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Recently fullerenes and their derivatives occupy the attention of many scientists of the world due to their interesting physical and chemical properties. The production of labeled fullerenes is interesting and important for studying the behavior of trace amount of fullerenes. In this work, the recoil implantation of radioactive carbon into fullerene network has been tried by cyclotron irradiation to study their reaction mechanism and open a new labeling method.

The production of ^{11}C labeled fullerenes was already succeeded in our previous experiment using photonuclear reaction¹⁾. In this case, ^{11}C is produced from carbon of fullerenes by $^{12}\text{C}(\gamma, n)^{11}\text{C}$ reaction. As the recoil energy of ^{11}C is extremely larger than the chemical bonding energy, it can be considered in our common sense that ^{11}C produced by photonuclear reaction can not stay in the skeleton of fullerenes and carbon network is broken by recoil energy. Beyond our expectation, it was confirmed by HPLC separation coupled with the UV- and BGO-detectors that the 60-70% and 30% of total ^{11}C activity remained in C_{60} and C_{70} , respectively. Furthermore, 80-90% of labeled ^{11}C existed in fullerene dimer. This ^{11}C labeled fullerene dimer is isolated in the state of carrier-free, because it could only be detected by BGO-scintillation detectors and could not be detected by UV-spectrometer. Two important questions are raised, that is, 1) why such a high yield of ^{11}C -labeled fullerenes can be produced? and 2) why ^{11}C -labeled fullerenes prefer the coalescence reaction?

It is very important to confirm whether the same experimental result can be obtained by charged-particle irradiation, in order to make clear the labeling mechanism. As ^{11}C was produced by using $^{11}\text{B}(p, n)^{11}\text{C}$, $^{14}\text{N}(p, \alpha)^{11}\text{C}$ and $^{10}\text{B}(d, n)^{11}\text{C}$ reactions, the mixture of fullerene/boron or fullerene/nitrogen compound was irradiated with proton or deuteron. Therefore the possible production process of labeled fullerene by charged-particle irradiation is the substitution reaction between carbon atom of fullerene and ^{11}C recoiled out of boron or nitrogen.

Experimental

Fullerenes, C_{60} and C_{70} are dissolved into CS_2 and mixed with the same amount of boron, Si_3N_4 , CH_2N_4 . After evaporation of CS_2 , 10mg of sample was wrapped with

aluminium foil of 10 μm thickness. Irradiation was done at the No.1 irradiation facility for radioisotope production of Cyclotron Radioisotope Center, Tohoku University. Samples were irradiated by 12 MeV proton and 10 MeV deuteron for 20 min at the average current of 1 μA . Sample surface was cooled by He-gas and the hidden side was cooled with water indirectly.

Irradiated samples were dissolved into CS_2 and filtrated by milipore filter to remove recoil sources such as boron powder and insoluble byproducts. After CS_2 was removed, CS_2 soluble fraction was dissolved into toluene-hexane mixture (7:3) and injected into HPLC column (Bucky-clutcher, 250 mm \times 10 mm id) to separate C_{60} and/or C_{70} and their derivatives. Flow rate was adjusted at 3ml/min. After separation, the absorbance and radioactivity of eluate were measured by UV-detector at 290 nm and BGO-scintillation detectors in series. After the absorbance measurement, a elution tube was coiled and sandwiched between a pair of BGO-scintillation detectors which were coupled with coincidence counting circuit to detect 511keV annihilation gamma-ray from labelled compounds. Eluate was collected by the fraction collector every 1 min and checked a radiochemical purity with the Ge-detector.

Results and Discussion

It was found from the result of 12 MeV proton irradiation of a pure C_{60} that the activity of ^{13}N and ^{11}C produced by the $^{13}\text{C}(\text{p},\text{n})^{13}\text{N}$ and $^{12}\text{C}(\text{p},\text{pn})^{11}\text{C}$ reaction respectively were negligible.

