J. Am. Chem. Soc. **1995,** *117,* 12869−12870

Observation of Radioactive Fullerene Families Labeled with ^{11}C

Tsutomu Ohtsuki* and Kazuyoshi Masumoto

Laboratory of Nuclear Science, Tohoku University
1-2-1, Mikamine, Taihaku, Sendai 982, Japan

Keisuke Sueki, Kanako Kobayashi, and Koichi Kikuchi

Department of Chemistry, Tokyo Metropolitan University
1-1, Minami-Osawa, Hachioji, Tokyo 192-03, Japan

Received August 24, 1995

Since fullerenes, a series of highly cohesive all-carbon molecules whose structures are closed bonding nets, were first reported in 1985,[1] many new findings concerning physical and chemical characteristics have been reported. In recent years, it has become possible to produce large amounts of fullerenes by means of electric arcs,[2] flames,[3] and resistive heating.[4] Various approaches have been developed for studying fullerene science, such as metallofullerenes,[5,6] fullerne molecules,[7,8] and various interesting properties, such as superconductivity,[9] in their fields. Recently there has been much interest in finding practical applications of fullerenes.

Radioactive labeling of fullerenes and their derivatives is of considerable interest in following the location and metabolism of these substances in living organisms. Previously[6] two radioactively labeled endohedral metallofullerenes, $^{159}Gd@C_{82}$ and $^{161}Tb@C_{82}$, were produced by neutron irradiation of $Gd@C_{82}$. However, a convenient means for labeling empty cage fullerenes is very desirable as empty cage species are much easier to synthesize and to handle.

Here, we demonstrate the observation of radioactive fullerenes labeled with ^{11}C which were produced by photonuclear reaction, namely, $^{12}C(\gamma,n)^{11}C$ (^{11}C nuclide decays to ^{11}B with a half-life of 20.4 min and emits a 511 keV annihilation γ-ray for β^+ decay[10]). These observations are of great interest because they indicate that the carbon network of a fullerene can survive the recoil energy when ^{11}C is produced by nuclear reaction. This gives us a simple means for producing radioactive fullerenes molecules, opening up not only new questions in basic science but also new applications, such as radioactive tracers for nuclear medicine[11] and other fields.

The experimental approach is as follows. About 10 mg of C_{60} and C_{70} fullerene powder was wrapped with Al foil and set in a quartz tube. To check the effects of the atmosphere inside the quartz tube during irradiation, experiments were done in vacuum, oxygen, helium, and air. The sample was irradiated with bremsstrahlung of $E_{max} = 30$ MeV which originated from the bombardment of a Pt plate 2 mm in thickness with an electron beam which was provided by a 300 MeV electron linac, Laboratory of Nuclear Science, Tohoku University. Irradiation time was set to 20 min, corresponding to a half-life of ^{11}C. The average beam current was typically 120 μA. The samples were cooled with a water bath during the irradiation. After the irradiation, the fullerenes were dissolved in carbon disulfide (CS_2). The CS_2 solution was then filtered to remove insoluble materials through a membrane filter (pore size = 0.45 μm). The radioactivity from the dissolved fraction and the membrane filter was measured with a Ge detector to obtain the specific activity of ^{11}C. After evaporation of the CS_2, the soluble fraction was dissolved in a toluene−hexane solvent (7:3). The solution was injected into an HPLC equipped with a Buckyclutcher column[12] for reversed-phase chromatography. The eluted solution with flow rate 1 mL/min was passed through a UV detector (the wavelength was set to 280 nm) for the confirmation of fullerene derivatives. Downstream of the UV detector, two γ-ray detectors consisting of a bismuth germanate photomultiplier (BGO PM) were installed in order to count the 511 keV annihilation γ-ray of β^+ decay from ^{11}C. Data of the radiochromatogram were accumulated with a multichannel scaler system (MCS), using a personal computer. The eluent fraction was collected in 1 min intervals, and the γ-ray activities of each fraction were measured with a Ge detector.

Panels a and b of Figure 1 show the radiochromatogram for C_{60} and C_{70} samples, respectively, measured with the coincidence counting system. The horizontal axis indicates the retention time after injection into the HPLC and the vertical one the counting rate of the ^{11}C radioactivity corrected for the decay of ^{11}C. It was clearly seen that at least two large distinct elution peaks appeared in each chromatogram, Figure 1a,b, respectively. Furthermore, a broad peak was observed after about 20−25 min for the chromatograph of the C_{60} sample. The first peak at 7 min for Figure 1a and at 10 min for Figure 1b corresponded to the peaks of the C_{60} and C_{70} fullerenes in the UV-chromatogram, respectively. No significant difference caused by the irradiation atmospheres (vacuum, oxygen, helium, and air) was seen in these results. These results indicate that fullerenes labeled with ^{11}C, namely, $^{11}CC_{59}$ and $^{11}CC_{69}$, were produced. The second giant peak in Figure 1a,b was observed after about 11 min and 22−23 min retention time for the C_{60} and C_{70} samples, respectively, though they could not be observed clearly in the UV-chromatogram at the same retention.

