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Isotopic Fractionation During Fullerene, Nanotube, and Nanopolyhedra Formation

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The production of fullerenes[1] by electrical arcing[2,3] or resistively heating[4] produces a number of other products[5,6] including nanotubes and nanopolyhedra,[7] microtubes,[8] and pyrolytic carbon.[9,10] The mechanism of formation of these different products is still speculative.[11] We report here that the isotopic distributions in the various products named above differ, and this sheds new light on the mechanism by which they are formed.

We electrically arced graphite rods of high purity (99.99% C) in a helium atmosphere according to the general procedure for preparing fullerenes.[2,3,6] In our experiments, a DC arc was used with a sawtooth wave function. The cathode was a 12-mm-diameter × 30-mm-length graphite rod, and the anode was an 8-mm-diameter × 100-mm-length graphite rod. The charge helium pressure was 121 kPa, and the operating pressure 135 kPa. The resulting soot was removed from the reactor and carefully weighed, sampled, and combusted according to the method described by Kaplan et al.[12] and analyzed for ^{12}C and ^{13}C in a Finnigan MAT252 isotope ratio mass spectrometer. The presence of fullerenes (C_{60} and C_{70}) in the soot was confirmed by infrared and UV–visible spectroscopy[5,6] of toluene-soluble extracts. Microtubes growing on the surface of deposits on the cathode were also carefully removed, weighed, homogenized, and combusted, and the product carbon dioxide was analyzed by the same mass spectrometer. The main deposit on the cathode, about 8 mm in diameter, was sectioned. The outer surface material (shell) was sampled, and samples of the inner material were collected at distances from the original cathode surface. We have shown[9] that the outer surface is pyrolytic carbon and the inner core material is a mixture of pyrolytic carbon, nanotubes, and nanopolyhedra. Shell and inner core material were also combusted, and the resultant carbon dioxide was analyzed by mass spectrometry using the instrument noted above.

Isotope distributions are reported in the δ notation relative to the international standard Peedee Belemnite (PDB):

$$\delta\,^{13}\mathrm{C}\ (\text{‰}) = \frac{(^{13}\mathrm{C}/^{12}\mathrm{C})\mathrm{sample} - (^{13}\mathrm{C}/^{12}\mathrm{C})\mathrm{standard}}{(^{13}\mathrm{C}/^{12}\mathrm{C})\mathrm{standard}} \times 1000$$

Table I shows that the fullerene soot is isotopically heavy compared with the original graphite and that the cathode core deposit is isotopically light. Repeat experiments showed this always to be the case, although some variations in isotopic distributions were found as discussed below.

When the yields of all four products were measured (e.g., experiment 2, Table I), the isotope ratio in the graphite (i_g) was found to be equal to the sum of the isotope ratios of the products (i_p) corrected for fractional yield (f_p). That is,

$$i_g = \sum_p f_p i_p$$

Hence slightly different isotope ratios may be obtained for experiments which give different yields.

The fact that the cathode deposit is isotopically lighter than the original graphite is strong evidence that ionization and atomization is a mechanism by which deposits form. The mass-to-charge ratio is higher for ^{13}C than for ^{12}C, so the ^{12}C species reach the cathode in greater numbers than the ^{13}C species relative to that observed for natural abundance. However, this is not to suppose that all carbon deposited comes from ions. It has been shown that nanotubes can be formed from carbon vapor.[13]

We have observed that the cathode deposit in arcing experiments is always formed opposite the anode electrode even when the electrodes are not placed directly opposite each other, i.e., the deposit is coaxial with the anode. Thus the species involved make the shortest path between electrodes because this is the region with strongest electric field gradient. These results and the isotope data are consistent with the concept that the nanotubes and nanopolyhedra composing the deposit form from small ionic species such as C_1. Moreover, it is difficult to visualize how the nanotube or nanopolyhedra morphology might form if not from individual ions or atoms. Nanotubes are never deposited in an ordered way,[9] although they may clump.

