From $^3He@C_{60}$ to $^3H@C_{60}$: Hot-Atom Incorporation of Tritium in C_{60}

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The introduction of tritium into the cavity of C_{60} using hot-atom chemistry was studied. Neutron irradiation of ^3He in $^3He@C_{60}$ produced tritium ions and atoms which enter the C_{60}. $^3H@C_{60}$ was detected with a scintillation counter. The Bingel reaction was carried out on this material under conditions so that the monoadduct formed predominantly, and the products were probed for tritium activity. Analysis with ^3He NMR gave a peak with the characteristic ^3He shift for the malonate product. The product fractions gave only 33% of the original activity; most was recovered in the unreacted C_{60} portion. No reaction was observed between C_{60} and the stable radical di-*tert*-butylnitroxide; all tritium activity was recovered in the C_{60} peak. These results suggest similarities in properties between $^3H@C_{60}$ and pure C_{60}, implying that the tritium exists as a free atom inside the molecule.

Introduction

Hot-atom chemistry involves the study of chemical reactions using species produced by nuclear reactions, with kinetic energies well above thermal energies.[1−3] The reagent can be "hot" by virtue of its radioactivity. The fast atom is decelerated by colliding with surrounding material, causing ionization before it is eventually thermalized. It may react before that happens, generating products quite different from those found in a thermal reaction. We used this technique to incorporate tritium in C_{60}, trapping it inside the fullerene cage where it is detected with a scintillation counter.

We have heated fullerenes in the presence of noble gases at a temperature of 650 °C and a pressure of 3000 atm and have incorporated gas atoms inside the fullerene cage.[4,5] The hot-atom reaction, on the other hand, provides the tritium atom enough energy to pass through one of the rings in the fullerene. Once inside, it may not have enough energy to escape.

We previously found that tritium can be incorporated inside C_{60} by first preparing the tris-lithium salt of the fullerene and then subjecting it to neutron irradiation in a nuclear reactor.[6] The nuclear reaction of ^6Li with thermal neutrons is

$$^{6}\mathrm{Li} + {}^{1}\mathrm{n} \rightarrow {}^{3}\mathrm{H} + {}^{4}\mathrm{He} + 4.8\ \mathrm{MeV} \qquad (1)$$

The exothermicity is calculated as $\Delta E = \Delta mc^2$. A 20-min irradiation of the salt yielded material containing tritium. Tritium undergoes β^- decay to form ^3He with an energy of 18.6 keV. By conservation of momentum, almost all the energy is carried away by the β^- particle and the antineutrino. The recoil energy of the ^3He is only a few electron volts, not enough to knock it into or out of the cage.

One main concern was that all or part of the detected tritium activity could have resulted from tritium bound chemically to the exterior of the fullerene cage. However, if that were the case, β^- decay would yield ^3He on the outside of the cage, which will diffuse away. A sample stored over 15 months yielded ^3He when heated and analyzed in a highly sensitive mass spectrometer by Poreda.[6] The amount of ^3He detected from this sample agreed closely with the amount of tritium that had decayed over this time. Therefore, the tritium must have been inside the fullerene.

There are two serious drawbacks in the preparation of $^3H@C_{60}$ using the tris-lithium salt precursor. The preparation of the salt is not trivial, since it must be done in the absence of air. The anion is a radical, which makes it susceptible to radiation damage. Each tritium atom produced in the reactor is accompanied by 4.8 MeV of energy and creates free radicals and ions that can react with the anion radicals. Finally, after the irradiation, the fullerene salt must be converted back to C_{60}. This may contribute to product loss.