Figure 1 shows the radiochromatogram after proton irradiation of the C_{60} and boron mixture. Horizontal and vertical axes are the retention time and radioactivity detected by the coincidence counting system. The count rate at each elution time was normalized as the count rate at the injection time according to the half-life of ^{11}C . The first peak appeared at the retention of 6 min was attributed as C_{60} molecule labelled with ^{11}C , such as $^{11}\text{CC}_{59}$. The second large peak appeared at 10 min seems to be a C_{60} -dimer. The third broad peak, which may be a C_{60} -trimer was observed around 20 min after injection. The peak area ratio of above three peaks was 1:5:1. The same chromatograph was also obtained in the case of the C_{60} mixture with Si_3N_4 and CH_2N_4

Figure 2 shows the result of the C_{70} and boron mixture. The first and second large peaks are assigned as C_{70} monomer and dimer. The second peak was broader than that of single component. It seems to be the compound peak of three types of geometrical isomer of C_{70} dimer, because the C_{70} molecule resembles a rugby ball in shape. Three small peaks appeared at 6, 10 and 14 min were caused by the small amount of C_{60} impurity and expected to be C_{60} -monomer, C_{60} -dimer and C_{60} - C_{70} , respectively.

Above results are the same as the results of bremsstrahlung irradiation¹⁾. Therefore, the ^{11}C labeling induced by nuclear reactions is mainly caused by the substitution reaction

between a stable carbon in fullerene and ^{11}C . When fulleren network is opened by the attack of ^{11}C , the open end of carbon network can easily combine with neighboring fullerene molecules.

Yoretzian *et al.* reported the coalescence products observed in a hot and dense vapor generated by laser desorption of a fullerene film.²⁾ McElvany *et al.* found that the coalescence reaction can be catalyzed by ozone and produces odd mass molecule, such as C_{119} ($\text{C}_{60} + \text{C}_{59}$), C_{129} ($\text{C}_{60} + \text{C}_{69}$ or $\text{C}_{59} + \text{C}_{70}$) and C_{139} ($\text{C}_{70} + \text{C}_{69}$).³⁾ They could not isolate these compound as chemically stable species. On the other hand, the Buckyclutcher column can separate these compound according to their molecular size. Our results are the first evidence that the chemically stable fullerene dimer and trimer can exist in liquid phase.

In the case of deuteron irradiation of C_{60} , ^{13}N labeled compound appeared at the retention time of 6 and 14 min. The retention time of the first peak is that of the C_{60} itself and the second peak seems to be a new ^{13}N labelled compound. As the insertion of hetero atom into fullerene cage is a recent theme of the fullerene chemistry, recoil implantation method is very effective to study this kind of work. The ^{13}N labeling experiment will be continued to confirm the structure of ^{13}N labeled compound.

As this labeling method is very simple, easy and rapid, this method is very useful for preparing a complex molecule labeled with a short lived radioisotope, such as ^{11}C and ^{13}N . This work will open not only several application fields, such as tracer chemistry and nuclear medicine, but also a new fullerene chemistry for the insertion of heteroatom into fulleren cage and/or the production of higher fullerenes.

