Evidence for Rare Gas Endohedral Fullerene Formation from γ Recoil from HPLC Studies

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Abstract: In this paper, we present the first direct evidence for the formation of endohedral fullerenes from prompt γ emission of neutron irradiated Xe held interstitially in the C_{60} lattice. Following neutron activation, solutions of the irradiated solid were analyzed by high-pressure liquid chromatography and γ spectroscopy which showed Xe radioisotopes to be present in fractions that eluted at longer times relative to untreated C_{60}. The observation of Xe radioisotopes at these particular times was attributed to elution of compounds based on Xe@C_{60}. Additional support for this conclusion was obtained from isotopic ratios measured by γ spectroscopy. The present results provide convincing evidence in support of the γ recoil mechanism for trapping radionuclides in fullerene cages which had previously been inferred from indirect evidence.

Introduction

Braun and Rausch,[1] by studying neutron activation of solid C_{60} samples which contained impurity levels of Ar (parts per million), found residual activity from ^{41}Ar in their solutions after all attempts had been made to expel the gas. They proposed that their results were attributable to endohedral formation by γ recoil. With our success in producing stoichiometric rare gas interstitial C_{60} fullerenes,[2−4] we decided to study in more detail the effects of neutron irradiation on these materials. We showed that the rare gas fullerenes survived neutron irradiation with no evidence for extensive damage or loss of rare gas after 4 h of irradiation[5] with a neutron flux of 5×10^{13} neutrons cm^2 s^{-1}. We similarly found residual activity in toluene solutions[6,7] (between 1 and 2% of the activity for an equivalent amount of undissolved solid, for each of the individual radioisotopes observed) after all efforts had been made to expel any free rare gas. In addition, further evidence for endohedral formation was found in that there was an indication of different propensities for encapsulation of different rare gas radionuclides, as evidenced from the γ spectra.

The effects of γ recoil following neutron activation have also been studied by Kikuchi et al.,[8] where they showed that neutron activation of Gd@C_{82} led to only 10% of the radionuclide ^{159}Gd remaining within the cage as a result of recoil out of the cage. Large losses were also found by Kobayashi et al.[9] studying La endohedral fullerenes. Grushko et al.,[10] on the other hand, found that about 70% of ^{153}Sm endohedral fullerene cages survived neutron capture. Overall these results show that a significant amount of the trapped endohedral atoms recoil out of the fullerene cage as a result of prompt γ emission, and this prompted our previous suggestion[6,7] that in order to make endohedral radionuclides it may be just as efficient to start with a mixture of fullerene and radionuclide precursor instead of the already synthesized endohedral fullerene and use γ recoil to produce the endohedral radionuclide itself. This method would also have the added advantage of being carrier-free in that all produced endohedral fullerenes would be radioactive, whereas using synthesized endohedral fullerenes, the activated material would still consist predominantly of unactivated endohedral fullerenenes. In any medical diagnostic or therapeutic treatment, carrier-free radioisotopes offer less chemical side effects. To show the possible validity of this approach, it is essential to obtain direct evidence for the recoil mechanism, and we do this for the first time using HPLC.

Experimental Section

The rare gas fullerenes were prepared by hot isostatic pressing (HIP) of C_{60} powder (99.95%+) in the presence of the desired rare gas at pressures of ∼170 MPa and elevated temperatures. The details of such experiments have been documented previously.[2−4] In these experiments, we irradiated a rare gas fullerene sample which had a stoichiometry of $\sim Xe_{0.26}C_{60}$ (±5%). The stoichiometry was determined from thermal gravimetric analysis (TGA) and powder X-ray diffraction with Rietveld analysis. A 50-mg sample was sealed in a titanium can and irradiated

