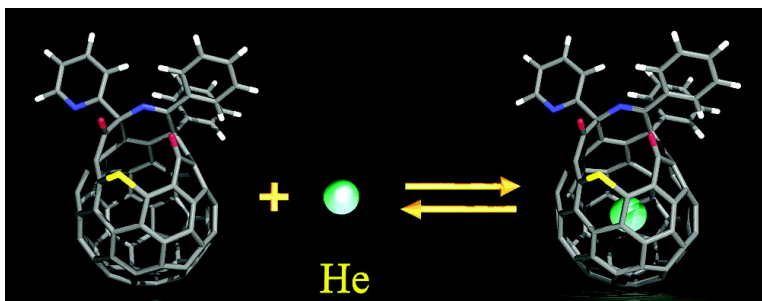Article

Helium Entry and Escape through a Chemically Opened Window in a Fullerene

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Helium Entry and Escape through a Chemically Opened Window in a Fullerene

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Abstract: [3]He has been inserted into the cavity of an open-cage fullerene derivative close to room temperature, reaching an incorporation fraction of 0.1%. The rate of escape of [3]He from this fullerene was monitored by [3]He NMR to yield the activation barrier and to compare the size of the orifice to those of other open-cage fullerenes. The equilibrium constant was also measured.

Since fullerenes were prepared in 1985, various methods have been devised to put atoms and small molecules inside their hollow cages. Metals were introduced by making the fullerenes in an arc by use of graphite rods doped with the metal.[1,2] We have used high temperature and high pressure to put noble gases and small molecules inside fullerenes.[3-6] Various groups have used beams of fast ions or atoms to shoot atoms inside[7-11] or used the recoil energy from nuclear processes to do this.[12,13] A more recent method has been to open a hole in the fullerene through chemical modification. The first attempt, by Wudl's group, resulted in an opening that was too small to allow helium to pass through it.[14] Rubin's group produced a fullerene with a larger opening,[15] and we were able to put [3]He and H_2 through

it and to measure the rate of escape of [3]He.[16] Last year Komatsu's group made a fullerene with a still larger opening.[17,18]
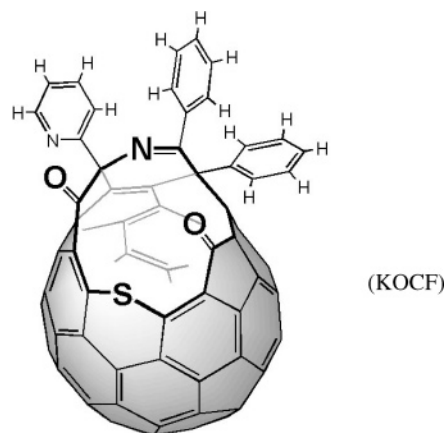
(KOCF)

Referring to Komatsu's open-cage fullerene as KOCF, we have measured the rate of the reaction

$$^3\text{He@KOCF} \rightarrow {}^3\text{He} + \text{KOCF} \tag{1}$$
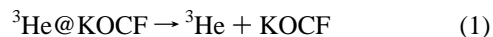
by using [3]He NMR and obtained its activation energy. We have also measured the equilibrium constant, the first measurement of an equilibrium constant for the incorporation of an atom into a fullerene. Since the equilibrium constant is the ratio of the forward and reverse rate constants, this gives the rate of the reverse reaction as well.

Experimental Section

Preliminary [3]He Incorporation. In our first experiments, we dissolved in 0.7 mL of *o*-dichlorobenzene (ODCB) about 4 mg of

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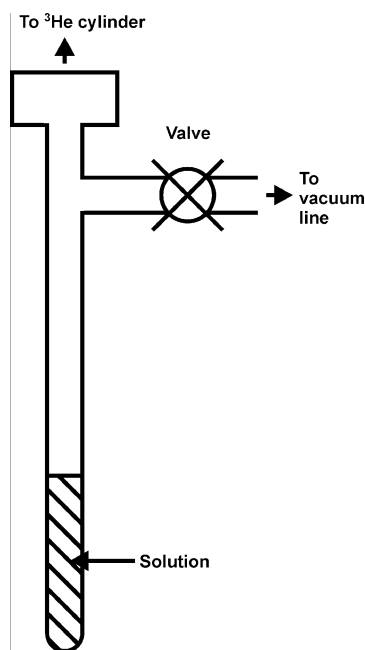
Figure 1. Schematic of the high-pressure cell used to put ^3He into KOCF. The drawing is not to scale. The cell is screwed to the lecture bottle of ^3He with a pipe thread. The air is pumped out, and the tube is immersed in liquid nitrogen. The valve on the lecture bottle is opened to let in several atmospheres of ^3He and then closed. The cell is then warmed, and the pressure increases to roughly 20 atm.

KOCF, a few milligrams of ^3He-labeled C_{60}, and ~1 mg of chromium acetoacetonate, Cr(acac)$_3$, an NMR relaxation agent. A few drops of benzene-d_6 were added for deuterium lock. This solution was placed in an NMR tube and attached to a vacuum line. The tube was cooled to 77 K, and ^3He was introduced into the line to a pressure slightly less than 1 atm. The tube was sealed and slowly warmed. As a result, the pressure of ^3He was about 2 atm. After heating for a few hours at 80 °C, the ^3He NMR spectrum could be acquired overnight, typically accumulating over 15 000 acquisitions with a pulse width of 6 μs (~60°) and a pulse delay of 3 s. The signal-to-noise ratio for $^3He@KOCF$ prepared in this manner was about 5:1, and the incorporation fraction was 0.01%. Higher incorporation would decrease the time for acquiring the NMR spectra and improve the accuracy in measuring the rate of release. The chemical shift for $^3He@KOCF$ was observed at −11.86 ppm relative to dissolved ^3He gas. ^3He inside Rubin's compound ($^3He@ROCF$) gives −10.10 ppm.[16] $^3He@C_{60}$ has a chemical shift of −6.06 ppm.