A possibly cleaner and easier preparation involves ^3He as the tritium source:

$$^{3}\mathrm{He} + {}^{1}\mathrm{n} \rightarrow {}^{3}\mathrm{H} + {}^{1}\mathrm{H} + 760\ \mathrm{keV} \qquad (2)$$

The nuclear reaction 2 dissipates only 16% of the energy of reaction 1, involving ^6Li; radiation damage should be reduced. Given our work with the high temperature and pressure incorporation of fullerenes, $^3He@C_{60}$ was clearly a natural choice for this investigation. Neutral C_{60} is likely to be less susceptible to radiation damage than the anion radical, as in the lithium salt. Moreover, isolation of the irradiated material is easily accomplished with any solvent that dissolves C_{60}. There is no fullerene recovery step. A further simplification is perhaps activation of free ^3He gas in the presence of the solid fullerene.

Wilson et al. reported that neutron activation of the metallofullerene $^{165}Ho@C_{60}$ yielded $^{166}Ho@C_{60}$, which subsequently decays to stable ^{166}Er with the emission of a β^- particle.[7] Conversion from ^{165}Ho to ^{166}Er occurs without release of the atom from the C_{60}. Similar investigations have also been made with La, Y, Tb, and Gd@C_{60} by other researchers.[8,9] Braun[10−12] and Gadd[13−15] have made $^{41}Ar@C_{60}$ by irradiating C_{60} in the presence of ^{40}Ar. Ohtsuki[16,17] has made Be@C_{60} by two nuclear reactions. If the nuclear reaction producing the hot atom yields two or more heavy particles as in reactions 1 and 2, the initial recoil energy of the hot atom is large enough to allow it to leave a fullerene cage and, subsequently, enter another. If the

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TABLE 1: Tritium Activity Prepared from Three $^3He@C_{60}$ Samples

	sample		
	1	2	3
irradiation time (hr)	2	10	10
sublimed	yes	yes	no
specific activity (dpm/mg)	4.0×10^4	2.2×10^5	2.5×10^5
soluble portion	~100%	~100%	~100%

nuclear reaction gives one heavy particle and one or more light ones (e.g., γ rays or β^- particles), the recoil energy of the heavy particle will be much less, and it may remain trapped in the fullerene cage.

An important question is the structure of $^3H@C_{60}$. Recent work by Weidinger et al.[18−21] involving ion implantation of nitrogen in C_{60} showed, by ESR spectroscopy, that the nitrogen is present as a free atom inside the fullerene. Thiel[22] has done ab initio calculations on $H@C_{60}$ and found two structures of roughly equal energy. One is a free atom inside the middle of the cage; the other is a puckered structure with the hydrogen atom bound to one of the carbon atoms of the cage. Similar results were reported by Smith et al.[23] If the tritium is bonded to one carbon, then a neighboring carbon must have a radical site on it. This species might be expected to abstract a hydrogen or some other groups from the solvent; bind to O_2 or some other radical present; or dimerize. During the irradiation in a reactor, there is a relatively high concentration of radicals due to radiation damage.

Results and Discussion

The Irradiation. The irradiation conditions for $^3He@C_{60}$ were chosen initially so that they would produce radiation damage similar to that in the ^6Li case. The irradiation time was increased to account for the smaller energy release of ^3He as well as the lower concentration of $^3He@C_{60}$. The number of tritium atoms, N_T, produced in a run is given by

$$N_T = \sigma F t \tag{3}$$

where σ is the thermal neutron cross section of the nucleus, F the neutron flux, and t the irradiation time. The cross section for ^3He is 5333 b (1 barn = 10^{-24} cm^2) and that for ^6Li is 940 b.[9] Most other nuclei have thermal neutron cross sections of the order of only 1 b. In the lithium case, there are three lithium atoms per C_{60} whereas for $^3He@C_{60}$, there is only 0.002 ^3He per C_{60}, the maximum yield obtained by the high temperature and pressure process. In addition to the longer irradiation time, a higher neutron flux was applied. The irradiation was done in the High-Flux Breeder Reactor at Brookhaven National Laboratory using a neutron flux of 7.5×10^{13} cm^{-2} sec^{-1}.