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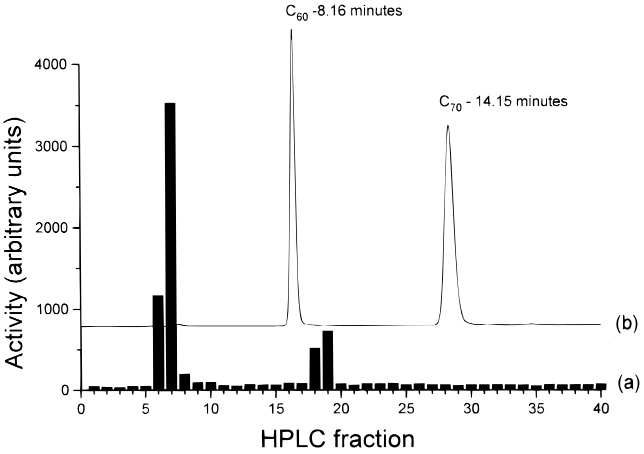

Figure 1. (a) Activity measured from the HPLC fractions using the assay counter, (b) UV absorption measured from an HPLC of a standard solution containing C_{60} and C_{70}. The absorption axis is not shown.

with a neutron flux of ~5 × 10^{13} neutrons cm^{-2} s^{-1} for a period of 4 h. γ spectroscopy was performed on both the solid and toluene solutions using a high-resolution γ spectroscopy system with a resolution of 1.9 keV at 1.33 MeV (^{60}Co). HPLC was carried out on 150−280-μL samples of toluene solutions using a Waters LC626 HPLC system with toluene as the mobile phase and using a Cosmosil packed column (no. 091−3113, SES Chemicals Inc.). The column had a capacity to handle up to ~110 mg of injected fullerenes at any one time. In our case we injected at most a ~0.1−0.2-mg fullerene sample. The HPLC had a Waters 486 tunable detector for measuring UV absorption, during the HPLC run. Activity from the HPLC fractions was measured using a Wallac Wizard 1470 γ counter.

Results and Discussion

The irradiated solid Xe fullerene was added to toluene and left to make a suitably concentrated solution. This was then decanted and processed further by (a) passing through a 0.2-μm filter, (b) shaking and nitrogen purge, and (c) complete evaporation and redissolving the solid in toluene. A solid sample of a few milligrams was used as a standard for γ spectroscopy. A γ spectrum from the solution was taken initially before any processing and subsequently after each step. As found previously[6,7] the activity from the Xe radionuclides as shown by γ spectroscopy reached a constant value.

If the residual activity is associated with an endohedral rare gas C_{60} species, we might expect that HPLC of this sample would show a discernible radioactive fraction associated with the proposed endohedral species and eluting after C_{60}. The use of HPLC to differentiate endohedral radionuclides has already been shown by Kikuchi et al.,[8] who found that ^{159}Gd@C_{82}, ^{161}Tb@C_{82}, and ^{153}Gd@C_{82} all eluted at the same time. Once the activity from the processed solution reached this constant level, a 150-μL sample was passed through a 0.22-μm filter using a microcentrifuge and then was injected into the HPLC and 0.5-mL fractions were collected every 0.5 min for 25 min. The UV spectrum was monitored continuously at a wavelength of 285 nm as the samples were collected. Before injection of the radioactive sample, a standard trace was run by injecting a 20-μL sample of C_{60} and C_{70} (each ~0.5 mg mL^{-1}). We found that C_{60} eluted at ~8.5 min wheras C_{70} eluted at ~14 min as shown in Figure 1b. Also seen in Figure 1b are the indication of weak peaks after the elutions of C_{60} and C_{70}. These are associated with epoxide $C_{60}O$ and $C_{70}O$ species, respectively. The processed radioactive Xe/C_{60} fullerene solution was then injected into the HPLC, and it was observed that the C_{60} eluted in fractions 16 and 17 as expected, which appeared red purple and purple, respectively, while fractions 15 and 18 were completely colorless. The actual UV chromatograph showed the C_{60} peak completely off scale and also showed the epoxide peaks more clearly. We expected the endohedral C_{60} rare gas species to elute somewhere between the times of C_{60} and C_{70}. The collected fractions were measured on the γ counter for activity with a 10-s count time and monitoring all X-ray/γ rays with energies within 5−300 keV. The results are shown in Figure 1a. As can be seen, activity appeared in only two elution periods. The first appears just after the dead time for elution and occurs in fractions 6 and 7 (collected between 3 and 3.5 min). This is obviously not associated with any fullerene species. The second period of activity was noted for fractions 18 and 19 with the latter having the higher activity (collected between 9 and 9.5 min). These two fractions occur after the fractions where free C_{60} is eluted and are attributed to endohedral C_{60} species.

