Article

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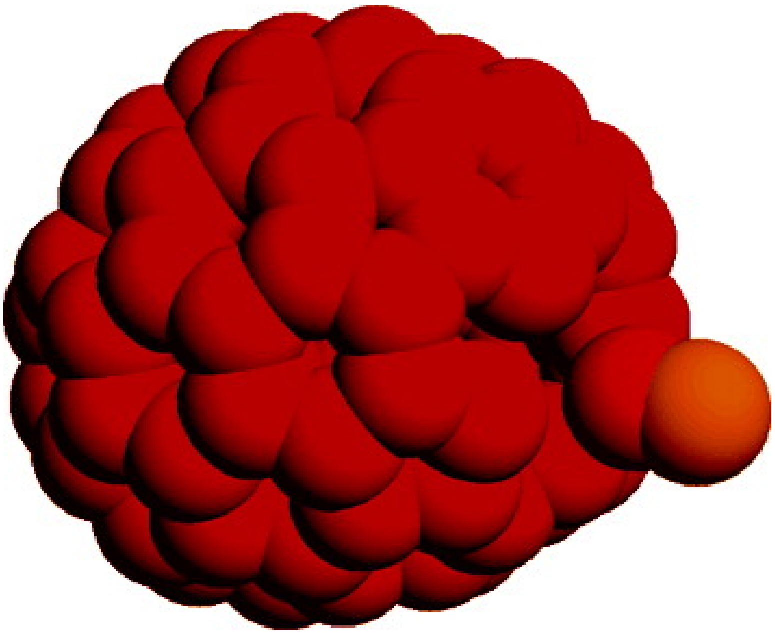

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Transmutation of Fullerenes

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Abstract: Fullerenes were pyrolyzed by subliming them into a stream of flowing argon gas and then passing them through an oven heated to ~1000 °C. C_{76}, C_{78}, and C_{84} all readily lost carbons to form smaller fullerenes. In the case of C_{78}, some isomerization was seen. Pyrolysis of $^3He@C_{76}$ showed that all or most of the ^3He was lost during the decomposition. C_{60} passes through the apparatus with no decomposition and no loss of helium.

Introduction

The formation of fullerenes by laser ablation of graphite or in a carbon arc is a complicated process. Initially, carbon atoms are produced, and they condense to form fullerenes, carbon nanotubes, and other less well characterized products. Although there has been much discussion about how these conversions might occur, it is fair to say that we do not know the detailed mechanisms. However, the products do not appear to be at equilibrium. For example, much more C_{60} is formed than C_{70}. Both theory and experimental thermodynamic results lead one to expect at least as much C_{70} to be present at equilibrium. Very high energy species, such as those which violate the isolated pentagon rule (IPR), are not found. Within each isomeric class of the higher fullerenes, the ratios of amounts seem to be much closer to the expected equilibrium distributions. It might well be that after the distribution of fullerene sizes is established, there is some kind of annealing process that interconverts isomeric structures. In an effort to detect such processes and to probe the latter stages of this complex sequence of reactions, we have heated fullerenes in the gas phase to study their reactions. To our surprise, we have found loss of carbon atoms at temperatures above 1000 °C as well as conversion of one isomer to another.

The current price of C_{60} is very roughly the price of gold. The price of C_{70} is about an order of magnitude larger, and that of higher fullerenes very much higher. A process to interconvert fullerenes could be useful in making higher fullerenes available at a reasonable price. So far, however, we have succeeded in the alchemist's equivalent of transmuting gold into lead.

The apparatus is shown in Figure 1. A long tube made of fused silica (quartz) is attached to an argon cylinder and passes through two ovens. A flow meter at the exit end measures the flow rate. A few milligrams of the fullerene sample are placed inside the tube in the middle of the first oven. At temperatures of 600−700 °C, the fullerene sublimes into the argon stream and is carried through the second oven. Reaction products then condense in the bend after the second oven. After the run, the products are dissolved and analyzed by high-pressure liquid chromatography (HPLC), using a PYE column.