We expected a comparable amount of insoluble material as in the earlier irradiation with the lithium salt but saw almost none. We irradiated the next two samples at five times the dose level and again found little decomposition. One recurring problem in the irradiation of the tris-lithium salt was radiation damage. Increasing the irradiation time led to a corresponding decrease in the yield of soluble product.[6] We thought, at first, that small amounts of solvent or air trapped between C_{60} molecules in the crystal lattice promoted decomposition when they dissociate into radicals during the irradiation and subsequently react with the C_{60}. Subliming the crude C_{60} prior to irradiation should remove these impurities. The data are given in Table 1. As the results show, these fears were ungrounded. The sublimation proved unnecessary. The same specific activity was obtained for the sublimed and unsublimed starting material. A specific activity of 2.5×10^5 dpm/mg corresponds to a fractional incorporation of 3×10^{-6} tritium atoms per C_{60}.

TABLE 2: HPLC Fractionation of $^3H@C_{60}$

fraction	normalized activity (counts/min)
parent	139.40
fract. 1	48.66
fract. 2	54.41
fract. 3	16.37
fract. 4	4.64
fract. 5	2.57
fract. 6	2.54
fract. 7	18.28
total (1−7)	147.47
$\Delta_{\text{total}-\text{parent}}$	8.07

The maximum specific activity of tritium obtained from the ^6Li irradiation was only as high as 410 disintegrations/min/mg. Irradiation of $^3He@C_{60}$, on the other hand, gave an enhancement of as much as 600 times in tritium activity! Moreover, sample recovery was excellent. Even after an irradiation period of 10 hours, almost all the material was recovered. In the lithium case, more than 58% of the fullerene decomposed after just 20 min of irradiation. Increasing the irradiation time gave a somewhat higher specific activity but with an accompanying increase in decomposition.

Forming $^3H@C_{60}$ from $^3He@C_{60}$ is indeed attractive. Not only is the yield of tritium-labeled material increased significantly, but also sample preparation and product isolation are greatly simplified. The high temperature and pressure process to prepare $^3He@C_{60}$ is also quite straightforward and routinely carried out in our laboratory. Its main limitations are, however, the low yield of $^3He@C_{60}$ and the decomposition of the fullerene material. We considered the possibility of producing a higher, if not similar, level of $^3H@C_{60}$ in a process independent of the initial amount of ^3He-labeled material. An obvious possibility is activation of free ^3He gas to form ^3H in the presence of the solid fullerene.

A sample containing 30 mg of pure C_{60} and $^1/_2$ atmosphere of ^3He gas sealed in a 3 cm-long quartz ampule was irradiated. The use of a relatively low pressure means that most of the tritium stops in the solid C_{60} rather than in the gas. The sample was irradiated for 2 h using the same neutron flux as before. A specific activity of 4.5×10^4 dpm/mg obtained from this material is comparable to a sublimed $^3He@C_{60}$ sample irradiated in the same amount of time. Recovery of the material is also ~100%.

Isolation of $^3H@C_{60}$. We have found[24−26] that column chromatography produces enrichment of $Kr@C_{60}$. Using high-pressure liquid chromatography (HPLC), we isolated over 90% pure $Kr@C_{60}$ from a mixture consisting of largely unlabeled fullerenes.[26] We wondered if the same methods can be applied to $^3H@C_{60}$. We found that separating the tritium-labeled fullerenes by chromatography can be challenging. At low resolution, $^3H@C_{60}$ chromatographed along with C_{60}. At higher resolution, using a four-foot long basic alumina column, the slowest fraction of the C_{60} peak has significantly higher radioactivity than preceding fractions, suggesting enrichment of the tritium-labeled C_{60}.

