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Release of Noble Gas Atoms from Inside Fullerenes

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Abstract

Noble gas atoms can be introduced into the interior of fullerene molecules. A procedure, using a mass spectrometer system, is described for measuring the rates and amounts of noble gas released on heating these compounds. We find that the half life for Ne@C_{60} reacting to Ne + C_{60} is at least many weeks at 630°C. Additionally, the rate of thermal decomposition of fullerenes can be very substantially faster if traces of trapped solvent are not removed. Copyright © 1996 Elsevier Science Ltd

I. Introduction

The properties and reactions of fullerenes containing atoms inside the cage continue to be of great interest.[1] Preparing fullerenes from graphite doped with metal atoms has been shown to result in their incorporation.[2] We have previously described a method for getting noble gas atoms inside intact fullerene molecules.[3-6] Our current procedure is to heat the fullerene in the presence of the noble gas for eight hours at a temperature of 620°C and at pressures of 3,000 atm.[5] Under these conditions, noble gas atoms are introduced into 0.1% of the fullerene molecules, except in the case of xenon where only 0.03% contain xenon. These compounds are very stable. They can be heated for hours without decay or loss of the noble gas. It has been shown that chemical reactions on the fullerene cage generally do not release the noble gas.[7,8] There have been many theoretical calculations of the properties of these noble-gas compounds, since they have unusual nonbonded interactions.[9] We have been interested in the mechanism and rates by which noble gas atoms enter or leave the fullerene cage and the associated equilibrium constants. To study them, we have constructed a mass spectrometer system capable of rapid analysis of the trace amounts of noble gas released from the fullerenes. Although our results are still preliminary, they demonstrate the remarkable stability of fullerenes and of their noble gas compounds when pure. We have found that even after outgassing for many hours under vacuum at temperatures around 200°C, there is enough residual contaminants to accelerate the thermal decomposition of the fullerene by over an order of magnitude. Below, we describe the mass spectrometer system and then give our preliminary results for the decomposition rates.

II. Mass Spectrometer

The mass spectrometer system was designed to measure the amount of noble gas contained in milligram samples of labeled fullerenes. One mg of Ne@C_{60} labeled at a level of 0.1% contains about 1 n mol of Ne (3×10^{-4} cc-atm at STP). We must be able to make the measurements in the presence of small

amounts of solvent and other impurities, and we must be able to do this in a time of several minutes so that we can compare a large set of samples to each other. Mass spectroscopy is the obvious method. However, quantitatively measuring the amount of noble gas containing fullerene in the presence of a large amount of empty fullerene is very difficult. Heating it to the high temperatures required to vaporize it may lead to decomposition. The same is true of fast-atom bombardment. We therefore elected to release the noble gas first by heating the sample to 1000°C for two hours in an evacuated fused silica ampoule and then to measure the amount of noble gas released. We have shown that the fullerene is completely decomposed under these conditions.

In a conventional mass spectrometer, the sample flows past the ionizing filament into a pump. As a result, the sensitivity is low and the quantitative accuracy from sample to sample is limited by the ability to reproduce flow rates and pumping speeds. Because the noble gas is not destroyed by the filament, we constructed the spectrometer to operate in a closed volume without pumping. In this mode, the spectrometer operates as a residual gas analyzer, measuring the partial pressure in the volume. We use an Ametek Dycor 1000 quadrupole mass filter mounted in a small stainless steel chamber attached to a liquid nitrogen trap (Edwards model NCT63). Below the trap is a butterfly gate valve and then a 63 mm Edwards Difstak diffusion pump (Model 63MM), chosen for its very low backstreaming rate. The chamber is thoroughly pumped out, the gate valve closed, and the sample introduced for measurement. Because there is no pumping during the measurement and because the mass filter will not operate properly above a pressure of 1×10^{-4} torr, the system is very sensitive to noncondensible gas leaking in or outgassing from the walls of the chamber. By baking the chamber for hours at 200° and by pumping on it continually, we can close the gate valve for as long as five minutes to take the measurement. The diffusion pump is backed by an Edwards model RV5 direct-drive forepump with a Lesker Micromaze sorption trap between the two pumps in order to prevent any forepump oil from entering the diffusion pump.