The radionuclides associated with the active HPLC fractions were identified by γ spectroscopy. Figure 2 compares the γ spectra for the solid, injected solution, and relevant HPLC fractions. All the spectra were taken within a period of ~3.5 h so that decay of the radioisotopes is small enough so as not to be a major issue in comparing the spectra. The spectra have been shifted and sized appropriately for the sake of comparison. The major isotopes to consider are ^{125}I, ^{125g}Xe, ^{133g}Xe, and ^{135g}Xe. The γ spectra from the processed solution before injection is shown in Figure 2b, and the residual Xe rare gas activity was found to be ~1−2% of an equivalent amount of undissolved solid, as found previously.[6,7] It was also found, by considering the X-ray emission of ^{125}I at 27.3 keV, that this was not effectively driven off in the process of evaporating the toluene solution to dryness and ~60−80% was retained. Whereas the residual rare gas indicates an endohedral species, similar arguments for the ^{125}I cannot be used. Figure 2d shows the γ spectrum from HPLC fraction 7, which as shown in Figure 1 had activity. The γ spectrum can be assigned solely to ^{125}I. This shows that ^{125}I passes through the column quickly with very little retention. Figure 2c shows the γ spectrum from HPLC fraction 19, which from Figure 1 is one of the later fractions which had activity. This fraction together with 18 is postulated as being associated with an endohedral C_{60} rare gas species. The γ spectrum supports these arguments further in that we observe the Xe radioisotopes with these fractions.

HPLC fraction 18 showed a γ spectrum similar to that of fraction 19. The other fractions were measured with γ spectroscopy, and from emissions associated with the individual radioisotopes, a plot of radioisotope activity (arbitrary units) versus HPLC fraction was constructed. This is shown in Figure 3. Included in the figure is a plot of the estimated weight (in milligrams and multiplied by a factor of 2000) of free C_{60} for each of the fractions 16 and 17. This was estimated from UV absorption. The activities from the Xe radioisotopes have also been multiplied by a factor of 25 so as to be comparable to the ^{125}I.

The fact that the Xe radioisotopes are eluted at a time just after the fractions of C_{60} and over a similar number of fractions is very convincing evidence that the eluted fractions 18 and 19 are associated with endohedral Xe@C_{60} species. It is expected that a Xe atom inside the cage will not appreciably change either the chemical nature of the C_{60} molecule nor its size, and hence, we might expect it to elute a short time after C_{60} on account of the heavier mass. Although C_{70} has a mass similar to that of a Xe@C_{60} molecule, its smaller size means that it will still elute