HPLC separation of the tritium-labeled C_{60} using a semi-preparative PYE [2-(1-pyrenyl)ethylsilylated silica] column corroborates our observations from column chromatography. Results are shown in Table 2. The C_{60} band was collected in seven fractions. The peak containing unlabeled C_{60} was divided approximately into two equal fractions, Fractions 1 and 2. These two fractions contain 70% of the overall activity. Activity of

TABLE 3: Tritium Activity of the Bingel Products of $^3H@C_{60}$

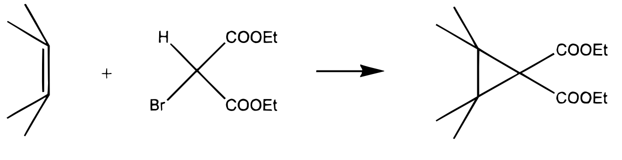
	specific activity (dpm/mg)	mass (mg)	product
starting material	8.9×10^3	25	C_{60}
fastest fraction	6.9×10^3	3	C_{60}
middle fraction	1.3×10^3	12	C_{60} and monoadduct
slowest fraction	2.1×10^3	13	mono- and bisadducts

subsequent fractions declined rapidly to background. The sum of the activity of all fractions is comparable to the activity of the original material. The increase in activity in Fraction 7 is most likely due to the monoxide product. Its retention time is comparable to $C_{60}O$ and was probably formed over time with storage of the material.

The HPLC results demonstrate the possibility of isolating $^3H@C_{60}$ from C_{60} as in the case of $Kr@C_{60}$.[26] More important, they provide a glimpse at the structure of $^3H@C_{60}$. If the tritium atom were unbound in the center of the cage, we would expect the retention time to be close to that of empty C_{60}. If the tritium were bound to one of the cage carbons, radical sites would be generated on the C_{60} when the carbon−tritium bond forms. In this case, HPLC might produce a large separation of the empty C_{60} from those fullerenes containing radical sites. The two species would be well resolved from each other. No activity should therefore be detected in the C_{60} fraction. This was clearly not the case. Instead, all activities were recovered in the C_{60} portion. The $^3H@C_{60}$ must have properties, at least those relevant to separation on a column, very similar to C_{60}, suggesting that the tritium has to be present as a free radical inside the C_{60}.

We also tried vacuum sublimation to enrich $^3H@C_{60}$. The sample was placed in the bottom of a fused silica tube and heated gradually. Solid was deposited on the cooler parts near the top of the tube. The sublimed material was radioactive, indicating that $^3H@C_{60}$ is volatile. However, the specific activity was only 5% of the starting material. The loss can be attributed to decomposition of the fullerene during the sublimation. We found that, typically, only 60−80% of the C_{60} sublimes. The tritium-labeled fullerene seems to be more sensitive to decomposition than the unlabeled fullerene. Trapped air and solvent molecules in the C_{60} crystal could have brought about decomposition of the molecules.

The Structure of $^3H@C_{60}$. Questions concerning the structure of $^3H@C_{60}$ were further investigated with a chemical reaction of C_{60}. The Bingel reaction[27,28] is a reaction that is simple and one in which the extent of functionalization can be easily controlled. The bromomalonate anion adds across one of the 6,6 double bonds (reaction 4). In our case, the reaction conditions were adjusted so that the monoadduct would form predominantly. The products were purified on a silica gel column using methylene chloride as eluent. Three bands were observed. Each was isolated and counted for tritium activity (Table 3).



The total product specific activity is only 3.4×10^3 dpm/mg, 33% of the activity of the resulting mixture. The specific activity of the first peak, the unreacted C_{60}, is about the same as the starting material, indicating that most of the loss occurred during the reaction. The cause of this discrepancy is unclear even as ^3He NMR indicates close to 90% conversion of the C_{60}. Perhaps a side reaction involving the radical character resulted in this loss. We wonder if the low tritium activities found in the products indicate differences in the reactivity of $^3H@C_{60}$ from C_{60} in which the former is discriminated in the Bingel transformation. This might explain the accumulation of counts in the starting material.

The presence of an appreciable portion of $^3He@C_{60}$ allowed additional analysis of the products with ^3He NMR spectroscopy.[29,30] The fastest eluting peak contains unreacted C_{60}, which gave a characteristic ^3He shift at −6.3 ppm. The second fraction contains the monoadduct, giving a peak at −7.9 ppm in the ^3He NMR spectrum. The third band contains a mixture of bisadducts which gave peaks between −8.5 to −9.8 ppm in the ^3He NMR.