The sample is introduced through a glass vacuum line which is rough pumped to 1 mtorr by a second Edwards model RV5 forepump. The sample is contained in a sealed, evacuated fused silica ampoule which is placed in a breaker made of stainless steel attached to the vacuum line by a standard tapered joint. After evacuating the breaker, the ampoule is broken by crushing it with a screw. The gas passes through a U-shaped liquid nitrogen trap and is further pumped out by an SAES model SORB-AC gettering pump before entering the mass spectrometer. These steps remove all components except the noble gases which are not condensed by liquid nitrogen and do not react with the getter. With this arrangement, we can measure four samples an hour. We prepared a glass bulb with known amounts of the noble gases for calibration.

Not surprisingly, our sensitivity is limited by the noble gases in air. Argon is the worst case, since it is a major constituent of air. The most common isotope of Ne, ^{20}Ne (90.5%), is limited by the large background of $^{40}Ar^{++}$. We therefore look at ^{22}Ne (9.3%). Our limit for detection of pure Ne@C_{60} is 1 ng. This could be increased by an order of magnitude by using enriched ^{22}Ne. We initially had problems with Kr and Xe. The signal intensity was not reproducible and slowly decayed after the sample was introduced into the mass spectrometer. We traced this to the adsorption of the noble gas on the liquid nitrogen cooled trap. Although the equilibrium vapor pressures of Kr and Xe at 77K are much higher than the ambient pressures in the mass spectrometer, the gases can adsorb on the cold surfaces. We now measure these gases with no liquid nitrogen in the trap. In retrospect, it might have been better to put the trap below the gate valve rather than above it. Helium presents an interesting case. Although it is present in air at a level of only 5.2 ppm, it readily passes through glass and fused silica, especially when hot. We therefore get a high background of helium. Mass spectrometers used for measuring trace quantities of noble gases in geological samples typically use metal inlet systems that are baked for hours for each sample. By using a high-resolution mass spectrometer capable of separating $^3He^+$ from the common contaminants H_3^+ and HD^+ one can get backgrounds of the order of 10^4 atoms of ^{3}He.[10] Such instruments cost an order of magnitude more than ours and require long times to measure samples.

III. Results and Discussion

We attempted to measure the rate of noble gas escape from the fullerene cage by heating samples of $Ne@C_{60}$ for varying lengths of time and then measuring the amount of free Ne present in the ampoule. We got data which fit a single exponential,

$$[Ne] = [Ne@C_{60}]_0 \left(1 - e^{-kt}\right).$$

The rate constant gave a reasonable fit to the Arrhenius equation. This experiment measures the sum of all reactions leading to the release of Ne, regardless of whether the fullerene survives or not. We found that the rates were close to those measured by Leifer et al.[12] for the thermal decomposition of fullerene to amorphous carbon. We therefore devised a method to measure the rate at which neon leaves C_{60} without the decomposition of the fullerene. We heated the samples, broke open the ampoules, scraped out the solid, and weighed it. We extracted the soluble fraction using CS_2, removed the solvent, and weighed the dried sample and analyzed it for the total neon content by heating it to 1000°C. We found that much of the sample had decomposed, but that the soluble portion contained roughly the same fraction of Ne as the original sample. This means that our initial rate data were determined largely by the decomposition of the fullerene,

$$Ne@C_{60} \rightarrow C + Ne,$$

where C is some form of amorphous carbon.

It is well known that the spaces between molecules in a crystal of C_{60} are large enough to hold molecules of common solvents such as benzene, toluene, or CS_2; and, when crystallized from a solution, solvent is trapped in the fullerene crystal. Several papers[11,12] claim that all the solvent is removed by pumping on the sample for several hours at moderately high temperatures, but we suspected that this is not the case. We therefore sublimed the $Ne@C_{60}$ under vacuum in a fused silica tube after outgassing it at 200°C for several hours. The rise in pressure during sublimation was evidence of solvent still left in the fullerene. The fused silica tube was then sealed below the sublimed material and then above it. Following the sublimation, the sample was never exposed to air. Analysis of the sublimed material showed that it contained the same fraction of noble gas as the starting material. In subliming the fullerene, if the temperature is raised too rapidly, a noticeable rise in pressure is observed and only ~50% of the sample sublimes; the rest appears to decompose. If the temperature is raised to 550°C, over many hours, the yield increases to 80-90%. This is further evidence that all the solvent is *not* removed by outgassing at 200-300°C for hours.