Acknowledgement

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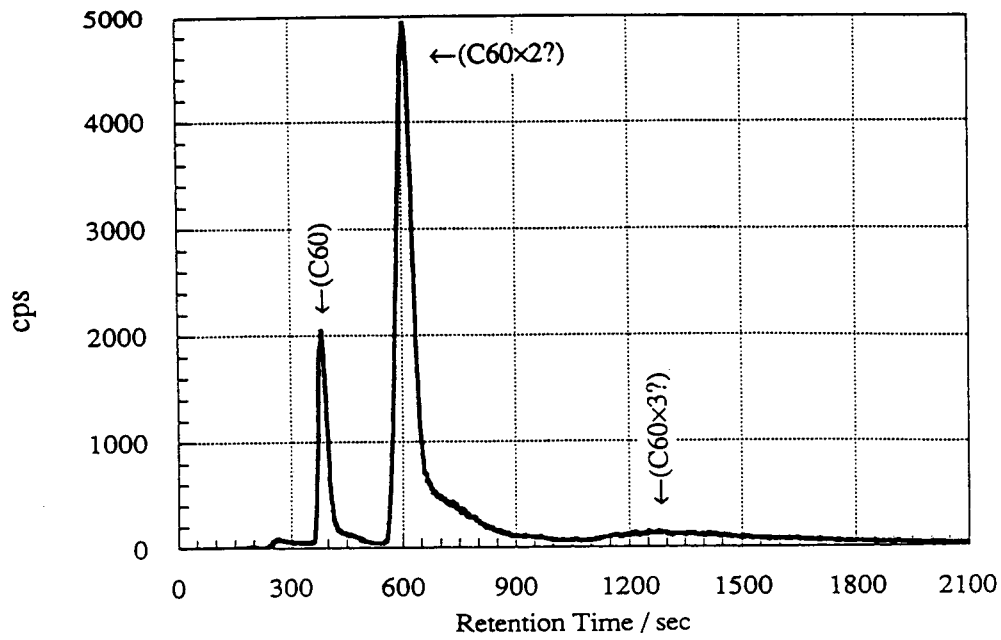


Fig. 1. Radiochromatogram of the C_{60} and boron mixture bombarded by 12 MeV proton.

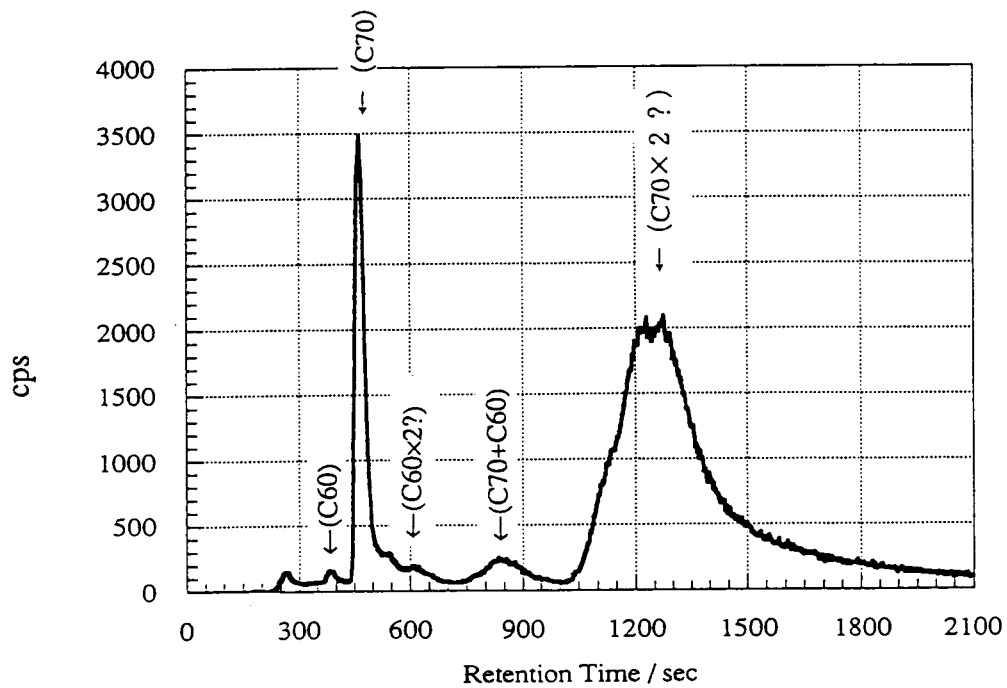


Fig. 2. Radiochromatogram of the C_{60} and boron mixture bombarded by 10 MeV deuteron.