ARTICLE

Noble Gas Atoms Inside Fullerenes

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Heating fullerenes at 650°C under 3000 atmospheres of the noble gases helium, neon, argon, krypton, and xenon introduces these atoms into the fullerene cages in about one in 1000 molecules. A "window" mechanism in which one or more of the carbon-carbon bonds of the cage is broken has been proposed to explain the process. The amount of gas inside the fullerenes can be measured by heating to 1000°C to expel the gases, which can then be measured by mass spectroscopy. Information obtained from the nuclear magnetic resonance spectra of helium-3–labeled fullerenes indicates that the magnetic field inside the cage is altered by aromatic ring current effects. Each higher fullerene isomer and each chemical derivative of a fullerene that has been studied so far has given a distinct helium nuclear magnetic resonance peak.

The structure of Buckminsterfullerene (Fig. 1A) was first suggested by Osawa in 1970 as a potential three-dimensional aromatic compound (*1*). In 1985 Kroto *et al.* reported that the molecule was formed by laser ablation of graphite (*2*). In 1990, Krätschmer *et al.* (*3*) reported a method for preparing substantial amounts of Buckminsterfullerene and related higher fullerenes, which has stimulated a huge volume of experimental and theoretical work.

One striking feature of fullerene structures that immediately attracted attention was the presence of a closed central cavity, clearly large enough to hold atoms (*2*) (Fig. 1B). The preparation of fullerenes with graphite that had been treated with metal compounds resulted in some incorporation of metal atoms (*4*). After much discussion about whether the metal atoms were inside or bound to the outside of the cage, isolation and purification of some of the more stable of these substances containing one or more transition metal atoms allowed conclusive demonstration that these atoms were inside the cage (*5*). Studies of structures indicate that the metal atoms are not in the center of the cavity, which suggests that these metal atoms are bonded to carbons of the cage in the manner of metal carbides and are not simply trapped.

Collision of helium, neon, and argon atoms with C_{60}^{+} or of the helium cation with neutral C_{60} was shown by mass spectroscopy to lead to ions with the noble gas added (*6*). The noble gas atoms were presumed to be inside the C_{60} cage. This idea was supported by additional neutralization-reionization experiments (*7*). Unfortunately, mass spectroscopy yields only indirect evidence for ion structures. One cannot be sure that the ions containing the noble gas atoms still have intact fullerene structures, and the number of ions formed is far too low to prepare sufficient quantities of neutral products to investigate their properties. Macroscopic amounts of these neutral compounds containing the noble gas atoms are needed.

At this point the following questions could be asked:

1) How can bulk quantities of fullerenes with noble gas atoms inside be prepared?

2) How can the amount of noble gas inside be detected and measured?

3) How will properties of the fullerenes be affected by the enclosed atoms?

In this article we will discuss answers to questions 1 and 2 and some preliminary results in answer to question 3.

Noble Gas Atoms Inside Fullerene Cages

Because the Krätschmer-Huffman procedure for preparing fullerenes uses an arc between graphite electrodes in 0.2 atm of helium, it seemed possible that fullerenes containing helium had already been made. As the fullerene structure is assembled from carbon atoms, there must come a point when the cage closes. If a helium atom happens to be inside at that moment, it will be trapped. On the basis of the estimated volume of the cavity and the density of helium atoms at the pressure used, there would be about one helium in $\sim 10^{6}$ molecules of fullerene. The detection of molecules containing helium in the presence of such a large excess of empty fullerene would be exceedingly difficult; however, if the helium were released, detecting and measuring just the helium would be much easier.

Geologists face a similar problem in analyzing the noble gas content of rocks. They grind samples, thoroughly degas them in high vacuum, and then heat them to release the gases, which are then measured in a very sensitive mass spectrometer designed for noble gases. On analyzing a sample of commercial fullerene with such a procedure, Poreda and co-workers were able to measure (*8*) one ^{4}He atom in every 880,000 molecules of fullerene and one atom of ^{3}He in every 10^{12} molecules. The ^{3}He/^{4}He ratio is approximately that found in tank helium (and greater than that in the atmosphere by a factor of 4). The helium was released during a period of hours over a temperature range from 600° to 850°C. The approximate rates of release are consistent with an activation energy of 70 to 80 kcal/mol for a simple first-order process.