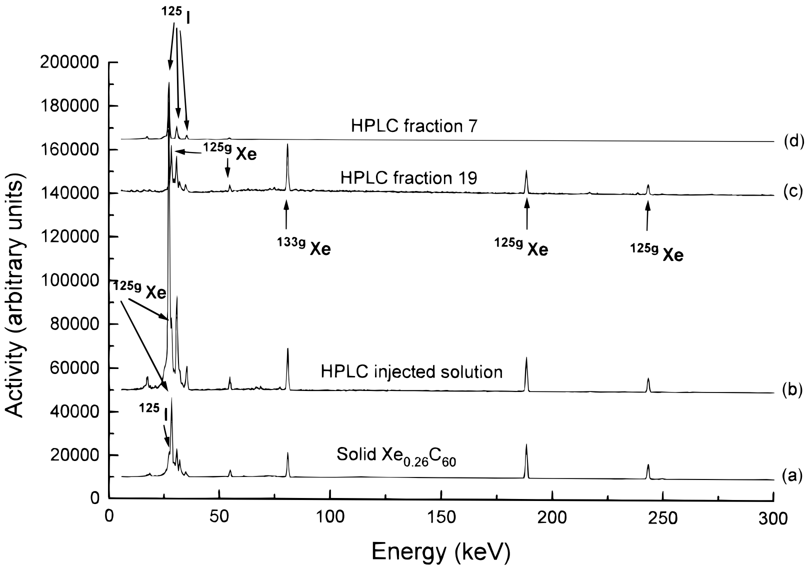

Figure 2. γ spectra showing the relevant radioisotopes from (a) solid $Xe_{0.26}C_{60}$, (b) the HPLC solution before injection, (c) HPLC fraction 19, and (d) HPLC fraction 7.

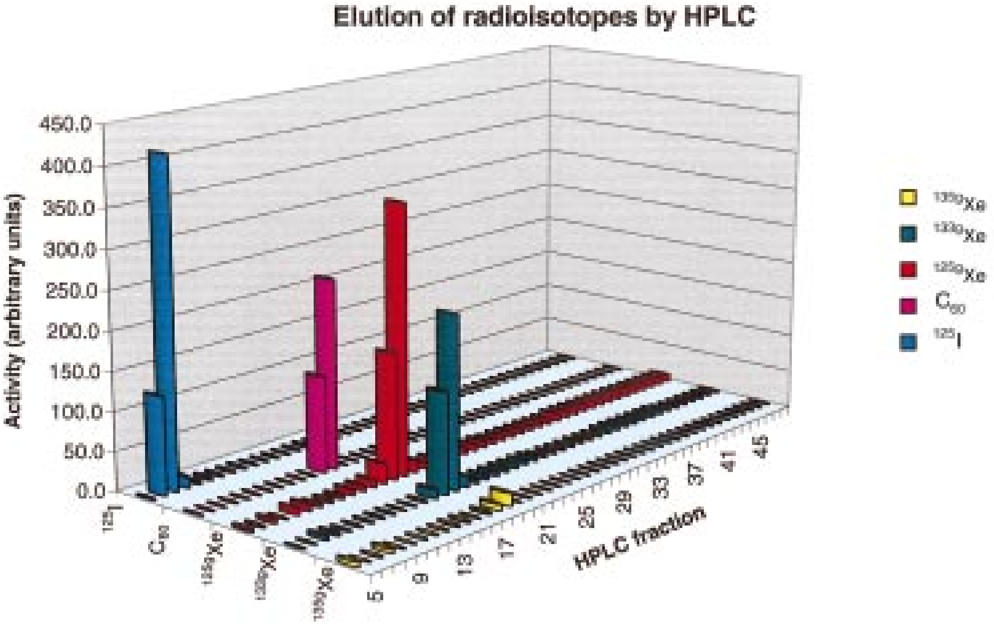

Figure 3. 3D plot showing the activity for the relevant radioisotopes as found in the HPLC fractions and deduced from the γ spectra. Also shown is the estimated weight of C_{60} as determined by UV absorption for fractions 16 and 17.

before C_{70}. Gromov et al.,[11] by studying HPLC of Li@C_{60}, found by using CS_2 and a Cosmosil analytic column that the endohedral species eluted after C_{60} with retention times of 5.8 and 4.5 min, respectively. Of more relevance to these experiments, Ohtsuki et al.[12] studying endohedral formation of Be atoms into C_{60} cages using the ^{7}Li (p,n)^{7}Be nuclear reaction found, by using HPLC with a Buckyclutcher column and using CS_2 as the elutant, that ^{7}Be@C_{60} eluted ~0.5 min after C_{60}, which eluted at ~7 min. In their HPLC runs they also used the activity to monitor the ^{7}Be and UV to monitor the free C_{60} elutions. Although the epoxide $C_{60}O$ elutes around fractions 18 and 19, the observed radioactivity cannot be associated with this species since any O and C radioisotopes produced have very short half-lifes. However, if we were able to achieve a higher level of detection, we might expect to observe activity in a fraction after 19 that might be assignable to Xe@C_{60}O.