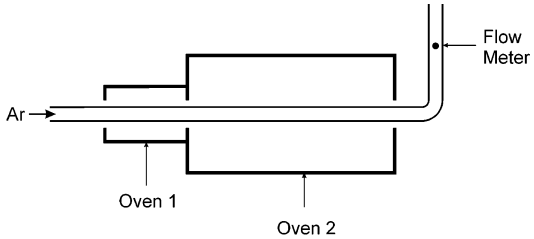

Figure 1. Schematic of the apparatus. The long tube is made of fused silica (quartz), 9 mm od and 7 mm id. It passes through two tube furnaces. The sample is placed inside the tube in the middle of the first oven. It sublimes into the argon stream and is carried through the second oven, condensing on the far side.

Experimental Details

Higher fullerenes were purchased from MER Corp. as a mixture. They were separated with HPLC using a semipreparative PYE column [2-(1-pyrenyl)ethylsilyl] (Cosmosyl 10 × 250 mm), with toluene as the eluent. The mixture contained a small amount of C_{70}, larger amounts of C_{76} and C_{78}, and some C_{84}. C_{70} and C_{76} are cleanly separated. C_{78} consists of three isomers that elute in two incompletely separated peaks, which we refer to as C_{78}A and C_{78}B. Previous work,[1] using ^{13}C NMR, has shown that C_{78}A is a mixture of one of the C_{2v} isomers and the D_3 isomer, while C_{78}B is the other C_{2v}' isomer and a small amount of the C_{2v} isomer. C_{84} is notoriously hard to resolve by straight HPLC analysis.[2,3] It comes off our HPLC as a broad peak containing a mixture of several isomers which blend into each other.

The fused silica tube is 9 mm od and 7 mm id. We introduce the fullerene sample as a solution in CS_2 into the tube using a long hypodermic needle and then evaporate the CS_2. The flow rate of argon is roughly 20 mL/s. The length of the second oven is 38 cm, so that the residence time at high temperature is about 40 s. Since the ends of

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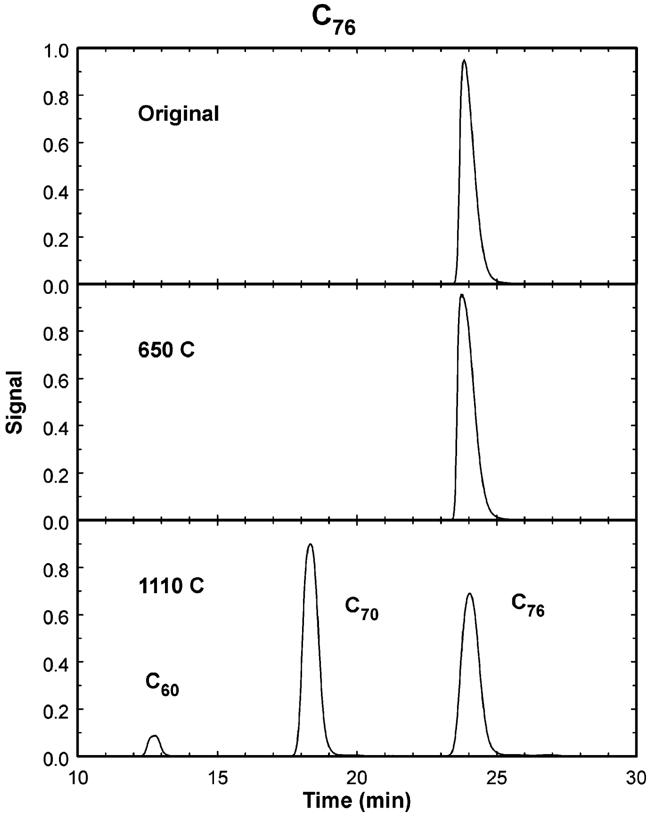

Figure 2. HPLC traces for C_{76}. The top panel shows the starting material. In the middle panel, the second oven is kept at 650 °C, the same temperature as that in the first oven. In the bottom panel, the second oven is at 1110 °C, and extensive decomposition occurs.

the oven are colder than the middle and since the flow rate fluctuates, this time is only approximate. The ovens are tube furnaces made by Omega Engineering and by Thermolyne. The temperatures are controlled by Omega controllers using Chromel−Alumel thermocouples positioned in the middle of the ovens.

