Insertion of Be Atoms in C60 Fullerene Cages: BeC60

Insertion of Be Atoms in C_{60} Fullerene Cages: Be@C_{60}

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(Received 31 May 1996)

Radioactive endohedral ^{7}Be@C_{60} can be detected using radiochemical and radiochromatographic techniques in the final solvent. Such a ^{7}Be atom can penetrate into the C_{60} cage to produce ^{7}Be@C_{60} by a recoil process of the nuclear reactions. An *ab initio* molecular dynamics simulation was carried out to demonstrate that a direct insertion process is really possible. Both the experimental and the theoretical results were consistent with each other. [S0031-9007(96)01431-7]

PACS numbers: 36.40.–c, 61.72.Ww

Currently, endohedral metallofullerenes attract much attention because of their interesting physical and chemical properties such as pseudoatom behavior, magnetism, and, possibly, superconductivity. Experimentally, metallofullerenes such as La [1,2], Y [3,4], and Sc [5,6] atoms encapsulated in C_{82} or C_{84} have been confirmed using arc-desorption or laser vaporization techniques. Here encapsulation occurs when fullerenes are created in a vapor phase. On the other hand, it may be necessary to insert atoms *a posteriori* into already created fullerenes in order to open up new production techniques for the endohedral fullerenes. Recently it has also been noticed that it is important to study the properties or the behavior of fullerenes by use of radiochemical techniques [7,8]. In our previous study [9,10], radioactive fullerenes such as $^{11}CC_{59}$, $^{11}CC_{69}$, and their dimers were produced in nuclear reactions, although the initial recoil energy was much higher than the intramolecular bonding energy level. This fact indicates the high structural stability and/or high flexibility of fullerene cages and it suggests that it might be possible to produce endohedral fullerenes using the recoil implantation process.

In this Letter, we present the first evidence that a second row element such as ^{7}Be can penetrate into the C_{60} cage to produce ^{7}Be@C_{60} in a nuclear recoil reaction. We proved the presence of endohedral fullerenes in the final product by the use of radiochemical and radiochromatographic techniques. This suggests that radioactive ^{7}Be is inserted directly into the C_{60} cage by the recoil implantation process following nuclear reactions. In order to check the possibility of the direct insertion process, we carried out an *ab initio* molecular dynamics simulation using our all-electron mixed-basis approach [11]. Our simulation confirms the existence of an insertion process. The direct insertion process may also occur in the plasma state of

a mixture of Li^+ and C_{60}^- without nuclear reaction [12]. Endohedral C_{60} plays an important role in the insertion process because of its relative abundance.

Two processes for producing the ^{7}Be isotope, namely the $^7Li(p,n)^7$Be and the $^{12}C(\gamma, \alpha n)^7$Be reactions were used for the experiments (^{7}Be decays to ^{7}Li with a half-life of 53.3 days and emits a 478 keV γ ray; see [13]). Sample preparations and irradiation procedures were as follows.

(1) $^7Li(p,n)^7$Be reaction: A homogeneously mixed sample of about 10 mg 99.5% purified C_{60} fullerene and Li_2CO_3 powder (mixed weight ratio = 1:1) was wrapped in thin aluminum foil and irradiated with 12 MeV protons. The irradiation was performed at the Cyclotron Radio-Isotope Center (CYRIC), Tohoku University. The beam current was typically 2 μA and the irradiation time was about 2 h.

(2) $^{12}C(\gamma, \alpha n)^7$Be reaction: Here also, a sample of about 10 mg 99.5% purified C_{60} fullerene was wrapped in aluminum foil and set in a quartz tube. The sample was irradiated by bremsstrahlung with $E_{\max} = 50$ MeV which was generated from a Pt target with the electron beam at the 300 MeV electron linac, Laboratory of Nuclear Science (LNS), Tohoku University. During the irradiation, the sample was cooled in a water bath. The average beam current was typically 120 μA and the irradiation time was about 12 h.

