, the PAHs chemically condense to form three-dimensional nanoparticles with some very unusual properties. At the temperatures where these particles form, the hydrocarbon species that compose the particles rapidly exchange hydrogen [6]. As a consequence of this exchange process, a large concentration of free radicals is formed. These free radicals permit rapid particle growth by hydrocarbon addition. They also permit rapid and continuous rearrangement of carbon structure inside the particle that accounts for the observed liquid nature of the precursor soot [6]. The liquid nature of precursor soot permits coalescence of the droplets to form larger singlet particles. This is yet another mechanism for rapid particle growth that helps explain the ability of the precursor soot to grow to observed micrometre sizes on millisecond timescales in flames [6].

Precursor soot is an ideal medium for fullerene growth because it is essentially a mass of reacting free radicals that are continuously rearranging their carbon skeletal structure. Because of the radical nature of the precursor soot, the hydrogen concentration is in equilibrium between the particle and gas phases. Therefore, it should be possible to regulate the hydrogen concentration in the precursor particle phase by regulating the hydrogen concentration in the gas phase. Moreover, the concentration of hydrogen in the particle phase could be optimized to yield the best reaction conditions.

## 2. Experimental

The chemical nature of precursor soot was investigated through the following experiment. Precursor soot was produced in a 3.85-mm I.D. 45-cm long quartz flow tube reactor by pyrolysis of a 40-ml min<sup>-1</sup> flow of pure atmospheric pressure acetylene at a constant temperature. Immediately, upon exiting the reactor, the effluent was rapidly diluted 100-fold and cooled with a 4-l min<sup>-1</sup> flow of pure room temperature nitrogen. A portion of the diluted effluent was directly sampled into our ion trap-based aerosol mass spectrometer. The configuration of this instrument has been described in detail elsewhere [6]. This experimental set-up permitted the analysis of the gas phase species alone by laser ionization or electron impact ionization. It also permitted the measurement of the laser ablation mass spectrum of individual particles from the effluent in a background of effluent gas phase species.

## 3. Results and discussion

The bizarre nature of precursor soot can be demonstrated by examining the averaged mass spectra of the gas phase and the averaged mass spectra from the particle plus

the gas phase. Fig. 1a shows the averaged mass laser ionization mass spectrum of the gas phase species obtained by deliberately mistiming the laser to avoid hitting the effluent particles. The gas phase mass spectrum shows a sparse and sharp distribution of PAHs and fragments. Examination of the averaged particle mass spectrum (Fig. 1b) in the ever-present gas phase background shows a very similar distribution with some subtle differences. The first obvious difference is a broadening of the local mass distribution around each of the PAH masses that has been previously observed [6] and attributed to rapid hydrogen exchange between the hydrocarbons in the particle phase. The second difference is the shift in the mass distribution toward higher mass indicating a higher concentration of hydrogen in the particle phase.

It has been previously suggested that the micrometre-sized particles observed in our experiments are the result of massive condensation of the gas phase PAHs during the dilution step. However, our comparison of the gas and particle phase spectra reveal that explanation would violate the law of the conservation of mass due to the mass shift in

the particle phase distribution. Furthermore, we have observed that the differences between the gas and particle phase spectra become more pronounced at higher temperatures. The spectra of the gas and particle phases at 800 °C are shown in Fig. 2a and b, respectively. Here it is clear that the particles could not possibly be the result of sampling or dilution-induced condensation. The differences in the gas and particle phase mass spectra are evidence of a large amount of chemistry occurring in the particle phase and can only occur in a high temperature environment.

In experiments reported in the literature, a white mist (precursor soot) was observed to form inside an industrial furnace used to make carbon black for tires under similar conditions without sampling [7]. Our results and those reported in the literature led us to conclude that the particles observed in our experiment were created inside the flow tube reactor at 700 °C. The fact that the boiling points of the observed species in the mass spectra, and identified by GC–MS of the filter-collected effluent, are all several hundred degrees below the reactor temperature