After the run, the products are dissolved in CS_2 and reinjected into the HPLC. Much of the original fullerene sample is left unsublimed at the beginning of the tube. Crystals of fullerene almost always contain solvent molecules as well as small amounts of oxygen. When heated to the temperatures required for sublimation, reactions occur that produce polymeric, nonvolatile products, so that only about 25% actually sublimes. We frequently find a trace of black residue at the end of the tube which is insoluble in CS_2. After removal of the product, the tube is filled with oxygen and flamed with a glass-blowing torch to burn out any residue. The process is then repeated to ensure a clean surface in the reactor for the next run.

Results and Discussion

Figure 2 shows the results for C_{76}. The top panel is the HPLC trace of the starting material. In the middle panel, the second oven is held at 650 °C, the same temperature as that in the first oven. The C_{76} emerges unchanged. In the bottom panel, the second oven is at 1110 °C. Here, there is extensive decomposition to form C_{70} and a small amount of C_{60}. The detector on the HPLC apparatus uses visible light at 400 nm. By injecting known amounts of C_{70} and C_{76}, we calibrated the detector. The molar extinction coefficient for C_{70} is 20% lower than that for C_{76}, so roughly a third of the C_{76} has decomposed. The temperature is critical. If the oven is 50 °C colder, there is little decomposition; at 50 °C hotter, most of the C_{76} is gone.

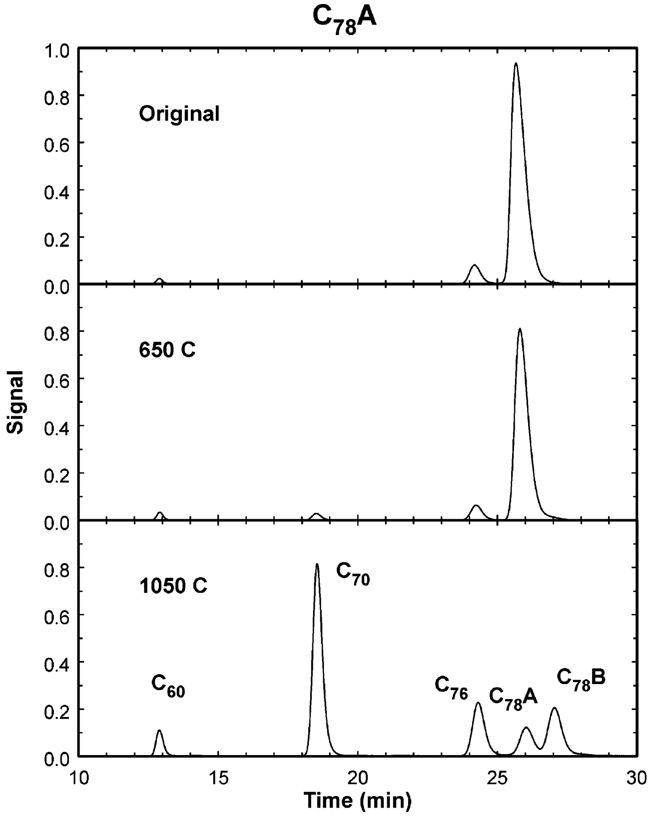

Figure 3. HPLC traces for $C_{78}A$. The original sample contains a small amount of C_{76} due to incomplete separation of the original mixture.