In order to assign these second peaks, two mixed samples for 7/3 and 3/7 weight ratios of C_{60}/C_{70} were prepared and irradiated. The results of the radiochromatogram for the mixed samples, which were irradiated, are shown in Figure 2a,b. Interestingly, it is clearly seen that a new peak is revealed after a retention time of about 15 min. The ratios of these five peak areas change systematically, as the mixed ratio for the amount of C_{60} and C_{70} fullerenes is changed. This fact may suggest that these radioactive products originated from the interaction between two C_{60}'s, C_{60} and C_{70}, and two C_{70}'s in coalescence reactions; the peaks at about 11, 22−23, and 15 min retention time can be assigned to fullerene dimers, such as ($^{11}CC_{59}-C_{60}$), ($^{11}CC_{69}-C_{70}$), and ($^{11}CC_{59}-C_{70}$) or ($^{11}CC_{69}-C_{60}$), respectively. The third broad peak in Figure 1a for the C_{60} sample was assumed to be trimer fullerenes, namely, ($^{11}CC_{59}-C_{60}-C_{60}$).

Another approach was used for investigating the second peak in panels a and b of Figure 1. Sulfur (S), which can easily dissolve in CS_2 solvent, was added to the initial C_{60} sample and mixed homogeneously with a C_{60} fullerene. C_{60} to S weight ratios of 4/1, 2/1, and 1/2, were used, respectively. The resulting radiochromatograms are shown in Figure 3b−d and compared with that of the irradiated pure sample in Figure 3a. It is clearly seen that the size of the second peak systematically decreases

---

* To whom correspondence should be addressed.

[1] Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Smalley, R. E. *Nature* **1985**, *138*, 162.

[2] Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

[3] Peter, G.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 223.

[4] Howard, J. B.; Mckinnon, J. T.; Makarovsky, Y.; Lafleur, A.; Johnson, M. E. *Nature* **1991**, *352*, 139.

[5] Chai, Y.; et al. *J. Phys. Chem.* **1991**, *95*, 7564.

[6] Kikuchi, K.; Kobayashi, K.; Sueki, K.; Suzuki, S.; Nakahara, H.; Achiba, Y.; Tomura, K.; Katada, M. *J. Am. Chem. Soc.* **1994**, *116*, 9775.

[7] Yeretzian, C.; Hansen, K.; Diederich, F.; Whetten, R. *Nature* **1992**, *359*, 44.

[8] McElvany, S. W.; Callahan, J. H.; Ross, M. M.; Lamb, L. D.; Huffman, D. R. *Science* **1993**, *260*, 1632.

[9] Hebard, A. F.; et al. *Nature* **1991**, *350*, 600.

[10] Lederer, C. M., Shirley, V. S., Eds. *Table of Isotopes*, 7th ed.; John Wiley & Sons, Inc.: New York, 1978.

[11] Fridman, S. H.; Sijbesma, D. L.; Srdanov, R. P.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.

[12] Welch, C. J.; Pirkle, W. H. *J. Chromatogr.* **1992**, *609*, 89.

0002-7863/95/1517-12869$09.00/0

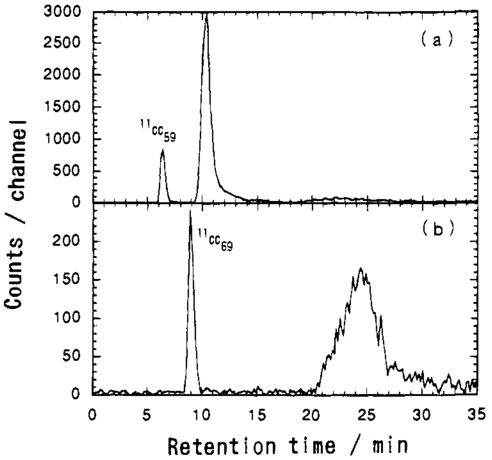

Figure 1. Radiochromatogram of radioactive (a) C_{60} and (b) C_{70} fullerenes labeled with ^{11}C. The horizontal axis indicates retention time, and the vertical axis is the counting rate of the 511 keV annihilation γ-ray, measured with two BGO detectors in coincidence.

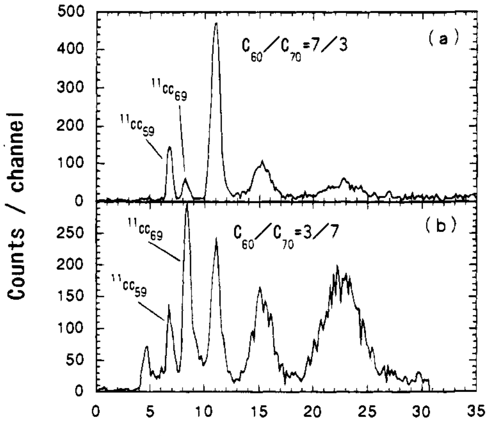

Figure 2. Radiochromatogram of C_{60} and C_{70} fullerenes containing (a) 7/3 and (b) 3/7 C_{60}/C_{70}. The horizontal and vertical axes are same as in Figure 1.

as the amount of S is increased. These results indicate that the coalescence reaction between C_{60} cages is reduced by dilution with sulfur.

