Se-Atom Incorporation in Fullerene and the MD Simulation(II. Radiochemistry)

Se-Atom Incorporation in Fullerene and the MD Simulation

T. Ohtsuki[1], H. Yuki[1], K. Ohno[2], K. Shiga[3], Y. Kawazoe[3],
K. Shikano[5] and K. Masumoto[6]

[1]*Laboratory of Nuclear Science, Tohoku University, Mikamine, Taihaku, Sendai 982-0826*
[2]*Department of Physics, Yokohama National University, Yokohama, 240-8501*
[3]*Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577*
[4]*NTT Opto-Electronics Laboratories, Tokai, Ibaraki, 319-11*
[5]*Radiation Science Center, KEK, Tanashi, Tokyo 188*

The formation of Se atom-incorporated fullerenes has been investigated by using radionuclides produced by nuclear reactions. From the trace of radioactivities of ^{75}Se after High Performance Liquid Chromatography (HPLC), it was found that the formation of endohedral fullerenes or heterofullerenes is possible by a recoil process following the nuclear reactions. To confirm the produced materials, *ab initio* molecular-dynamics simulations based on an all-electron mixed-basis approach were carried out. We found that the insertion of Se atom into C_{60} cage is much easier than that of As and Ge atoms.

§ 1. Introduction

Fullerenes are the new type of carbon compounds and show very interesting physical and chemical properties. Especially, chemical interaction between C_{60} and a variety of atoms is becoming a very new field of cluster research. So far, numerous experimental studies for endohedrally doped [1-10] or exohedrally doped [11-13] fullerenes with foreign atoms have been undertaken by resorting to arc-desorption or laser-vaporization techniques. On the other hand, it has become possible to synthesize the heterofullerenes, where the foreign atom is incorporated into the carbon cage. Experimentally, heterofullerenes doped with foreign atoms, such as boron (B) [14, 15] nitrogen(N)[16, 17] silicon (Si) [18, 19] have been reported. In our previous studies, we have studied not only the endohedral doping of Be [20], Kr and Xe [21] but also the substitutional doping of ^{11}C [22], ^{13}N [23], ^{69}Ge and ^{72}As [24] by a recoil-implantation process following nuclear reactions. In spite of the intense research, only partial facts for the formation process and the produced materials have been unveiled on the nature of the chemical interaction between a foreign atom and a fullerene cage. Therefore, it is important and intriguing to synthesize new complexes, such as several foreign-atom incorporated fullerenes, and to investigate their properties so that knowledge about how to produce large amount of these complexes is gained.

In this paper, we show evidence of Se atom-incorporated fullerenes on the collision between a C_{60} cage and an Se atom, which was generated from a recoil process following nuclear reactions. We performed *ab initio* molecular-dynamics (MD) simulations: whether the Se atom can be incorporated in the fullerene with the endohedral doping: Se@C_{60}. Furthermore, the chemical nature of the Se atom in a fullerene is compared with that of the Ge and As atoms.

§ 2. Experimental Procedure

In order to produce Se atom-incorporated fullerenes, about 10 mg of C_{60} fullerene powder was mixed homogeneously with 10 mg of As_2S_3 (200 meshes), and used to the target material. Deuteron irradiation with beam energy of 16 MeV was performed at the Cyclotron Radio-Isotope Center (CYRIC), Tohoku University. Radioisotopes of ^{75}Se can be produced by ^{75}As (d, 2n) ^{75}Se reactions. The beam current was typically 5 μA and the irradiation time was about 1 hour. The sample was cooled with He-gas during irradiation. After the irradiation, the samples were left for one day to cool down the several kinds of short-lived radioactivities of byproducts. After the one-day cooling, radioactivities, such as ^{11}C or ^{13}N, e.g., ^{11}C decays to ^{11}B with $T_{1/2}$=20 min, the radioactivities of ^{75}Se could be measured with its characteristic γ-rays. The typical γ-ray and the half-life ($T_{1/2}$) of ^{75}Se are 136 keV (and 265 keV), 120 days, respectively.

The fullerene samples were dissolved in o-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size = 0.2 μm). The soluble fraction was injected into a High Performance Liquid Chromatograph (HPLC) equipped with a 5PBB (silica-bonded with the pentabromo benzyl group) column of 10 mm (inner diameter)×250 mm (length), at a flow rate of 3 ml/min. The eluted solution was passed through a UV detector, the wavelength of which was adjusted to 290 nm in order to measure the amount of fullerenes and their derivatives. The fraction was collected at 30 sec intervals, and the γ-ray activities of each fraction were measured with a Ge-detector. Therefore, the existence of ^{75}Se could be confirmed by their characteristic γ-rays.

