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Using Cyanide To Put Noble Gases inside C_{60}

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Abstract: After fullerenes are heated in the presence of a noble gas or an unreactive molecule at 650 °C and 3000 atm pressure, a small fraction of the fullerene molecules contain the atom or molecule. The incorporation fraction is greatly enhanced by adding potassium cyanide to the reaction mixture. The details of the preparation are described here.

Several years ago, we discovered that we could put noble gas atoms and other small molecules inside fullerenes by heating the fullerene in the presence of the gas for 8 h at 650 °C at a pressure of 3000 atm.[1−5] These noble-gas fullerene compounds are van der Waals molecules, since there is no chemical bond between the included atom or molecule and the carbon cage. They are very stable, nevertheless, since several C−C bonds must break in order for the molecule to escape. They can be sublimed under vacuum without decomposition.[6] Chemical reactions on the outside of the cage do not release the included atom.[3] In the case of ^{3}He[3,5,7,8] and, more recently, ^{129}Xe,[9] we can use NMR spectroscopy to study the compounds and their derivatives. However, the incorporation fraction, the fraction of recoverable fullerene containing the noble gas, was quite low: 0.1% for He, Ne, Ar, and Kr and about 0.03% for Xe. Many more experiments could be done if the incorporation were increased substantially.

Although we have used the high-pressure technique extensively, the mechanism for the incorporation is not yet known. Calculations show that it takes roughly 220 kcal/mol to push a helium atom through a six-membered ring,[10] far too high for a thermal reaction. Other processes involving bond breaking or the formation of triplet states require similar energies.[10] Thus, we are forced to conclude that the reaction involves more than a single fullerene molecule and a noble gas atom. It seems to require some sort of promoter that attaches to the fullerene, weakening bonds. The cage then opens, allowing the gas atom to enter. Finally, the process reverses to give the fullerene with the gas atom inside. Evidence for this comes from several experiments. If the reaction is allowed to go six times longer, the fraction of fullerene containing the noble gas increases only slightly, even though most of the fullerene and most of the gas are unused. However, if we dissolve the product, remove the insoluble component, and use the soluble part in a second high-pressure run, the incorporation fraction doubles. Repeating the labeling process six times shows a nearly linear relationship between the incorporation fraction and the number of times the sample was labeled. The linearity shows that the incorporation fraction is still well below the equilibrium value.[11,12] We tried using vacuum sublimed C_{60} without exposing it to air. The incorporation fraction dropped by a factor of 2. Clearly, there is something promoting the reaction, but it is being used up as the reaction proceeds. Discovery of a suitable promoter or catalyst might greatly enhance the incorporation fraction.

We tried traces of O_2, various organic solvents, and several hydrocarbons. None gave more than 20% increase. We then tried KCN. Komatsu and co-workers[13,14] found that finely ground mixtures of C_{60} and KCN reacted in the solid state to form appreciable amounts of C_{120}, a dimer where two C_{60} molecules are attached to each other by a four-membered ring. One possible mechanism is the addition of CN^- to a double bond in C_{60} to form a radical anion which then adds to the double bond of a neighboring C_{60} molecule. The resulting radical site on the second C_{60} then causes the elimination of the CN^- to form the dimer. Since KCN is a stable, molten salt at 650 °C, it seemed a likely choice. Grinding a small amount of KCN and C_{60} in a mortar and pestle gives twice the normal incorporation of neon. Since C_{60} is almost certainly insoluble in molten KCN, the reaction probably takes place at the interface between the two. Therefore, grinding the mixture more finely should lead to a higher level of incorporation. Using a ball mill leads to an enhancement by over 1 order of magnitude compared to pure C_{60}. A recent mass spectrometric measurement on ^{3}He@C_{60} and ^{4}He@C_{60} showed incorporation fractions of 1%.[15] Measurement on Kr@C_{60} prepared with KCN showed an incorporation fraction of 0.26%.[16] We describe below the detailed experimental procedure and the results of some experiments comparing the incorpo-

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TABLE 1. Yields and Incorporation Fractions

sample	incorp fract[a]	yield[b] (%)
single[c]	1	11
double[d]	2.1	7.5
no KCN[e]	0.04	87

[a] Fraction of C_{60} molecules containing ^4He. The numbers are relative to the singly labeled sample. An absolute determination was done on a singly labeled sample prepared in the same manner and gave and incorporation fraction of 1%.[15] [b] The amount of soluble fullerene product divided by the initial amount of C_{60}. [c] Prepared with KCN as described in the text, starting with C_{60}. [d] Prepared with KCN as described in the text, starting with the singly labeled sample. [e] Prepared without KCN.

ration between samples with and without KCN and with a sample that was labeled twice using KCN.