The soot formed in the reaction is found on the condensor and walls of the reactor chamber. That is, the species from which soot is formed are not captured by the cathode. This suggests that the soot forms from larger species with higher mass-to-charge ratios than those which are involved in cathode deposit formation. It is possible that the soot precursors may have time to combine with an electron and become electrically neutral and thus escape from the arc's electromagnetic field. Convection will also assist in helping these materials to escape the arc.

The observation[14] of isotopic scrambling in fullerenes generated from ^{13}C-enriched mixtures of carbon does not contradict this hypothesis, since statistical incorporation may occur before large species are formed. Once the large species form, they migrate from the influence of the electrodes and may close to form fullerenes and other components of the soot. However, we should reflect on other pathways by which fullerenes may form. We have amassed a considerable amount of evidence (albeit in laser ablation rather than arcing studies) that the chemical structure of the starting material greatly influences the ease by which fullerenes can be produced,[15,16] so individual ions or atoms may not always be a requisite of fullerene formation. Fullerene

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Table I. Isotope Distributions (δ ^{13}C, ‰) in Products from Electrically Arcing Graphite[a]

product	experiment 1	experiment 2
graphite	−29.4 ± 0.2	−29.3 ± 0.2
fullerene soot	−26.7 ± 0.2	−27.8 ± 0.2
shell, pyrolytic carbon	−28.6 ± 0.2	−30.5 ± 0.2
microtubes	−29.8 ± 0.2	−29.9 ± 0.2
nanotube core (base)	−30.4 ± 0.2	−29.0 ± 0.2
nanotube core, 5 mm		−33.1 ± 0.2
nanotube core, 12 mm	−30.7 ± 0.2	−31.9 ± 0.2
nanotube core, 15 mm		−31.9 ± 0.2
nanotube core, 25 mm	−30.7 ± 0.2	−31.7 ± 0.2
nanotube core, 30 mm	−30.4 ± 0.2	
total core	−30.6 ± 0.2	−31.7 ± 0.2

[a] Two typical sets of experimental results are given. Slightly different yields are obtained in different experiments depending on variations in distance between the electrodes and other experimental factors. Typical yields (experiment 2) were soot 0.7370 g, filaments 0.0227 g, core deposit 0.2164 g, shell 0.8018 g. Thus isotope ratios differ between different experiments since the sum of the isotope ratios of the products corrected for fractional yield must equal that of the original graphite (see text).

formation is easier when extensive aromatic networks like those in graphite do not need to be broken down. Thus nanotubes readily form C_{60},[17] and so do appropriate alicyclic compounds.[18] Thus an isotope effect could be due to the fact that the larger molecular ions, which are fragments of the original anode material, would have larger mass-to-charge ratios and would be enriched in ^{13}C due to preferential ^{12}C–^{13}C bond breakage. This explanation is not consistent with the studies using ^{13}C-labeled pure carbon as anode; however, it could be proven or disproven as a mechanism for other reactions using ^{13}C-labeled materials such as polycyclic aromatics.

Pyrolytic carbon on the shell of the cathode deposit has an isotopic ratio close to that of the graphite. This is strong evidence that the pyrolytic carbon is formed by a mechanism different from nanotube, nanopolyhedra, or soot formation. It may form from species which are not monoatomic but have mass-to-charge ratios that do not allow them to escape from the magnetic field of the arc. This is consistent with pyrolytic carbon being deposited with the nanotubes and on the surface of the deposits but not in the soot. The microtubes also isolated here are formed by growth from a catalyst metal particle[8] and thus would also not be expected to differ greatly in isotopic distribution from the graphite, and this was observed.

We conclude that nanotubes and nanopolyhedra, pyrolytic carbon, microtubes, and fullerene soot in the arcing process are formed by different mechanisms. The nanotubes and nanopolyhedra are produced preferentially from ions with lowest mass-to-charge ratio and atoms. It is probable that the nanotubes and nanopolyhedra are formed by direct electrode–electrode interchange of charged monoatomic ions. Fullerene soot is formed from species with higher mass-to-charge ratios which can escape the electromagnetic field of the arc. Larger isotope effects should be observed for isolated nanotubes and nanopolyhedra, since the cathode deposits also contain pyrolytic carbon. Moreover, within the soot, isotopic fractionation may also occur. Work to this effect is in progress.

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