In contrast with metal atoms, noble gas atoms would not be expected to stick strongly to the outside of fullerene cages. The high temperature required for the release of helium is strong presumptive evidence that helium was trapped inside the cage. Previous calculations had indicated that the energy necessary to push a helium atom through an intact ring was ~200 kcal/

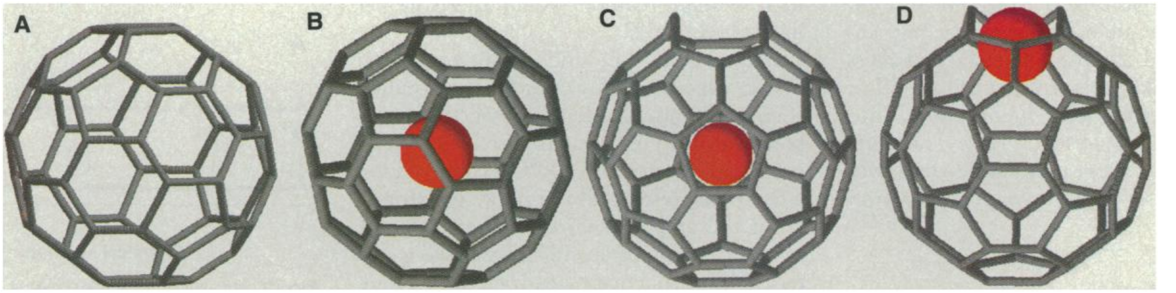

Fig. 1. (**A**) C_{60} or Buckminsterfullerene. (**B**) C_{60} with an atom inside. (**C**) C_{60} with an atom inside and with a bond broken (open window). (**D**) Same molecule as in (C) but with the atom moving out through the window.

mol (6). The lower activation energy found by Saunders and co-workers (8) suggested that the thermal release must have a different mechanism. It seemed reasonable that breaking a C–C bond would cost much less than 200 kcal/mol. Breaking a bond would open what could be described as a "window" in the fullerene cage (Fig. 1C), through which the helium atom could then come out (Fig. 1D).

If helium could come out through such a window, it follows that atoms could also go in when the window was open, and if the window reclosed, this would lead to incorporation of the atoms. Heating fullerene with 3 atm of ^{3}He at 600°C for 1 hour led to the incorporation of about 5×10^6 times as much ^{3}He as was present in the original sample. When the experiments were then done with neon and krypton (argon was skipped because the 1% abundance of ^{40}Ar in the atmosphere leads to a high blank in mass spectrometers), these atoms were incorporated at similar levels, as predicted by the window mechanism (9).

Incorporation of noble gas atoms on the order of about one per 10^6 molecules of fullerene can be measured easily, but further investigation of these interesting molecules requires a larger fraction of molecules to contain the noble gas. The obvious thermodynamic variable that would increase the equilibrium fraction of incorporation is the pressure of the noble gas. We developed a procedure for labeling fullerenes with noble gases at pressures of up to 3000 atm at temperatures of up to 650°C (9). A copper ampoule containing the noble gas and ~100 mg of fullerene is sealed and placed in a high-pressure vessel that is partially filled with water and then closed. On heating the vessel, the pressure increases and is measured by a gauge. The soft copper tube collapses and transmits the pressure to the fullerene and the gas. This procedure for labeling fullerenes with noble gases is now carried out routinely at Yale.

At 3000 atm, the fractional incorporation at equilibrium should be increased to a few percent, large enough to enable a conventional mass spectrum of the fullerene to show observable peaks at higher mass corresponding to the addition of the noble gas atoms. High-pressure labeling with neon, argon, krypton, and xenon produced samples that showed mass spectrum peaks, demonstrating that all of these noble gases were incorporated into both C_{60} and C_{70} at levels of several parts per thousand, except for xenon, which was incorporated at lower levels (9). Krypton and xenon have many isotopes, and the characteristic multiplets seen in the mass spectra reflected the expected normal isotopic abundances (including the normal abundance of ^{13}C).

Murry and Scuseria calculated the energy required to break each of the two kinds of bonds in C_{60} to yield singlet and triplet "window opened" structures (*10*). Their values are in rough agreement with the activation energy inferred from the experimental results (8). It was suggested that opening the window by photochemical means might be an alternative procedure for getting atoms inside the fullerenes, but this would be true only if it could be performed at very high pressures. At atmospheric pressure, very low amounts of gas would be expected inside at equilibrium. For example, even with no energy cost for putting a helium atom inside C_{60}, it is predicted that, with helium gas at 1 atm, roughly one in a few thousand molecules would be occupied at equilibrium. This conclusion follows from the estimated volume inside the fullerene and the density of helium at atmospheric pressure.