In both cases, the irradiated samples were dissolved in CS_2, and filtrated with a millipore filter (pore size = 0.45 μm) to remove insoluble by-products and Li compounds. After evaporating the CS_2 solvent, the soluble fraction was dissolved again into the eluent, toluene-hexane (7:3), and injected into a HPLC (high pressure liquid chromatography) column, Buckyclutcher column [14], at the flow rate of 3 ml/min. The elution behavior of ^{7}Be

in this chromatography was monitored in 40 sec intervals. The γ ray spectra of all fractions (0–40, 40–80, 80–120, ...sec) were measured with the Ge detector coupled to the 4096 channel pulse height analyzer which conversion gain was set 0.5 keV per channel. The energy resolution of the Ge detector was 1.5 keV in FWHM at 478 keV photopeak. Therefore, the ^{7}Be could be uniquely confirmed by its characteristic γ ray and its half-life and any other γ sources were ruled out.

The solid circles in Fig. 1 show the results of the γ ray measurements for each fraction in the experiment of case (1). The horizontal time-scale axis represents the retention times (20, 60, 100, ...sec), which corresponds to each fraction collected at 40 sec intervals, after the injection into the HPLC. The vertical axis represents the counting rates of 478 keV γ ray from ^{7}Be. One sharp peak of ^{7}Be radioactivity was observed in the retention of 7–8 min. No activities of ^{7}Be were observed in other time intervals (0–7 min and >8 min). Activities of ^{7}Be on the fraction were estimated to be of the magnitude of 10 Bq/mg. The solid curve in Fig. 1 indicates the absorbance monitored continuously by a UV detector for the irradiated sample. Only one strong peak was observed in the elution curve. This peak position corresponds to the retention time of C_{60} which is confirmed by the calibration run using the C_{60} sample before the irradiation. A similar result was obtained in the $^{12}C(\gamma, \alpha n)^7$Be reaction although the specific activity seems to be less than that of the $^7Li(p, n)^7$Be reaction. It is noted that the peak position of ^{7}Be (solid circle) exactly coincides with the UV chromatograph of C_{60}. This observation corroborates the formation of ^{7}Be@C_{60} following the nuclear reactions, since alkali-earth atoms such as ^{7}Be cannot combine with carbon atoms of fullerene cages covalently and are removed in the solvent if they were exohedral. The retention time of ^{7}Be@C_{60} seems to shift to a slightly later time than that of C_{60}. The same trend was observed in the elution behavior of ^{159}Gd@C_{82} [7].
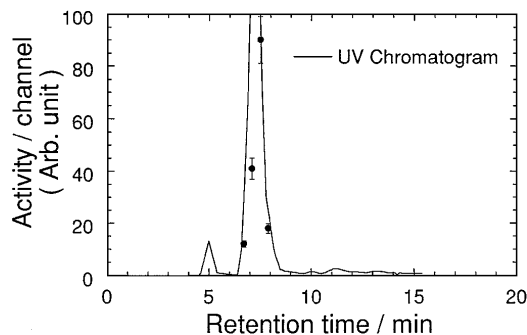

FIG. 1. HPLC elution curves of the soluble portion of the crude extracted in the proton irradiated sample of ^{7}Li and C_{60}. Solid circles indicate the radioactivities of ^{7}Be in each fraction. The vertical axis shows an absorbance of UV chromatogram of C_{60}. Small peaks in the figure correspond to by-products.

The energetic ^{7}Be should destroy the fullerene cages because their initial kinetic energies produced by the nuclear reactions are estimated to be several order of magnitude higher than the energies (eV) of intramolecular C-C bonding. Our observations suggest the following sequence of events during the recoil implantation process which will be presented in detail elsewhere [9,10]: The ^{7}Be atoms are produced from ^{7}Li and ^{12}C by the nuclear reactions. Then the kinetic energy of ^{7}Be is decreased in the sample to an appropriate value and the charge state of ^{7}Be still becomes 2+ during a collision and ionization process. Finally ^{7}Be penetrates into the C_{60} cage to produce the endohedral fullerene. Since the C_{60} is an electron acceptor and Be is an electron donor, the Be@C_{60} complex can be easily neutralized as well as the examples of La@C_{82} [2] and Y@C_{82} [3,4].