§ 3. Results and Discussion

The elution curve shown by solid line in Fig. 1 indicates the absorbances monitored continuously by a UV detector for the irradiated samples of $C_{60}+As_2S_3$. The horizontal axis indicates the retention time after injection into the HPLC, and vertical one indicates the absorption intensity of the UV and the γ counting rate of the ^{75}Se radionuclide produced by ^{75}As (d,2n) ^{75}Se reaction. A strong absorption peak

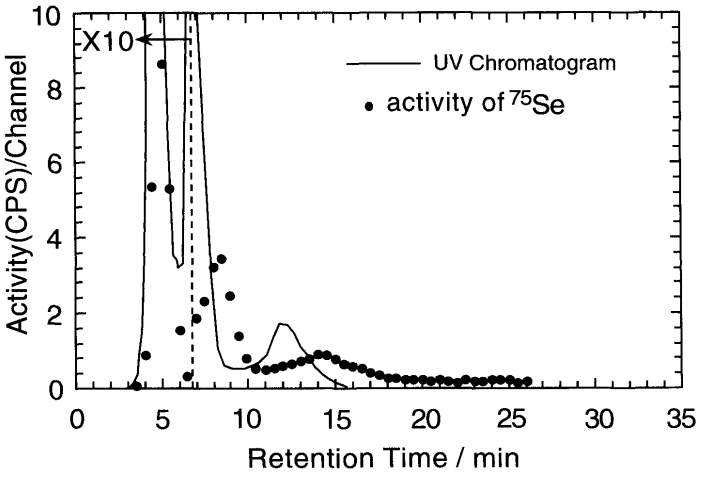

Fig.1. HPLC elution curves of the soluble portion of the crude extracted in the deuteron irradiated sample of C_{60} mixed with As_2S_3. The horizontal axis indicates retention time, while the vertical axis represents the counting rate of the radioactivities of ^{75}Se (solid circles) measured with a Ge-detector and the absorbance of a UV chromatogram of C_{60} (solid line).

was observed at the retention time of 4.2 - 5.2 min in the elution curve (solid line) which was measured by the UV detector. This peak position corresponds to the retention time of C_{60} which was confirmed by the calibration run using the C_{60} sample before the irradiation. Following the first peak, two peaks at around 6.5 - 7.2 min and 10 - 15 min were consecutively observed in the UV chromatogram. This fact indicates that the second and smaller third peaks can be assigned to C_{60} dimers and C_{60} trimers, respectively, with resorting to TOFMAS measurements. These materials can be produced by the interaction between C_{60}'s in coalescence reactions after ionization by the incident or produced charged particles. Three peaks appeared in the curve of the ^{75}Se radioactivities in the radiochromatogram. Aside from a slight delay, the first peak (5.0 min) corresponds to the C_{60} UV absorption peak. The second as well as the relatively broad third peaks were observed at the retention time of 7 - 10 min, and of 11 - 18 min, respectively. Though there is a delay in the elution peaks of the radioactivities against that of the UV absorption peaks, it seems that the elution behavior is similar. This result indicates that the radioactive fullerene monomers and their polymers (dimers and trimers) labeled with ^{75}Se possibly exist in the final fractions.

In order to understand the present experimental results, *ab initio* molecular-dynamics simulations were carried out. The method, which is used here, is based on the all-electron mixed-basis approach [26-28] using both plane waves (PW's) and atomic orbitals (AO's) as a basis set within the framework of the local density approximation (LDA). In the present study, all the core atomic orbitals are determined numerically by a standard atomic calculation based on Herman-Skillman's framework with logarithmic radial meshes. For the present system,we use 313 numerical AO's and 4,169 PW's corresponding to a 7 Ry cutoff energy. For dynamics, we assume the adiabatic approximation where the electronic structure is always in the ground state. We utilize a supercell composed of $64\times64\times64$ meshes, where one mesh corresponds to 0.196 Å. We set the basic time step as $\Delta t = 0.1$ fs and perform five steepest descent (SD) iterations after each updation of atomic positions. We do not impose any velocity control, so that the system is almost microcanonical with a little energy dissipation from the SD algorithm.