The sum of the activities from fractions 18 and 19 as compared to an equivalent amount of Xe/C_{60} solid provides the best measure of estimating the efficiency of the recoil process. The HPLC fractions can be related to an amount of dissolved Xe/C_{60} solid by using UV absorption to estimate the amount of free C_{60} in fractions 16 and 17. We found the residual activity for the radioisotopes, as compared to their activity in an equivalent amount of solid, to be much lower than we previously found for the processed solutions, but they still showed the same trend. The residual activities were found to be ~0.2, 0.35, and 0.65% for ^{125g}Xe, ^{135g}Xe, and ^{133g}Xe, respectively. These results probably represent the lower limit while the solution values[6,7] represent an upper limit. At this stage, we feel on account of

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the complexity of measuring these values accurately that our figures are only semiquantitative. These residual values also indicate that the radioisotopes do not have the same propensity for encapsulation, and it appears that ^{133g}Xe has the highest propensity for forming the endohedral species. This can be seen from the γ spectra shown in Figure 2. If we compare the γ spectrum from fraction 19 (Figure 2c) to the γ spectrum from the Xe/C_{60} solid (Figure 2a), there appears to be relatively more ^{133g} Xe than ^{125g} Xe in the former spectrum. If fractions 18 and 19 were associated with free Xe gas, which for some strange reason eluted only in these two fractions, we would have expected a γ spectrum identical to that of the solid. The HPLC solution before injection does appear to have contained some free Xe since its γ spectrum shown in Figure 2b is between that of the solid and HPLC fraction 19. However, there was no evidence of Xe radioisotopes eluting in the fractions where ^{125}I eluted (fractions mainly 6 and 7). However, the γ spectra of the fractions from ∼10 onward did show a very weak contribution from Xe radioisotopes. The sum of the contributions for each of the Xe radioisotopes from fractions 10−48, excluding the γ spectra from 18 and 19, was found to be comparable to the sum of those found from fractions 18 and 19. This activity is attributed to free Xe gas as well as from a broad distribution of other encapsulated species, e.g. smaller and larger cages produced from C_{60}. This is also based on the fact that the ratio of activities for ^{125g}Xe and ^{133g}Xe was found to be between that of the solid and HPLC fractions 18 and 19.

In conclusion, these preliminary results, which have been shown to be consistent in repeated experiments, indicate strong evidence for endohedral formation by γ recoil from (n,γ) reactions as proposed by Braun et al.[1] As mentioned in our previous papers,[6,7] there is no correlation between the maximum recoil energy available and the postulated percentage of encapsulation. The amount of recoil energy of the Xe radionuclides is more than enough to penetrate a C_{60} cage. For ^{133g}Xe, it is 256 eV, whereas for ^{125g}Xe, it is 165 eV. Regardless of these values, we find a higher yield for ^{133g}Xe. To understand the mechanism, the actual nuclear decay scheme for the produced radionuclide needs to be known in order to obtain the recoil energy distribution. Unfortunately full details on prompt γ emission from Xe radioisotopes are not currently available. Not only this but also processes in the solid as well as in the actual C_{60} molecules that allow excess energy to be dissipated need to be addressed. Other interesting aspects which we are still investigating include the fate of ^{125g} Xe@C_{60} as the ^{125g}Xe decays to ^{125}I. Due to the long half-life and hence low activity of the ^{125}I, we have not as yet conclusively identified a fraction associated with ^{125}I@C_{60}. This also does not rule out that the ^{125}I recoils out of the cage on formation. We also observed in our later experiments a very weak activity for the Xe radioisotopes peaking at about ∼20 min and spread over at least 10 fractions. This could well represent Xe encapsulated in larger dimerized fullerene species. This is not apparent from Figure 1 in this paper, which collected activity over a whole range of energies, but is slightly apparent in Figure 3 constructed from the γ spectra. Similar broad peaks were observed by Ohtsuki et al.[13] and Mitch et al.[14] in HPLC studies of ^{11}C production in fullerene cages which they have attributed to either dimers or graphite nanoparticles. γ spectra collected over longer periods showed this more clearly and will be discussed further in a future paper.

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