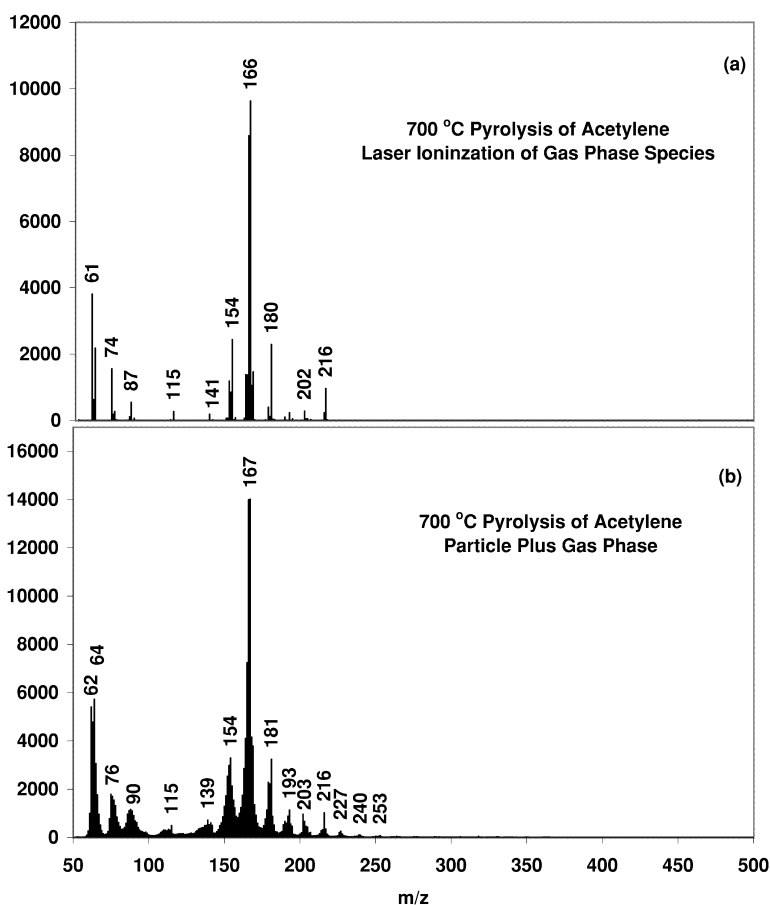


Fig. 1. (a) Averaged laser ionization mass spectrum of the diluted effluent from the 700 °C pyrolysis of acetylene (501 spectra averaged). (b) Averaged laser ablation/ionization mass spectrum of the effluent particles in a background of effluent gas from the 700 °C pyrolysis of acetylene (494 spectra averaged).

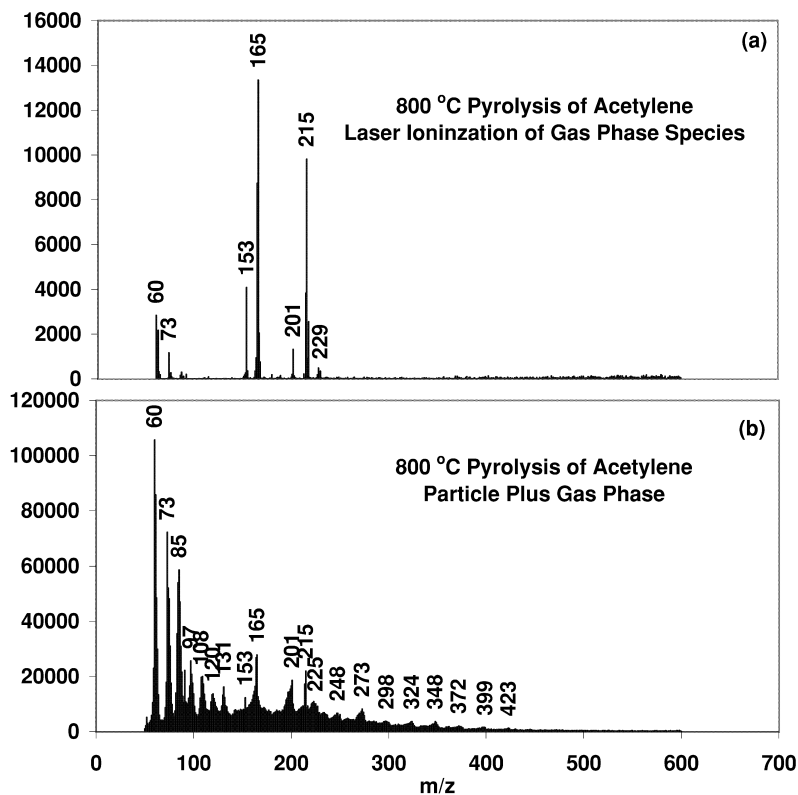


Fig. 2. (a) Averaged laser ionization mass spectrum of the diluted effluent from the 800 °C pyrolysis of acetylene (329 spectra averaged). (b) Averaged laser ablation/ionization mass spectrum of the effluent particles in a background of effluent gas from the 800 °C pyrolysis of acetylene (550 spectra averaged).

reveal that a vast amount of chemistry occurs in the condensed or particle phase of the reactor borne aerosol. More importantly, there must be a change in the chemical nature of the precursor soot as it is cooled to room temperature. It is our contention that this chemistry results from a large concentration of radicals in the particle phase that is the consequence of rapid hydrogen exchange in the high temperature environment. This large concentration of radicals causes the carbon skeletal structure of the species that make up the particle to continuously rearrange and thereby gives the particle the physical properties of a liquid and accounts for the high temperature stability of the material. When the precursor soot cools, the hydrogen exchange ceases and the hydrocarbons convert to thermodynamically stable forms, namely an oil of low boiling PAHs and other small hydrocarbons as observed in our GC–MS analysis of the reactor effluent.