Three samples of $^4He@C_{60}$ were prepared as described above and combined. About 100 mg of the product was used as the starting material for another run. A third sample was prepared with no KCN. The results are shown in Table 1. It is clear that, while the yield of soluble product was considerably higher in the sample without the KCN, the incorporation fraction is 20 times higher using KCN. Overall, more $^4He@C_{60}$ is formed using KCN. The higher incorporation fraction makes an important difference in most experiments. The length of time required to take an NMR spectrum is inversely proportional to the square of the incorporation fraction. Separation of the product using HPLC is greatly facilitated by using a higher initial concentration. As Table 1 shows, the doubly labeled sample gave twice the incorporation of the singly labeled sample. Thus, even at 1% incorporation, we are still well below equilibrium.[11,12]

How can we increase the incorporation fraction still further? The one factor that consistently appears important is how finely ground the sample is. Grinding for only 4 min decreases the incorporation fraction; grinding for 20 min makes no further improvement. Putting more C_{60} in the ball mill decreases the incorporation. There are devices that grind much finer than our ball mill. Perhaps that would give an increase, but they are quite expensive, and there are problems handling very fine powders, particularly in pumping the air out of them. There may be other promoters that are more efficient than KCN. We tried KOH and LiI, but the first destroyed the sample completely, and the second did nothing. The material must be stable at 650 °C and should be a liquid so it covers the crystals of fullerene. These conditions severely limit the choices.

How does the KCN promote the reaction? Unfortunately, we really do not know. This is obviously a complex series of reactions. CN^- is known to add to C_{60}. Somehow the addition of one or more CN^- groups must weaken the C–C bonds so that the molecule opens up enough to get a xenon atom inside. The process must be reversible, at least some of the time, to produce $X@C_{60}$. There seems little that we can do experimentally to pin down the mechanism, but perhaps theoretical calculations might help. We have found that KCN enhances the incorporation in C_{70}, but the yield of soluble product is very small. Since the incorporation without cyanide is considerably higher than in C_{60} and since the cost of C_{70} and higher fullerenes is so much greater, it does not appear to be worth using cyanide for these cases.

We have already used the cyanide technique in several experiments. We were able to separate $Xe@C_{60}$ from the unlabeled C_{60} using HPLC.[9] The time-consuming step is the first stage of separation, where a great many small samples must be injected. If we had to start with 10 times the amount of material with one tenth the incorporation, the separation would have been impossible. We have used the cyanide technique to make quantities of $Kr@C_{60}$. This has led to an X-ray structure[17] and will probably lead to other measurements. In experiments involving ^3He NMR we can now take spectra in several minutes that once took 8 h.

Experimental Section

To summarize, a copper tube is crimped sealed at one end. The crimp forms a cold weld that gives a high-vacuum seal. A mixture of fullerene and KCN is put into the tube. The air is pumped out, and the appropriate gas is added, and the other end of the tube is crimped to form a sealed ampule. Two of these ampules are placed in a high-pressure vessel, which is then filled with water and closed. The vessel is then heated to 650 °C. The pressure increases to 3000 atm, and the soft copper ampule collapses, pressurizing the gas inside.

Oxygen-free, high-conductivity (OFHC) copper tubing $^1/_4$ in. in diameter is cut into 4 in. lengths. The cut ends are deburred, and the tubes are washed, inside and outside, with detergent. They are rinsed and dried with acetone. Using a die, about $^1/_4$ in. on one end of each tube is flattened in a hydraulic press. The tubes are then vacuum annealed. They are placed in a stainless steel cylinder, which is then connected to a vacuum line. The cylinder is put into a large tube furnace and slowly heated to 800 °C. At this point, about $^1/_4$ atm of dry hydrogen gas is admitted into the cylinder for about 20 min and then pumped out. The hydrogen reduces any copper oxide on the tubes. The tubes are heated for about 30 min longer at 800 °C and then slowly cooled. The annealing softens the copper, making the crimp seals stronger and more reliable. It is very important that the copper surfaces on the inside of the tubes be clean, or else the seal will leak, and the ampule will fill with water during the high-pressure run. After annealing, the tubes must be stored under vacuum to prevent them from oxidizing.