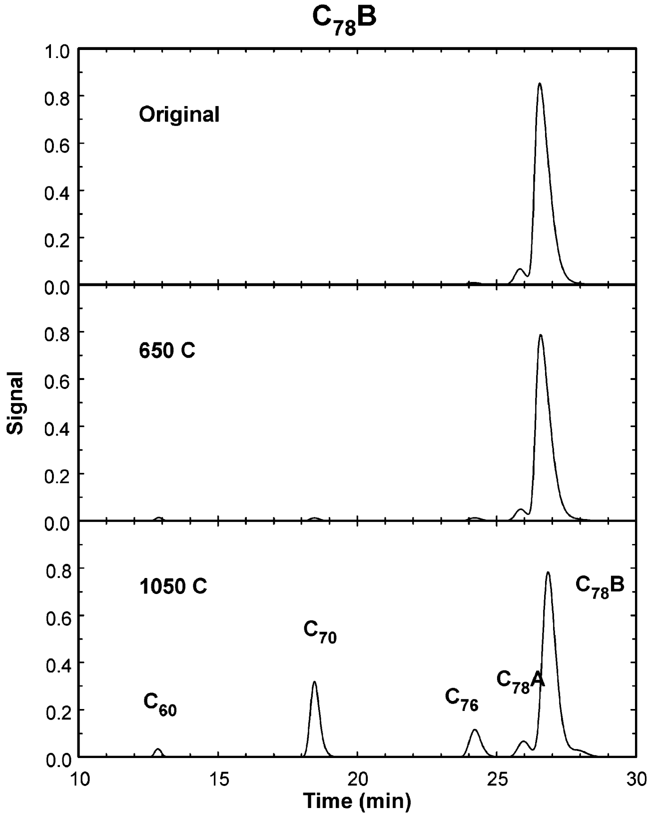

Figure 4. HPLC traces for $C_{78}B$. The original sample contains a small amount of $C_{78}A$.

Figures 3 and 4 show the results for the two peaks for C_{78}: $C_{78}A$ and $C_{78}B$. As the top panels show, the samples are not

Table 1. Calculated Energies

species	symmetry	E/C (kJ/mol)[a]
C_2	$D_{\infty h}$	426
C_6	$D_{\infty h}$	167
C_{60}	I_h	0.0
C_{70}	D_5	−3.8
C_{76}	D_2	−4.6
C_{78}	D_{3h}	−5.2
C_{78}	D_{3h}'	−4.1
C_{78}	D_3	−4.9
C_{78}	C_{2v}	−5.2

[a] Energies are calculated as energy per carbon atom, relative to C_{60}.

initially pure, due to incomplete separation in the initial HPLC run. C_{78}A has a small amount of C_{76}, and C_{78}B has a small amount of C_{78}A. Again, there is extensive decomposition to smaller fullerenes: C_{76}, C_{70}, and even C_{60}. In the case of C_{78}A, there is apparently a small amount of isomerization to C_{78}B since the size of the C_{78}B peak is significantly larger than it is in the starting sample.

We ran the first part of the peak for C_{84} at 1100 °C. As in the other cases, there was extensive decomposition to C_{78}A, C_{76}, C_{70}, and a small amount of C_{60}. There also appeared to be rearrangement to isomers appearing later in the HPLC separation. We ran C_{70} at 1110 °C and found no trace of C_{60}. Since our oven is rated at 1200 °C, we did not attempt a higher temperature. Since we saw small amounts of C_{60} formed at lower temperatures from C_{76}, C_{78}A, and C_{78}B, it would appear that this C_{60} cannot have been formed by a process that passes through C_{70} as an intermediate.