Two sets of sublimed samples were heated over varying lengths of time, one at 900°C and and the other at 630°C. In each case the ampoule was broken, and the soluble fraction was extracted and weighed to obtain the rate of thermal decomposition of the fullerene. The concentration of Ne in the soluble portion was measured to obtain the rate of the reaction

$$Ne@C_{60} \rightarrow Ne + C_{60}.$$

The results are shown in Figure 1. The circles (short dashes) give the amount of soluble material divided by the initial amount. The curve is the best fit single exponential. Since the initial value is no more accurate than the rest of the points, it was included in the fit, and the intercept is not precisely 1.0. The curve with long dashes is the ratio of amounts predicted by the rate data of Leifer et al.[12] for material that was "thoroughly outgassed" but not sublimed. The rate constants are six to 100 times larger than the ones we observe. The rate constants are given in Table 1. Note that the ordinate is in hours in the top panel and in weeks in the bottom panel. The triangles (solid curve) gives the ratio of Ne concentration to that in the starting material, and the curve is again the best fit to a single exponential. It is not clear that any release of Ne is observed at 630°C without the decomposition of the fullerene. The apparent release at 900°C may be due in part to a difference in the rates of decomposition of C_{60} and $Ne@C_{60}$. A curious feature of these results is that Leifer et al. used toluene as a solvent and we used CS_2, yet the

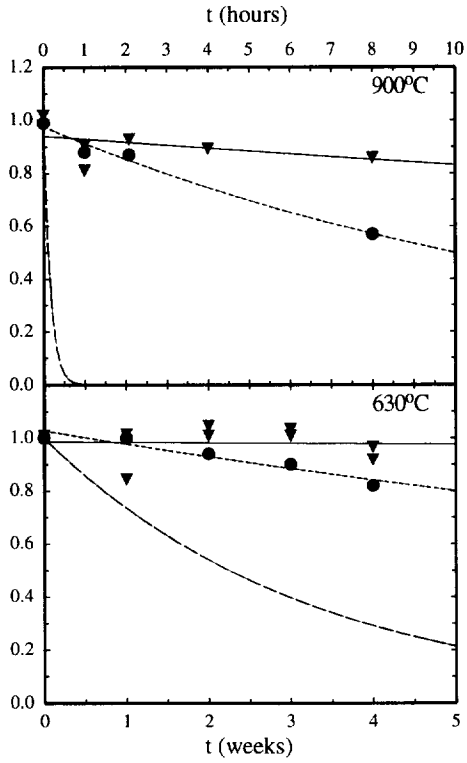

Figure 1: The circles show the amount of soluble fullerene divided by the initial amount. The triangles show the concentration of Ne in the Ne@C_{60} divided by the initial amount. The curves are the best fit to a single exponential. The curve with the long dashes is the decomposition rate predicted by the data of Leifer et al.

rates of decomposition of fullerene with trace quantities of the two solvents were very similar. When we measured the rate of decomposition of sublimed C_{60}, subsequently exposed to air, the rate fell in between that for the unsublimed and the sublimed material not exposed to air. Very pure C_{60} is an extraordinarily stable molecule, but even trace quantities of solvent or possibly air absorbed in the crystal can catalyze its decomposition. Further purification might well decrease the rate of decomposition still further.

We have now seen reactions where noble gas atoms both enter and leave the fullerene cage without destroying the molecule. This cannot occur by forcing the noble gas atom through one of the rings in the fullerene. Calculations[13] and experiments[14] on helium give a threshold of roughly 8 eV for the penetration of a six-membered ring. The energy required for the heavier noble gases is almost certainly higher still. We have proposed[3] a "window mechanism" where one or more bonds of a fullerene breaks to open a larger ring allowing noble gas atoms to enter or leave. The broken bond then recloses. If

Table 1: Rate Constants for the decomposition of C_{60} and for the escape of Ne from Ne@C_{60}

Temp.	Decomposition	Liefer et al.	Escape
630°C	$(3.0 \pm 0.3) \times 10^{-4}\text{hr}^{-1}$	$1.83 \times 10^{-3}\text{hr}^{-1}$	$(1.3 \pm 9.2) \times 10^{-5}\text{hr}^{-1}$
900°C	$0.067 \pm 0.003\text{hr}^{-1}$	6.4hr^{-1}	$0.012 \pm 0.007\text{hr}^{-1}$

we can assume that this is a normal first-order process with the normal pre-exponential factor of 10^{13} sec^{-1}, then we obtain a rough activation energy of 90 kcal/mol. The more rapid processes previously studied for both incorporation and release of the gases require the presence of impurities. They might occur via a "modified window mechanism." A radical might add to the fullerene, considerably weakening nearby carbon-carbon bonds of the fullerene and allowing the opening of a window with a lower activation energy. After the entry or release of the noble gas atom and the closure of the window, the radical can be eliminated, regenerating the fullerene.

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