Yeretzian et al.[7] have reported evidence of coalescence reactions by means of mass spectrometric measurements of hot and dense vapors of C_{60} and C_{70} fullerenes, and McElvany et al.[8] have demonstrated the production of odd-mass dimer fullerenes from coalescence reactions using pure C_{60} and C_{70}, and a mixture of C_{60} and C_{70} fullerenes in an ozone-gas phase. These early reports support the view that the giant second peaks in Figure 1a,b can be regarded as dimer fullerenes produced by the coalescence reaction which is caused by the $^{12}C(\gamma,n)^{11}C$ reaction. For confirmation of the coalescence reaction, mass spectrometry should be performed, but presently it may be impossible to apply it, because the amount of radioactive fullerenes produced is estimated to be only about 10^{10} molecules.

By a quantitative measurement of the γ-rays using a Ge detector, the specific activity of ^{11}C for C_{60} and C_{70} fullerenes was estimated to be about 0.3 MBq/mg. The activity of the dissolved fraction for the C_{60} fullerene was about 60−70% of the total activity when the C_{60} sample was irradiated, but that for the C_{70} fullerene was about 20%. Thus, the radioactive C_{60} fullerene labeled with ^{11}C yields has led to high yields, while the radioactive C_{70} fullerene yields are poorer than those of C_{60}. This may indicate that the structural durabilities of C_{60} and C_{70} are quite different.

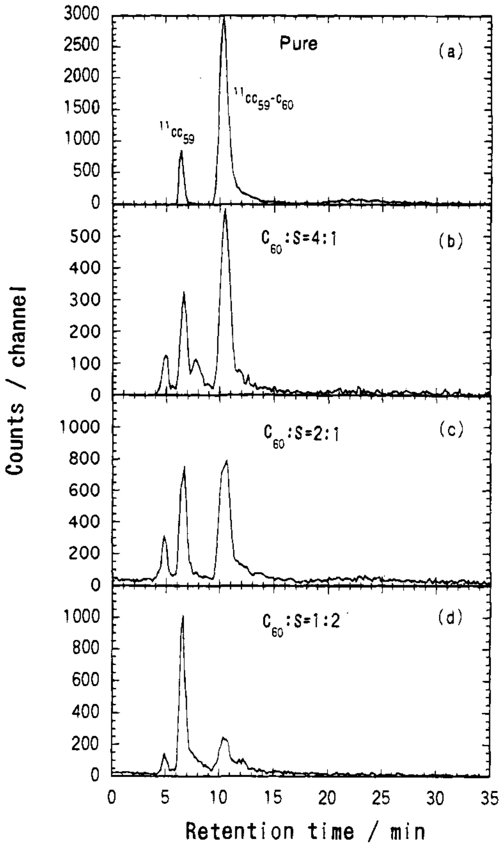

Figure 3. Radiochromatogram of C_{60} fullerenes containing (a) pure C_{60}, (b) 4/1 C_{60}/S, (c) 2/1 C_{60}/S, and (d) 1/2 C_{60}/S. The horizontal and vertical axes are same as in Figure 1. The small peaks in panels b−d are assumed to be unknown byproducts.

The present study is of interest because several radioactive fullerenes, such as monomer, dimer, and trimer fullerenes, can be produced easily and the production rate of radioactive fullerenes is not much affected by the kinetic energy of the recoiled ^{11}C in the $^{12}C(\gamma,n)^{11}C$ reaction (the form of the emitted neutron spectrum is expected to be approximately Maxwellian, and the average neutron kinetic energy seems to be about 2−3 MeV,[13] while the initial kinetic energy of the recoiled ^{11}C is estimated at about a few hundred kiloelectronvolts). The energetic ^{11}C should destroy the fullerene cages because their kinetic energies are estimated to be of a quite different order of magnitude than the energies (electronvolts) of molecular bonding. Surprisingly, our observations suggest that such energetic ^{11}C nuclei are successfully recombined into fullerene cages to include the ^{11}C. Further, the disrupted cages react with neighboring cages with a high degree of probability.

In conclusion, experimental evidence seems to show that radioactive C_{60} and C_{70} fullerenes and products, such as fullerene dimers labeled with ^{11}C, have been isolated and detected in a liquid phase by radiochromatography. These species were produced by a photonuclear reaction. The ^{11}C nuclide exists in fullerenes to the extent of about 60−70% of the total amount of ^{11}C produced when the C_{60} sample was irradiated, but at about 20% of the total ^{11}C when C_{70} was irradiated. This successful production of fullerenes labeled with ^{11}C demonstrates the structural stability and/or flexibility of fullerene cages.

Acknowledgment. We thank the technical staff of Laboratory of Nuclear Science at Tohoku University. This work was supported by the Inamori Fund and by a Grant-in-Aid for Co-operative Research (a) No.07213201 from the Ministry of Education, Science and Culture.

JA952916P

---

(13) Fultz, S. C.; Caldwell, J. T.; Berman, B. L.; Bramblett, R. L.; Hervey, R. R. *Phys. Rev.* **1966**, *143*, 790.