First, we show the results of the following simulation; an Se atom with a kinetic energies (K.E.) 40 eV hits vertically the center of a six-membered ring (u-C_6) of C_{60}. From the simulation, we found that an Se atom can penetrate into C_{60} easily when its initial speed is 40 eV, and stop at the inside of the C_{60} cage (see Figure 2). Although, an Se atom goes out again from the opposite side of the cage when its initial speed is greater than 100 eV. For an interaction with the K.E. lower than 40 eV, the Se atom first touches u-C_6, carbon atoms are pushed to open u-C_6, but the u-C_6 soon recovers its initial configuration. Similar simulations were performed for the case of As. In this case, we found that an As atom can penetrate into C_{60} if its K.E. is greater than 70 eV, although, an As atom goes out again from the opposite side of the cage when its initial energy is greater than 160 eV. Comparing Se and As, we found that the formation of Se@C_{60} seems to be easier than that of As@C_{60}, because the energy range of the insertion for Se atom is relatively lower than that for As atom.

Second, we put additionally one Se atom on the radial axis by 1.39 Å inward from the original C position of C_{60}. Then, starting the simulation with zero initial velocity. We found that there is a force acting on the Se atom to accelerate it inward, and finally, the Se atom stops at around the center of C_{60}

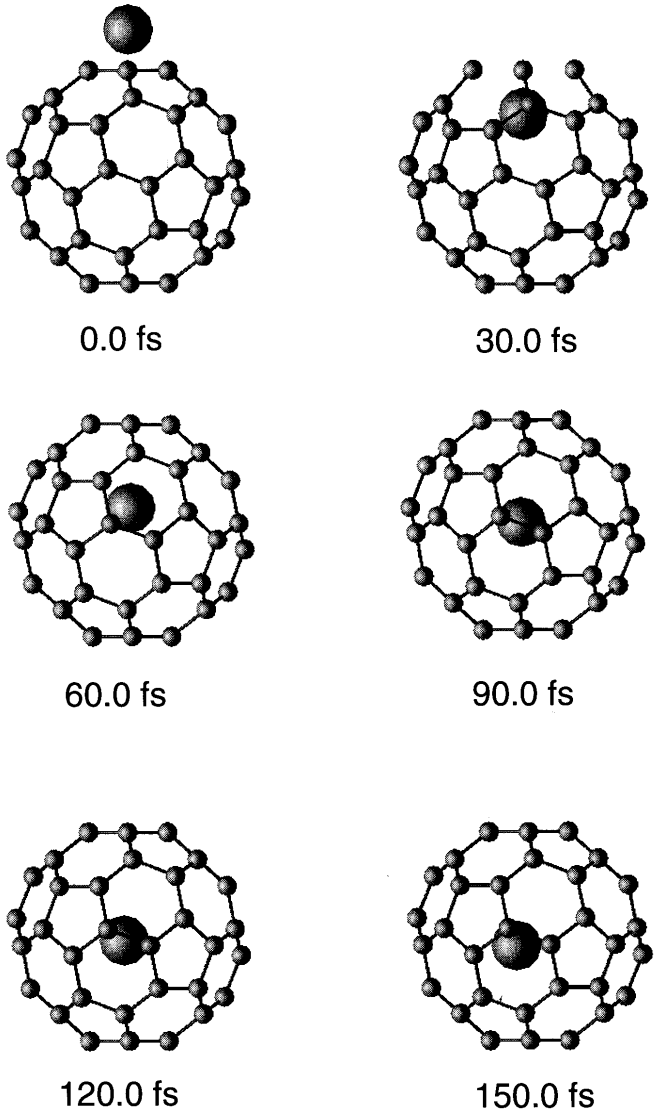

Fig.2. Simulation of Se hitting the center of a six-membered ring (u-C_6) of C_{60} with a kinetic energy of 40 eV. Here, the local skeleton disappears from the figure when the bond length is elongated to more than by 1.5Å.