Equilibria and Kinetics for Noble Gas Atom Capture and Release

The fraction of incorporation of noble gas atoms at equilibrium in fullerenes as a function of pressure is of interest. A number of theoretical studies of noble gas atoms inside C_{60} have been published and some of them (*11*) predicted that krypton and xenon are too big to fit. This kind of prediction is very sensitive to the values chosen for the size of the noble gas atom and to the effective size of the fullerene carbons on the inside of the cage. With a chosen set of sizes the equilibrium incorporation can be calculated with what might be called a hard sphere model. A factor that is left out in this model, however, and which might be particularly important for the larger noble gas atoms, is the van der Waals attractive interaction between the carbons and the noble gas atom. A large atom like krypton might fit inside the cavity snugly so that all 60 carbons of the fullerene would interact with it at the same time. The interaction energy with a single carbon would therefore be multiplied by 60.

Experiments are under way to try to obtain experimental values for the equilibrium constants. We have shown that samples sealed in evacuated fused-silica ampoules and heated to 1000°C in an oven for a few hours release all the noble gas atoms. After the ampoules cool, they are opened inside a vacuum line and the released gas is measured with a mass spectrometer. Recent results indicate that the labeling procedure described does not achieve equilibrium labeling with neon in our high-pressure bomb in one run. When fullerene, which has been labeled once, is isolated and relabeled, the neon content is increased. Even after four successive labeling runs equilibrium was not achieved (*12*).

The "Hot Atom" Method for Introducing Tritium into Fullerenes

How else can atoms be introduced into fullerenes? Atoms with enough kinetic energy should be able to penetrate the fullerene cage without a window being opened first. A barrier for helium of ~200 kcal/mol has been calculated and also observed for ion-neutral reactions (6). Nuclear reactions can be used to generate atoms with much more kinetic energy than this. ^{6}Li nuclei absorb slow neutrons with a large cross section, producing α particles and tritium cations as products. The T^+ is formed with several million electron volts of kinetic energy. With such large energies, the tritium would smash through any molecule, produce ionization, and break many bonds. Each encounter results in the tritium losing energy. After many collisions, T^+ slows down enough to pick up an electron and become a neutral tritium atom. As the tritium continues to travel, its energy continues to decrease. When it gets to the appropriate energy range, tritium can penetrate the cage of a fullerene with a good chance of not destroying the molecule and also of remaining inside.

Even a small fraction of incorporation can be detected with high sensitivity through tritium's radioactivity. When lithium salts of fullerenes were exposed to neutrons, material having the properties of fullerenes but with significant tritium radioactivity was formed (*13*). There was still the question of whether the tritium was actually inside or chemically bound to the outside of the fullerene. A very sensitive method for measuring tritium involves sealing a sample for a period of time (usually months) and then measuring the ^{3}He that is produced by its decay. In the case of tritium inside fullerene, the cage is an ideal bottle. The β decay of tritium occurs with a very small

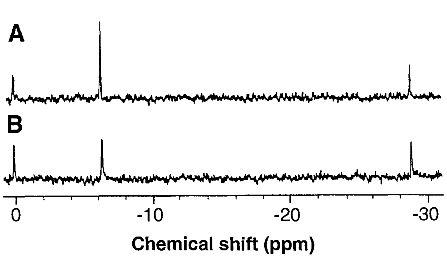

Fig. 2. ^{3}He NMR spectra of (**A**) a mixture of dissolved helium, C_{60}, and C_{70} and (**B**) the same mixture enriched in C_{70}.

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energy release, most of which goes into the recoil of the electron because of conservation of momentum. The ^{3}He produced has so little kinetic energy that we did not expect that it could escape from the fullerene if it started out inside or penetrate if it began outside. When a sample of tritium-labeled fullerene that had been stored for more than 1 year was examined, approximately the amount of ^{3}He predicted for the decay of the tritium over this time was found (*13*). This is strong evidence for the tritium being inside the fullerene. It is not yet known whether it is there as a free atom or is bound chemically to the inside.