The *ab initio* calculation is based on an all-electron mixed-basis approach within the framework of the local-density approximation. The method of simulation employed here is the same as our previous work concerning the stability and reactivity of C_{60} [11] and the Li insertion into C_{60} [12]. We put one C_{60} molecule and one Be atom in a supercell with zero and 5 eV initial velocites for C_{60} and Be, respectively. The wave functions are expanded by 300 Slater-type atomic orbitals and 2969 plane waves. The supercell is divided into $64 \times 64 \times 64$ meshes with 2.7 meshes corresponding to 1 a.u. = 0.52918 Å. We performed six steepest-descent iterations between two adjacent updates of atomic positions in order to converge the electronic states, and chose $\Delta t = 4$ a.u. ~ 0.1 fs as the basic time step. For rescaling velocity and assuming a Fermi-Dirac distribution of electronic states, the simulation temperature of the whole system was set to be $T = 1000$ K.

In the case where a ^{7}Be^{2+} ion with 5 eV kinetic energy hits the center of a six-membered ring of C_{60}^{2-} perpendicularly, we find that the Be ion penetrates into the cage through the center of the six-membered ring very easily. It is trapped at 1.0 Å depth from the center of the same six-membered ring toward the cage center; see Fig. 2. The reason why the insertion proceeds very easily is that the ionic radius of Be^{2+} is 0.45 Å, much smaller than the radius of the hole of a six-membered ring. If a Be ion with the same kinetic energy hits a C-C bond of a C_{60} ion, the bombardment gives a considerable shock and deformation to the C_{60} cage. If a Be ion with higher kinetic energy, e.g., 100 eV, hits a C_{60} molecule at any location, we find that the C_{60} cage is damaged considerably.

These results suggest the following scenario of the present experiment: A lot of C_{60} fullerenes are destroyed before the ^{7}Be ions have lost their kinetic energies during the recoil process in the sample, and once sufficiently low kinetic energies are reached, the insertion process ^{7}Be + $C_{60} \rightarrow {}^7$Be@C_{60} occurs. During the solvation process only ideal ^{7}Be@C_{60} and undamaged C_{60} molecules are ex-
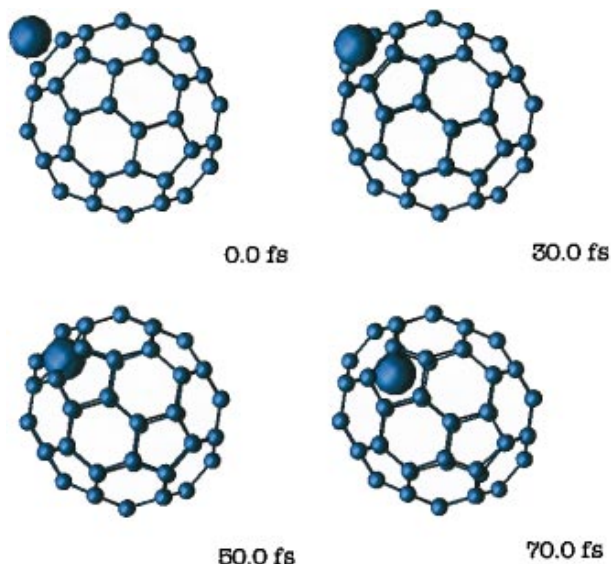
0.0 fs   30.0 fs

50.0 fs   70.0 fs

FIG. 2(color). Snapshots of the simulation, where ^{7}Be^{2+} hits with 5 eV kinetic energy the center of a six-membered ring of C_{60}^{2-}. In this case, after 60 fs, ^{7}Be@C_{60} is created.

tracted. The presence of ^{7}Be@C_{60} and C_{60} can be verified with the Ge and UV detectors. This fact is consistent with the result of an *ab initio* molecular dynamics simulation using the all-electron mixed-basis approach.

For confirmation of the endohedral Be@C_{60} more closely, further study is needed. We will currently try to measure the mass spectrum.

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