Our flow tube pyrolysis experiments were performed at 800 °C as well as 700 °C, because the production of mature black soot begins to happen during this temperature transition. The presence of mature soot is generally represented by the observance of carbon cluster ions in the mass spectra. These can be seen in our previous work [6] where we directly observed the evolution of precursor soot

into mature soot during the carbonization process that occurs during soot production in a flame. The conversion of precursor soot into mature soot was observed to occur by build-up of the rate of hydrogen exchange. Hydrogen exchange and scrambling of the carbon skeletal structures can be seen as broadening of the PAH mass lines and an increase of the intensity along the baseline over the range of masses. This increase of the intensity along the baseline is more pronounced in the flow tube experiments due to the increased concentration of hydrogen in this system relative to the flame environment. The carbon cluster ions are most pronounced at  $m/z$  60, 73, 85, 97, 108 and 120. Some of the carbon ions are partially hydrogenated. This was also observed in our flame spectra [6]. The lack of evidence of this carbon cluster ion pattern in the 700 °C spectra means that no mature soot was produced in the particles at that temperature.

Further proof of the chemistry occurring in the particle phase can be seen by examining the high mass region of the spectrum using resonant ejection from the ion trap [8]. No ion intensity was observed in this mass range for the gas phase species by electron impact or laser ionization. The averaged high mass spectrum of the particle phase is presented in Fig. 3a. On the right side of the averaged

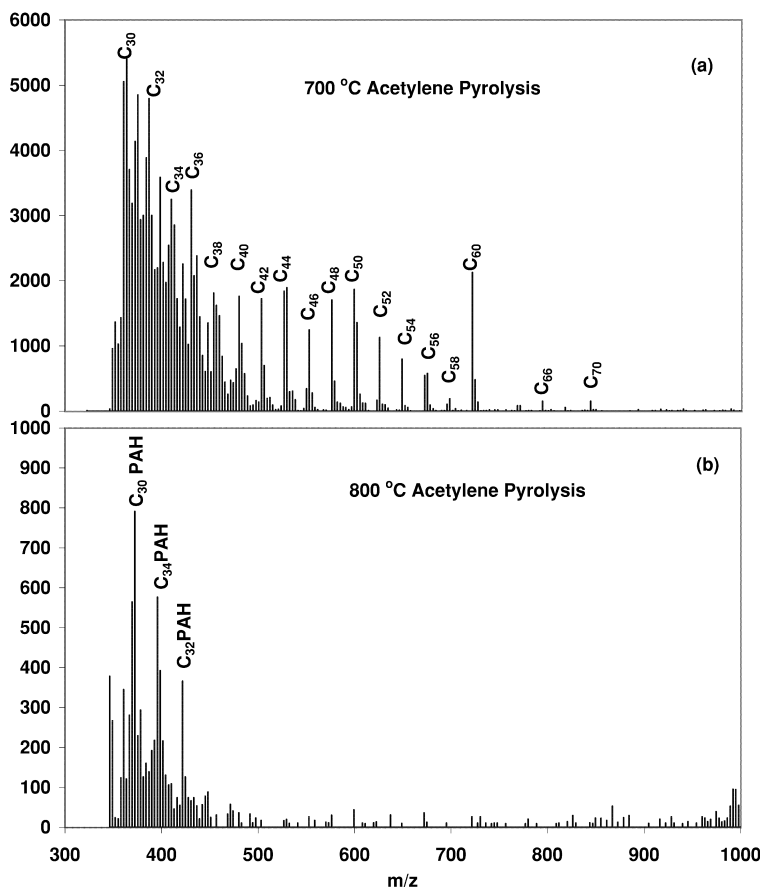


Fig. 3. (a) Averaged laser ablation/ionization high mass spectrum of the effluent particles in a background of effluent gas from the 700 °C pyrolysis of acetylene (all spectra averaged). (b) Averaged laser ablation/ionization high mass spectrum of the effluent particles in a background of effluent gas from the 800 °C pyrolysis of acetylene (all spectra averaged).

spectrum, the tail end of the PAH distribution can be seen tapering off just above 400 Da. Emerging from the PAH distribution is another distribution with a 24-Da spacing. These peaks are readily identified as carbon clusters because of the asymmetric local mass distribution caused by the addition of hydrogen. The dominant peak at 720 Da ( $C_{60}$ ) marks it as a fullerene distribution. Our group has observed similar distributions in the particle phase of a diffusion flame [9]. The fact that no ion intensity was observed in this mass region in the gas phase suggests that the observed fullerene distribution was produced in the particle phase and not the gas phase (this observation also further supports the validity of our analytical technique). In our previous discussion of the formation of fullerenes, it was suggested that the production of soot competed with the production of fullerenes. It was also suggested that if the leaving group (in this case hydrogen) was eliminated too quickly then soot production occurs and fullerene production should decrease. These suggestions were confirmed by raising the temperature of the flow reactor until black particulate matter (soot) was present in the effluent.