NMR of ^{3}He Inside Fullerenes

The first special property of fullerenes containing noble gas atoms to be investigated was helium nuclear magnetic resonance (NMR). ^{3}He is an excellent NMR nucleus. Its spin of 1/2 and high gyromagnetic ratio make its spectroscopy quite sensitive. The presence of a large amount of empty fullerene does not interfere with the helium spectrum. Labeling runs were made at successively higher pressures of ^{3}He and analyzed by helium NMR by Anet and coworkers at the University of California at Los Angeles (*14*). No peaks were seen until the labeling was done at very high pressure. The chemical shift of the helium at −6.4 parts per million (ppm) (upfield of dissolved ^{3}He used as the reference) was a surprise. A shift of only 1 ppm had been predicted. The shift of ^{3}He in C_{70} was also surprising at −28.8 ppm (Fig. 2).

Why should the NMR chemical shift of the helium be so different inside the cage? Certainly, one would not expect any significant bonding to the helium that might affect the shift. The electrons of the helium atom are in a very tightly bound, closed shell; therefore, the NMR shift should be simply a measure of the magnetic field experienced by the nucleus. The helium shift indicates that the field inside the fullerene is reduced from the field outside. What could cause this change? Benzenoid aromatic rings are very diamagnetic and this diamagnetism is strongly anisotropic. It is well known that nuclei constrained to be close to the flat side of benzene rings are strongly shifted upfield. This phenomenon is often described as being due to an "aromatic ring current." The chemical shifts of helium inside fullerenes may indicate that there is a ring current in their π electrons. The sign of this shift indicates that the ring current is diamagnetic in C_{60}. C_{70} is therefore much more diamagnetic than C_{60}. The bulk diamagnetic susceptibilities of C_{60} and C_{70} are in accord with the helium shifts.

The presence of a ring current and its magnitude are related, in turn, to a question about fullerenes that has been discussed at length: Should the fullerenes be described as aromatic compounds or as polyolefins? Aromaticity is a major topic in organic chemistry. All organic textbooks are divided into sections describing aromatic and nonaromatic chemistry, because the reactions and concepts are very different in these two areas. Stabilization due to aromatic character or "resonance energy" is an important criterion for evaluating ordinary aromatic compounds. Obtaining an unambiguous quantitative value for the resonance energy is difficult and controversial even in the prototype, benzene. The experimental and theoretical difficulties in estimating resonance energies for any of the fullerenes are daunting. The comparison of ring currents obtained from helium NMR with those expected from various theoretical models is probably the best handle we have for experimentally observing aromaticity for fullerenes. By this criterion, C_{60} is mildly aromatic and C_{70} much more strongly aromatic. Ab initio calculations have reproduced the observed helium shifts within a few parts per million (*15*). A recent review by Haddon discusses theoretical and experimental work on the magnetic properties of the fullerenes thoroughly (*16*).

In addition to C_{60} and C_{70}, fullerenes with more carbon atoms have been found in the "soot" produced in the Krätschmer-Huffman procedure. C_{76}, three isomers of C_{78}, three isomers of C_{84}, and many larger fullerenes have been reported. The same high-temperature high-pressure procedure that was found to label C_{60} and C_{70} produced a number of fullerenes labeled sufficiently with ^{3}He so as to yield peaks in the helium spectrum (*17*). Because there is one helium atom in each labeled molecule and no coupling with other nuclei, a single peak is seen for each isomer. The peaks are very sharp and the range of chemical shifts is large. It was discovered from helium spectra that there are at least five detectable C_{78} isomers and nine C_{84} isomers (*17*) (Fig. 3). Note that the helium NMR peak shifts 22 ppm upfield on going from C_{60} to C_{70} but then goes downfield as one goes to still higher fullerenes.