Two tubes are then crimp sealed on the flattened end. The crimping tool is a modified bolt cutter, where the cutting edges have been replaced by two steel cylinders $^1/_{16}$ in. in diameter. The middle of the seal is about 10 μm thick. If clean and annealed, the seal is vacuum tight and can be flexed without breaking. A seal on unannealed copper is brittle and breaks easily. Each tube is fitted with a funnel connected to a thin glass tube going halfway down the tube. This prevents the sample from contacting the top of the tube where the second seal will be made. Four samples are weighed out, each containing 100 mg of C_{60} and 20–30 mg of dry KCN. One sample is placed in the cup of the ball mill, Gilson model LC153. It is then ground for 8 min and poured through the funnel into the first tube. A second sample is then ground and added to the first. We have found that grinding 200 mg of C_{60} and 60 mg of KCN together produces a lower incorporation fraction, presumably because the large amount of material prevents it from being ground as finely. The funnel is then removed, and the top of the tube is cleaned with a small piece of Kimwipe wrapped around a wooden stick and moistened with benzene. Since the amount of KCN is roughly the lethal dose, the preceding steps should be carried out in a hood using gloves.

The tube is then attached with an adaptor to a vacuum line. The adapter consists of a glass joint, a stopcock, and a length of tubing. A short length of Tygon tubing connects the copper tube to the end of the glass adapter. The second tube is prepared in

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the same manner. Both tubes are then slowly pumped down. If the air is removed too rapidly, the fine powder will be blown up into the vacuum line and will cover the region on the copper tube where the top crimp seal is to be made, causing the seal to leak. The vacuum line is equipped with Teflon stopcocks that can be opened very slowly. After several hours the stopcocks can be opened fully, and the samples are pumped out overnight under diffusion-pump pressure.

Each tube is then filled to about 3 atm with the appropriate gas. For noncondensable gases such as He or Ne, the tube is cooled with liquid nitrogen and filled with an atmosphere of gas. For condensable gases such as krypton and xenon the ampule is filled with a fraction of an atmosphere, and the gas in the whole vacuum line is then condensed into the tube using liquid nitrogen. The tube, still cooled to liquid nitrogen temperature, is then sealed by crimping near the top. It is warmed and removed from the glass adapter. Each ampule is then slightly flattened with a pair of pliers parallel to the two crimp seals. This makes them fit more easily into the high-pressure vessel and, when they collapse, they flatten uniformly. Otherwise, they twist into a pretzel shape, and it is difficult to remove them from the vessel.

The high-pressure vessel was custom-made by Autoclave Engineers. It consists of a cylinder of René steel 7.6 cm in diameter and 44 cm long with a hole 1.3 cm in diameter bored down the center. The two ampules are placed in the bore and pushed to the bottom. The bore is then filled with water, and a calibrated amount of water is removed. The final pressure is determined by the temperature and the amount of water used. The top of the vessel is a large nut connected to a high-pressure Bourdon gauge. The seal is made with a hollow O-ring made of inconel steel, plated with silver. The O-rings are made by Advanced Products Corp. The lower two-thirds of the vessel is placed in an oven and slowly heated to 650 °C. The pressure and temperature must be carefully monitored to prevent the vessel from bursting. The vessel takes about 2.5 h to reach 650 °C. After 8 h, the heater is turned off, and the vessel is allowed to cool overnight. Under no circumstances should it be removed from the oven while hot. If it is bumped while hot and pressurized, it could explode in the operator's hands.

The ampules are removed from the vessel and dried. They are opened by cutting off the flattened end and squeezing them in a vise. The contents are then ground in a ball mill for 1 min and placed into a centrifuge test tube. Since KCN is molten at 650 °C, the sample is granular, making it difficult to dissolve the C_{60} without grinding it. We then add 4 mL of CS_2 to each tube and sonicate them to dissolve the C_{60}. The tubes are then centrifuged. The solution is removed and filtered with a 0.2 μm syringe filter into a second pair of centrifuge tubes. About 8 mL of acetone is added to each of the second set of tubes, and the C_{60} precipitates. The tubes are centrifuged, and the solvent is discarded. More CS_2 is added to the first set of tubes, and the process is continued until no more C_{60} is extracted. Starting with 400 mg of C_{60}, we can recover roughly 50 mg of labeled product. While some of this is lost in the handling of a fine, often sticky powder, much is left as an insoluble black powder (which contains cyanide). Without the cyanide, we can recover 80% of the fullerene as soluble product but with a much lower incorporation fraction.

The analysis has been described previously.[6] Briefly, 1 mg of sample is placed in a tube of fused silica (quartz). It is evacuated and sealed under vacuum. The ampules are then heated to 1000 °C for 2 h to decompose the fullerene and release the noble gas. The ampule is then broken under vacuum. The contents then pass through a liquid nitrogen trap and a getter pump into a quadrupole mass spectrometer, Ametek Dycor model 1000. During the analysis, the gate valve between the spectrometer and the diffusion pump is closed to give a closed volume, pumped by the liquid nitrogen trap and the getter pump, neither of which removes the noble gas. The signal on the mass spectrometer is then a step, whose amplitude is proportional to the amount of noble gas.

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