There are several possible mechanisms for the observed reactions. The simplest is that the fullerene molecule eliminates one or more carbon fragments, such as C_2 or C_6. To test this, we ran calculations using Gaussian 2003[4] using the B3LYP method and a 6-31G(d,p) basis set. The results are shown in Table 1. They are tabulated in energy per carbon atom relative to C_{60} to facilitate comparison. We see that the reaction

$$C_{78}\ (C_{2v}) \rightarrow C_{76}\ (D_2) + C_2 \tag{1}$$

is endothermic by 905 kJ/mol (216 kcal/mol), and that the reaction

$$C_{76}\ (D_2) \rightarrow C_{70}\ (D_{5h}) + C_6 \tag{2}$$

is endothermic by 1090 kJ/mol (260 kcal/mol). Reactions that are this endothermic are unlikely to occur to any extent in the gas phase. However, both reactions are favored in terms of entropy. The calculations for reaction 1 were extended to calculate the vibrational frequencies and, hence, the thermodynamic data. At 1050 °C and 1 atm, $\Delta G = 681$ kJ/mol (163 kcal/mol). This corresponds to an equilibrium constant of 1×10^{-27} (using a standard pressure of 1 atm), far too small for the reaction to be important.

There are two ways to overcome the large endothermicity. One is a radical chain reaction. A small amount of decomposition could give rise to small fragments that then add to other fullerene molecules causing them to decompose as well. Alternatively, the reaction could occur on the surface of the fused silica tube. The binding energy of the fragment to the silica surface greatly reduces the endothermicity. We ran the reaction with C_{76} as before, except that the tube was loosely packed with quartz wool, greatly increasing the surface area. If the reaction goes by way of radical intermediates, the rate should decrease substantially since collisions with the surface should remove the radicals. On the other hand, if the reaction occurs on a surface, the rate should increase. The experimental results were unchanged.

One mechanism, which avoids these problems, is where two fullerene molecules collide, join, and then separate into a larger and a smaller fragment. The problem with this mechanism is that we have never seen any fullerenes larger than the starting material. Of course, these larger species could be, or ultimately form, the insoluble residue that we find at the end of the tube. To distinguish between a unimolecular and a bimolecular reaction, we ran two samples of C_{76} under conditions as closely matched as possible. One sample was four times as large as the other. If the reaction is unimolecular, the fractional decomposition should remain unchanged. If it is bimolecular, the decomposition should increase. The larger sample gave much less decomposition than the smaller sample, 7 versus 50%. Clearly, the mechanism is more complicated than a simple unimolecular or bimolecular reaction.

Our group has developed techniques for putting noble gases inside fullerenes,[5,6] so it is natural to ask if the decomposition reactions open up a hole in the fullerene large enough to allow a helium atom to escape. We labeled a sample of higher fullerenes with ^{3}He using our high-pressure method. Since the yield of soluble product is low for higher fullerenes, we did not use the cyanide catalyst which works so nicely for C_{60}.[7] The labeled fullerenes were separated, as before, with HPLC. We then ran ^{3}He-labeled C_{76}. A ^{3}He NMR spectrum showed only the peaks for ^{3}He@C_{76} and ^{3}He$_2$@C_{76}, both seen before,[8] but no signal for ^{3}He@C_{70}. The sample was separated with HPLC and clearly showed the presence of C_{70} and a trace amount of C_{60}, although the extent of decomposition was not as much as that shown in Figure 2. From the peak area in the HPLC trace and our calibration of the detector sensitivity to C_{70} and C_{76}, we can predict both the position and the magnitude of the expected NMR signal for ^{3}He@C_{70}. This predicted value is approximately four times the noise level. Thus, most or all the helium escaped in the decomposition reaction. In a similar experiment, we ran ^{4}He@C_{60} through the reactor at 1100 °C.

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The fraction of C_{60} containing a helium atom (about 1%) was identical to that of the starting material. We have evidence[7] that when we put a noble gas atom inside C_{60} at 650 °C, some promoter, such as cyanide, is added reversibly to the C_{60} to open up the cage. We do not understand the detailed mechanism here either, but perhaps the two are related.

We set out to investigate the late reactions involving the formation of fullerenes in a carbon arc. We find at temperatures above 1000 °C that carbons are easily lost, and that rearrangements of isomers occur, but the mechanism is clearly complicated.

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