Chemical Derivatives of Fullerenes Containing ^{3}He

There are many chemical reactions of fullerenes where groups form bonds to the carbons (*18*). Because the helium chemical shifts are different in the various fullerene isomers as a result of different diamagnetic ring currents in the π orbitals, it might be expected that chemical reactions that alter the π structure would also change the helium shift. The most common type of reaction produces an adduct where two groups add to adjacent carbons. If the groups are connected, a new ring is formed attached to the fullerene. The majority of such addition reactions add the groups across the fusion between two six-membered rings and form products called 6,6 adducts. In a formal sense, this has the effect of removing one double bond from the π system. If the ring current was an additive function of the number of formal double bonds, one might expect that this would reduce the diamagnetism and produce a downfield shift. An

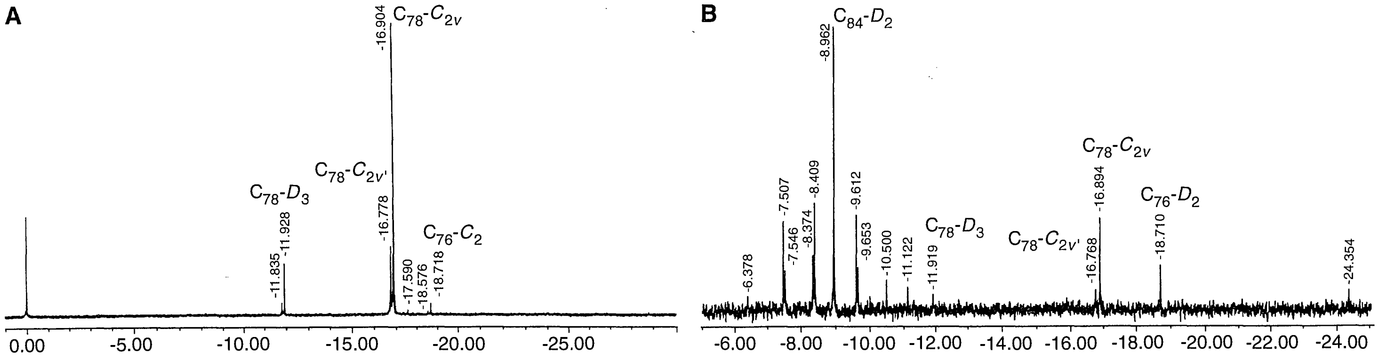


Fig. 3. ^{3}He NMR spectra of the higher fullerenes C_{76} and C_{78} (**A**) and higher fullerene C_{84} (**B**).

addition reaction, first studied by Prato and Scorrano, was carried out on a C_{60}-C_{70} mixture that had been labeled with ^{3}He (*19*). The spectrum (Fig. 4) showed that the reaction did result in downfield shifts of the helium in C_{70} adducts, but in the adduct of C_{60} the helium shifted upfield. Two small peaks further upfield were assigned to bis-adducts of C_{60}.

As yet, there is no qualitative explanation for these shifts. Ab initio calculations on $^3He@C_{60}H_2$ do predict an upfield shift (*20*), but they do not provide a reason for the shift. The helium shifts in a number of mono-adducts across 6,6 bonds of C_{60} are listed in Table 1 (*21, 22*). Such addition reactions all produce the same π system with 29 remaining formal double bonds. It is interesting that the helium shifts are all about 3 ppm upfield of $^3He@C_{60}$ (but different enough to be distinguished). The epoxide and the CH_2 (cyclopropane) adduct are exceptional in that these two compounds shift upfield only ~2 ppm (*22*). This would be consistent with the notion that three-membered rings have properties that are similar (in certain ways) to double bonds. The 5,6 CH_2 adduct is also interesting. Its helium shift is only 0.2 ppm upfield from $^3He@C_{60}$ (*22*). Other evidence indicates that this adduct is present in the open, homoannulene form (it therefore still has 30 formal double bonds). Thus, in a similar manner to other homoannulene aromatics, the 5,6 CH_2 adduct might be expected to behave very much like its parent substance. The small spread in the helium shifts of 6,6 mono-adducts in Table 1 (except those with three-membered rings) is in accord with the π system (29 formal double bonds) being the principal source of the change in magnetic field that leads to the shift. The small differences could be due to the effect of the different groups on the π system or due to a direct effect of these groups on the helium.

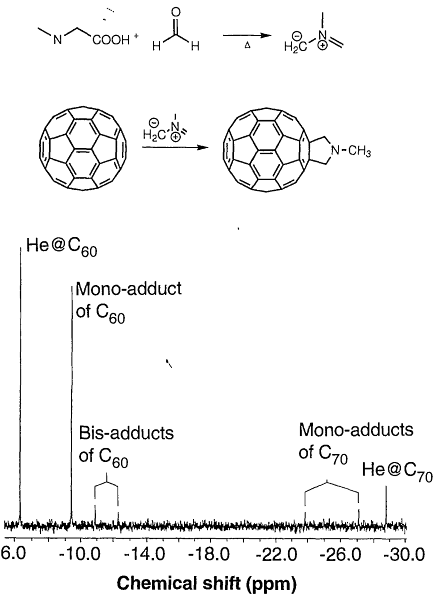


Fig. 4. ^{3}He NMR spectrum of the addition reaction in a mixture of C_{60} and C_{70} that were labeled with ^{3}He.