Another reaction was carried out in which some of the tritiated material was mixed with di-*tert*-butylnitroxide, a stable free radical. If radical sites were indeed generated as a result of the tritium bonding to a carbon inside C_{60}, a reaction with di-*tert*-butylnitroxide might occur. This would result in a significant loss of activity in the C_{60} peak when the mixture is chromatographed. A new peak in a different position containing most if not all the radioactivity would be found instead. Our results did not seem to support the presence of radical species in the material. All the radioactivity was recovered in the C_{60} portion. No activity was detected in the di-*tert*-butylnitroxide fraction that eluted much later.

Experimental Section

Preparation of $^3He@C_{60}$ for Neutron Irradiation. ^3He-labeled C_{60} was prepared as reported previously: by heating C_{60} in the presence of ^3He gas at high temperature and pressure.[4,5] The $^3He@C_{60}$ sample used in this case was labeled twice: the product of one high-pressure run was used as the starting material for a subsequent run. This procedure doubled the fraction of C_{60} molecules containing ^3He to about 0.2%.

Neutron Irradiation of $^3He@C_{60}$. Between 30 and 40 mg of the $^3He@C_{60}$ sample was sealed in a fused silica tube under vacuum. It was irradiated in the High-flux Breeder Reactor at Brookhaven National Laboratory in port V-11 at a thermal neutron flux of 7.5×10^{13} n/cm^{2}sec. This port has a very low flux of fast neutrons and γ-rays, which can cause further radiation damage. In all, three $^3He@C_{60}$ samples were irradiated, each under slightly different conditions. Two samples were prepared with sublimed $^3He@C_{60}$. One was irradiated for 2 h, the other for 10 h. The starting material in the third sample was not sublimed; it was irradiated for 10 h. All the material was extracted in toluene for at least 7 days and purified by column chromatography, using basic alumina as the stationary phase and toluene as eluent. The activity of each sample before and after purification was measured with a liquid scintillation counter.

HPLC Fractionation of $^3H@C_{60}$. About 1.26 mg of tritium-labeled C_{60} was dissolved in 120 μL of *o*-dichlorobenzene, of which 30 μL of the solution was injected into a [2-(1-pyrenyl)-ethylsilylated silica] semipreparative column (COSMOSIL 5PYE, 20 mm i.d., 250-mm length, Phenomenex Inc.) to determine the distribution of radioactivity in the C_{60} peak. An injection of 60 μL of the remaining solution was made, and the C_{60} peak was collected in seven fractions. Each fraction was counted for radioactivity.

Bingel Transformation. To a 25-mg fraction of the irradiated material in toluene, one equivalent of diethyl bromomalonate was added. The reagents were mixed as one equivalent of DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) was introduced. The mixture was stirred for 1 h, concentrated to 1 mL, and chromatographed (SiO_2, CH_2Cl_2) to recover unreacted C_{60}, the monoadduct, and the bisadducts. The fractions were counted for tritium activity and analyzed with ^{3}He NMR.

Conclusions

Tritium incorporation inside C_{60} was accomplished using hot-atom chemistry by neutron irradiation of ^{3}He. The amount of radiation damage was very much smaller than was observed from the irradiation of the ^{6}Li salt of C_{60}. Yield was increased significantly: by more than 600 times over the neutron irradiation of ^{6}Li. The presence of large amounts of $^3He@C_{60}$ after the nuclear reaction provides an additional tool for the characterization of the isolated material by ^{3}He NMR spectroscopy.

Results from HPLC and the Bingel transformation show that the presence of radicals in the irradiated material is rather unlikely, implying that the tritium is not bound to a carbon atom inside C_{60} but more likely exists as a free atom inside the cage.

The ability to generate tritium from ^{3}He makes the incorporation process attractive from the standpoint of sample preparation, extraction, and yield. Forming greater quantities of tritium-labeled C_{60} might eventually allow its use as a radioactive tracer in a host of applications.

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