Fig. 3b reveals the averaged high mass particle spectrum of the effluent of the 800 °C reactor. Here it was noted that when soot production begins in the particle phase, fullerene production ceases. It is our contention that these results are consistent with the too rapid removal of hydrogen from the vicinity of the rearranging carbon structure at the higher temperature making it energetically too difficult to convert to the more ordered fullerene structures.

The observation of pyrolysis-induced production of fullerenes by itself is rather mundane. However, the observation of the production of fullerenes from the liquid phase has never been observed before. More importantly, these fullerenes were produced without co-production of mature soot or amorphous carbon. The absence of soot in the effluent at 700 °C was concluded by comparison of our experimental observations on the effluents of the reactor at the two temperatures. The logic follows.

The quantity of effluent collected on the filters was of the order of grams. Because of the optical properties of mature soot and amorphous carbon and their known

tendency to aggregate and settle in solution, minute quantities of these species can be observed on pristine white filter paper or on the wall of the glassware of the extracted effluent. The best yields of  $C_{60}$  are of the order of a few percent of the mass of soot produced [10]. If we were producing fullerenes in the same manner as that observed in the literature then there should be two orders of magnitude more soot produced than fullerenes. The best reported detection limits for single particle mass spectrometry (our technique) are of the order of parts per million in a single particle. For a single 1- $\mu$ m diameter particle (our precursor soot particle size), this is an attogram detection limit. This extreme of sensitivity occurs when there is a charge transfer-induced enhancement by the matrix [11,12]. No such enhancement is expected for fullerenes in a precursor soot matrix. However, assuming that the maximum sensitivity for  $C_{60}$  and the production ratio of soot to  $C_{60}$  remains the same as typically found in the literature, then we should detect soot in the parts per thousand range in the precursor soot material. This quantity of soot should be readily observable to the naked eye on the filter or in solution. No black material was observed in the 700 °C effluent.

Furthermore, when the temperature was raised to 800 °C, we readily observed soot in the effluent on the filter and in the filter extract. The majority of the effluent was still liquid precursor soot under these conditions, yet the fullerene ions are no longer present in our mass spectra. In light of the relative yields of  $C_{60}$  and soot that have been reported in the literature [10], the fullerene ion intensities were expected to increase rather than decrease when soot production is increased. Our results indicate that the soot production competes with fullerene production in the manner suggested in the Introduction. They also suggest that our production method is quite different than any method currently described in the literature.

Given the comparison of our results from acetylene pyrolysis at 700 and 800 °C without and with the presence of soot in the effluent, respectively, we conclude that there was no observable production of soot at 700 °C. It is our contention that if soot were present in any quantity relative to the presence of  $C_{60}$  then we would have observed it in our mass spectra because the carbon cluster ion yield is 100 times greater for mature soot than it is for the PAHs in the precursor soot [6]. It is also our contention that we would have seen it optically in the extract or on the filter as well. Consequently, we conclude that fullerenes were produced without soot at 700 °C in the precursor soot particles.

We point out that this process has not been optimized for the production of fullerenes. To do so the concentration of hydrogen in the gas phase surrounding the particles would have to be carefully adjusted to hasten fullerene growth during the carbonization process without producing soot. This task is not trivially accomplished by adding a diluent. Unfortunately, adding diluent at the reactor inlet

also rapidly changes the rate of particle growth below our observation threshold (>200 nm). Consequently, the particles would have to be made in one reactor and subsequently diluted and allowed to carbonize in yet another reactor.

#### 4. Conclusions

These results have interesting implications. Firstly, fullerenes can be produced in this medium without producing soot or other carbonaceous material if careful attention is given to the gas phase hydrogen concentration and the temperature. Secondly, these products form in a liquid medium that is completely soluble in standard solvents and should be easily manipulated. Thirdly, the co-produced PAHs and other product hydrocarbons can be recycled back into the reaction medium to minimize reactant waste and create a more efficient process. Furthermore, we speculate that this process can be applied to the production of nanotubes. We feel justified in making this prediction because every medium that has been reported to produce fullerenes also produces nanotubes upon the addition of an appropriate catalyst. Moreover, it is the current assumption in the literature that the catalyst acts primarily to keep the cage structure from closing so that carbon addition can continue thereby forming a tube. We can foresee no reason why this will not also occur for catalyst particles incorporated into the precursor soot medium. Finally, we predict that nanotubes formed in this medium could be easily aligned to form ribbons and ropes of nanotubes [13].

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