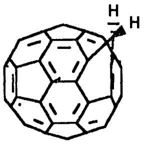
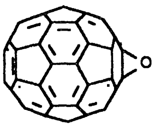
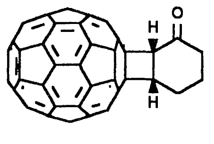
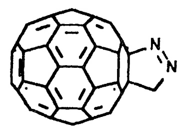
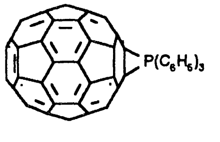
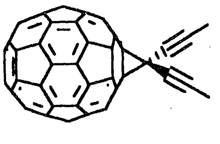
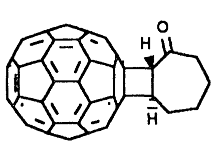
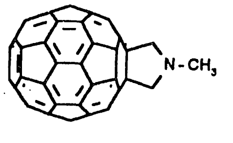
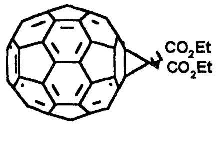
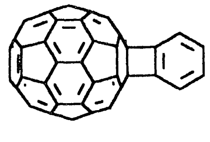
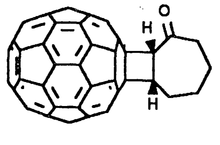
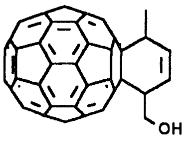
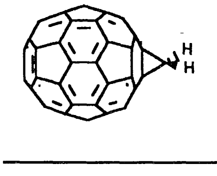
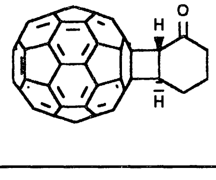
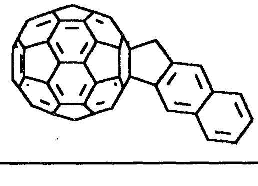
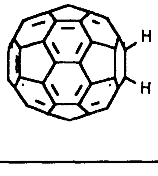
When a second addition reaction to C_{60} occurs, the helium shift moves further upfield. However, in contrast with the first addition, the bis-adduct shifts span a range of several parts per million. In place of the ortho, meta, and para disubstituted benzenes, there are eight different bis-6,6 adducts if each reagent that adds has two planes of symmetry. The different arrangements of the 28 remaining (formal) double bonds must be the cause of these different shifts. When enough sets of these isomers have been studied carefully, it will be known whether the helium shifts can be used to assign regiochemistry to these isomers. Each different helium-labeled fullerene examined so far has yielded a separately resolved peak.

Frequently Asked Questions

Could more than one atom be placed inside a fullerene? Even if there was no extra energy cost (debatable), at the present incorporation level of several atoms per thousand, the level of dilabeled molecules expected drops to the per million level simply on the basis of probability. There is no obvious way of detecting these double-labeled molecules in the presence of an excess of unlabeled and monolabeled fullerenes.

Ingenious and elegant chemical and photochemical schemes for reversibly opening holes in the fullerene cage to introduce atoms or molecules are often suggested. As mentioned above, these methods do not overcome the extremely low equilibrium incorporation levels expected if they are done at ambient pressure, because the free volume inside fullerenes is so small. The suggested new methods have been compared with the "brute force" high-tempera-

Table 1. ^{3}He chemical shifts of C_{60} mono-adducts. Et, ethyl.

	-6.63		-8.24		-9.34		-9.29
	-7.20		-8.38		-9.21		-9.45
	-8.06		-9.11		-9.29		-9.71
	-8.11		-9.28		-9.23		-9.66

ture high-pressure technique. Although not on most lists of useful procedures for accomplishing objectives in synthetic chemistry, the high-temperature high-pressure method has the practical advantage of working. With the proper apparatus, it can be conveniently carried out routinely on a scale that readily produces sufficient product for many investigations. This process can be thought of as simply a thermal reaction of A with B to make AB.