We also put additionally one As atom on the same radial axis by 1.39 Å inward from the original C position of C_{60}. we found that there is a strong force acting on the As atom to accelerate it outward and, as a result, to repel the outward C atom. Finally, the As atom stops at 0.50 Å from the cage sphere. Thus, it seems that the As atom put inside the cage is relatively unstable and has a strong tendency to repel the closest C atom of C_{60}, and is stabilized slightly outside the cage sphere after the removal of the closest C atom. Therefore, a heterofullerene, such as AsC_{59}, may exist stably under realistic conditions. It should be noted that similar results for the case of a Si atom have been reported by Pellarin *et al* [18, 19] (however, the possibility for endohedral doping, As@C_{60}, can not be completely excluded at present, there seems to be a local stable point inside the cage).

Radiochromatogram of ^{69}Ge, ^{72}As and ^{75}Se are shown in Fig. 3 (a) and 3 (b), respectively. The area ratios, the peak area assigned by "A" and "B" in Figs. 3 (a) and (b), are shown in Fig. 3 (c) for Ge, As and Se atom, respectively. It is interesting and important to note that the area ratio, A/B (monomer/

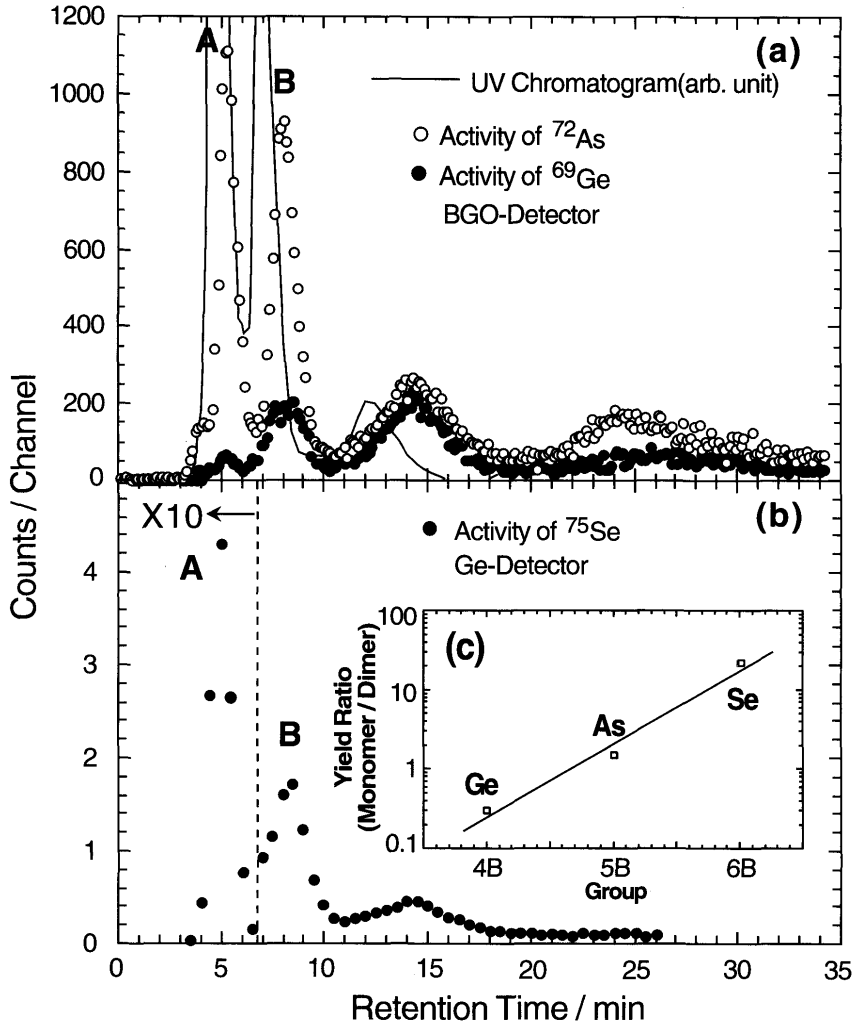

Fig.3. (a) HPLC elution curves of the soluble portion of the crude extracted in the deuteron irradiated sample for the production of ^{69}Ge and ^{72}As taken from ref. [24]. The horizontal and the vertical axes are same as Fig. 1, but for ^{69}Ge and ^{72}As. (b) Same as (a), but for ^{75}Se for comparison with the ^{69}Ge and ^{72}As cases. The difference in vertical scale between (a) and (b) is due to the efficiency of BGO- and Ge-detectors. (c) Area ratio, monomer/dimer indicated by the peaks "A" and "B" in (a) and (b), in the radiochromatogram of 4B～6B (Ge～Se) atoms.

dimer), in the radiochromatogram of ^{75}Se is much larger than that in the radiochromatogram of ^{72}As (and further much larger than that in the radiochromatogram of ^{69}Ge). This trend indicates that the shock caused by collision with higher K.E. (e.g. ～70 eV, for As atom) most probably induced the cage to create dimers with a higher rate. The difference can be due mainly to the nature of the covalent bonding between the C atom and the 4B～6B (Ge～Se) atoms.