Can molecules be inserted inside the fullerenes? There should be room for small molecules such as H_2 and CO inside C_{60}. Probably even CH_4 would fit. Larger fullerenes might be able to contain still larger molecules. The high-temperature high-pressure incorporation method is likely to pose difficulties because of decomposition of the reagent or reactions with the outside of the fullerene cage. There is neither difficulty with the noble gases.

Potential Uses of Fullerenes Containing Noble Gas Atoms

When fullerenes labeled with ^{3}He are used as a starting material for a reaction, the helium NMR spectrum of the reaction mixture has been demonstrated to be a powerful tool for following the reaction (*18, 19*). The fraction of starting material that has been consumed can be determined, and the number of peaks and their intensities indicate how many products have been formed and their relative amounts. One can then use separation methods to isolate the products and follow the separation with helium NMR. With more experience, it is likely we will be able to infer structures and regiochemistry from the helium shifts. No solvents, impurities, excess reagents, or products from the reagents can give extraneous helium peaks. As far as is known, an intact fullerene cage is necessary to retain helium, so all the peaks seen must be due to fullerene derivatives. It should also be possible to readily study any chemical or photochemical process that releases helium from the cage. The NMR signal for helium inside the cage should disappear and be replaced by the characteristic signal of dissolved helium gas. Without the noble gas, a reversible process that opens a window in the fullerene cage would be invisible. Clearly, ^{3}He NMR spectroscopy of the products of reactions using ^{3}He-labeled fullerene starting materials will be a powerful method for following fullerene chemistry.

Helium or other noble gases inside fullerenes could also be used as tracers to allow detection and measurement of these substances or their chemical derivatives at phenomenonally low concentrations, if the noble gas is released and measured by using the very high sensitivity of the mass spectrometer. If 1 mg of ^{3}He-labeled fullerene were dissolved in a 50-m swimming pool and the pool water thoroughly mixed, the helium could later be detected in 1 ml of the water with this method.

There has been much recent interest in nonbonded interactions in many areas of chemistry. Nonbonded forces are responsible for the nonideality of gases and lead to the formation of the liquid state and molecular crystals. Significant interactions of biologically important molecules such as the formation of the DNA double-strand helix and native three-dimensional structures of proteins, membranes, and complexes between enzymes and their substrates all involve multiple nonbonded interactions. Many experimental and theoretical tools are used to study them. Systems where small molecules can go into and out of larger cage molecules (host-guest systems) are currently the focus of considerable attention. These might be models for enzyme-substrate complexes. Typically, ionic forces or hydrogen bonding hold them together, but other (van der Waals) attractive and (especially) repulsive forces are important in determining their structures.

In contrast with these systems, the fullerenes are completely closed cages, allowing atoms to be trapped without regard to attractive interactions. When an atom is put inside, it simply cannot get out without extreme treatment. (Cram used the term carcerand to describe such systems.) We therefore can observe consequences of interactions that would not persist without the fullerene cage. The noble gas family is particularly valuable for this purpose because its members range from helium, which has two electrons in a very strongly bound, closed shell and is very small, to xenon, which has many electrons and is very much more polarizable and is quite large. Noble gas atoms are constrained to be in (or close to) the center of the cage. The distances to the carbons are therefore fixed (with some vibrational motion). In species with noble gas atoms inside C_{60}, the noble gas nucleus is about 3.5 Å from the carbon nuclei. Without constraint by the cage, it would take a pressure on the order of 1×10^6 atm to produce appreciable populations of situations where atoms approach noble gas atoms at this distance. Such arrangements in fluid media at high pressure would have very short lifetimes.

Gentry and co-workers have shown (*23*) that the dimer He_2 can be observed, but its bonding energy is so weak that temperatures above 0.01 K would lead to its dissociation. It has one very low-frequency stretching vibration with a He–He distance that extends to ~10 Å. Such weakly bound, easily dissociated species are often called van der Waals complexes. In contrast noble gas atoms inside fullerenes are extraordinarily stable. Pure Ne@C_{60} requires heating for weeks at 1200 K to get significant reaction. From any of the usual definitions, these species should be called compounds. If this idea is accepted, these are the first stable, neutral compounds of helium or neon to be described. Their number is now around 100 and growing rapidly.

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