§ 4. Conclusion

In this study, the formation of atom-incorporated fullerenes has been investigated by the trace of radioactivities of ^{75}Se produced by nuclear reactions. It was found that 6B element, like Se, remained in the final C_{60} portion after a HPLC process. This fact suggests that the formation of ^{75}Se atom-incorporated fullerenes can be possible by a recoil process following nuclear reactions. Carrying out *ab*

initio molecular-dynamics (MD) simulations on the basis of the all-electron mixed basis approach, we showed possibility of the formation of endohedral fullerene for Se atom. In comparison with 4B~6B (Ge~Se) atoms, we found that the insertion of Se atom into C_{60} cage is much easier than that of As and Ge atoms.

Acknowledgments

The authors are grateful to the staff of the Cyclotron Radio-Isotope Center (CYRIC) for handling the beam, and are grateful to the technical staffs, working at IMR, Tohoku University, for their continuous support, for the supercomputing facilities of HITAC S 3800. This work was supported by the Grants-in-Aid for Co-operative Research No. 12640532 from the Ministry of Education, Science and Culture of Japan.

References

[1] Y. Chai *et al.,* Phys. Chem. **95** (1991) 7564.
[2] R.D. Johnson *et al.,* Nature (London) **355** (1992) 239.
[3] J. H. Weaver *et al.,* Chem. Phys. Lett. **190** (1992) 460.
[4] H. Shinohara *et al.,* Nature (London) **357** (1992) 52.
[5] M. Takata *et al.,* Nature (London) **377** (1995) 46.
[6] W. Sato *et al.,* Phys. Rev. Lett. **80** (1998) 133.
[7] M. Saunders *et al.,* Science **271** (1996) 1693.
[8] T. Braun and H. Rausch, Chem. Phys. Lett. **288** (1998) 179.
[9] T. Braun and H. Rausch, Chem. Phys. Lett. **237** (1995) 443.
[10] G.E. Gadd, *et al.,* J. Am. Chem. Soc. **120** (1998) 10322.
[11] L.M. Roth, *et al.,* J. Am. Chem. Soc. **113** (1991) 6298.
[12] Y. Huang, and B.S. Freiser, J. Am. Chem. Soc. **113** (1991) 9418.
[13] S.W. McElvany, *et al.,* J. Phys. Chem. **96** (1992) 4935.
[14] T. Guo, *et al.,* J. Phys. Chem. **95** (1991) 4948.
[15] H.J. Muhr, *et al.,* Chem. Phys. Lett. **249** (1996) 399.
[16] T. Pradeep, *et al.,* J. Phys. Chem. **95** (1991) 10564.
[17] J.F. Christian, *et al.,* J. Phys. Chem. **96** (1992) 10597.
[18] M. Pellarin, *et al.,* Chem. Phys. Lett. **277** (1997) 96.
[19] C. Ray, *et al.,* Phys. Rev. Lett. **80** (1998) 5365.
[20] T. Ohtsuki, *et al.,* Phys. Rev. Lett. **77** (1996) 3522.
[21] T. Ohtsuki, *et al.,* Phys. Rev. Lett. **81** (1998) 967.
[22] T. Ohtsuki, *et al.,* J. Am. Chem. Soc. **117** (1995) 12869.
[23] T. Ohtsuki, *et al.,* J. Radioanal. Nucl. Chem. **239** (1999) 365.
[24] T. Ohtsuki, *et al.,* Phys. Rev. **B60** (1999) 1531.
[25] R.B. Firestone, *et al.,* Eds. Table of Isotopes, 8th Ed. Vol.I. John Wiley & Sons, Inc. 1996.

[26] K. Ohno, *et al.,* Phys. Rev. Lett. **76** (1996) 3590.

[27] K. Ohno, *et al.,* Phys. Rev. **B56** (1997) 1009.

[28] K. Shiga, *et al.,* Modelling Simul. Mater. Sci. Eng. **7** (1999) 621.