Achieving Higher Incorporation. A small stainless steel vessel was constructed that could be pressurized with ^3He. A schematic is shown in Figure 1. The vessel was designed to have as small a volume as possible to limit the use of ^3He. It consists of a stainless steel "tee" to which were welded the following components: a hollow, narrow tube into which the sample would be placed as a solution; a pipe fitting to attach the ^3He lecture bottle; and a bellows valve to pump the air out. The tube was 12 in. long, and the sample solution filled it only halfway. The sample consisted of ~12 mg of KOCF, ~6 mg of ^3He-labeled C_{60}, ~3 mg of Cr(acac)$_3$ in 3 mL of ODCB, and 5 drops of benzene-d_6. After the vessel was evacuated and the solution was degassed, the vessel was sealed by closing the valve. The tube was cooled in liquid nitrogen approximately 6 in. above the level of the solution. The lecture bottle was opened to introduce ^3He and then closed while the tube was still cooled to liquid nitrogen temperature. Warming the apparatus to room temperature then increased the pressure within the vessel to approximately 20 atm. The tube was warmed to 80 °C for a few hours to reach equilibrium. After cooling, the pressure was relieved, and the 3 mL sample solution was divided among four NMR tubes. Preliminary

experiments indicated a slow rate of escape of ^3He at room temperature, so the samples were stored at 0 °C.

Monitoring the Kinetics of Escape. The higher incorporation achieved by the stainless steel vessel allowed NMR spectra to be acquired in about 3 h with typical signal-to-noise ratios of 15:1. Before and during acquisition of ^3He NMR spectra, the probe was cooled to 0 °C to slow escape of ^3He. The rate of escape was monitored in the following manner. An initial spectrum was acquired, the sample was heated, and another spectrum was taken. After heating, the integrated intensity of the signal for $^3He@KOCF$ relative to the signal for $^3He@C_{60}$ decreased; $^3He@C_{60}$ served as a stable internal standard. At least five data points were taken in this manner for each of four temperatures: 30, 40, 50, and 60 °C.

Measurement of Equilibrium Constant for $^3He@KOCF$. To measure the equilibrium constant for encapsulation of ^3He by KOCF, it was necessary to know the equilibrium concentrations of empty KOCF and $^3He@KOCF$. These were determined by comparing the integrated intensity of the signal for $^3He@KOCF$ to the integrated intensity of a calibrated, standard sample of ^3He-labeled C_{60}. It was also necessary to know the absolute pressure of ^3He. A mercury manometer was constructed that allowed accurate measurement of pressures of ^3He up to 2 atm.

To prepare the sample, 1.383 mg of the standard sample of ^3He-labeled C_{60} was mixed with 4.563 mg of KOCF. About 1 mg of Cr-(acac)$_3$ was added, and the mixture was dissolved in ~0.7 mL of ODCB with a few drops of benzene-d_6. The solution was placed in an NMR tube, which was then attached to the vacuum line. Equilibrium incorporation was achieved by introducing ^3He at a pressure just under 2 atm, as measured by the manometer, and then heating for approximately 4 h. After heating, the region of the NMR tube containing the solution was cooled with liquid nitrogen to freeze the reaction, the vacuum line was evacuated, and the NMR tube was sealed under vacuum. Comparing the integrated intensities of the ^3He NMR signals for $^3He@KOCF$ and $^3He@C_{60}$ allowed for the determination of the fraction of KOCF molecules incorporating a helium atom at equilibrium.

Measuring the Incorporation Fraction of $^3He@C_{60}$. To get the absolute amount of $^3He@KOCF$, we measured the relative NMR signals for $^3He@KOCF$ and for $^3He@C_{60}$. We then had to obtain the fraction of C_{60} molecules containing ^3He. A standard sample of ^3He-labeled C_{60} was prepared by our high-pressure−high-temperature method, described in detail previously:[6] a sample of C_{60} powder is ground with potassium cyanide and sealed in a copper tube under a helium atmosphere, and this copper tube is then heated in a high-pressure vessel. About 100 mg of this product was dissolved in CS_2, mixed thoroughly, and recrystallized to ensure uniform composition.

To measure the incorporation fraction, samples of a few hundred micrograms of unlabeled C_{60} and of ^3He-labeled C_{60} were placed on a sample plate and the mass spectra were acquired on a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. No matrix was necessary to ionize the fullerene. The signal-to-noise ratio and resolution of the spectra are quite sensitive to instrumental parameters. The ratios of the intensities of the peaks corresponding to C_{60} with one or more atoms of the ^{13}C isotope were affected by slight adjustments of the operating parameters. When the signal becomes so large that the detector nears saturation, there are coincidence losses in the signal due to the dead time between acquisitions of data points. This results in measured isotopic abundances that deviate from predicted values. There are two other difficulties. The peaks for $^3He@C_{60}$ containing varying numbers of ^{13}C atoms overlap those of the empty C_{60}. The incorporation fraction (~1%) requires the measurement of the ratio of peak intensities of very different magnitudes. In acquiring the mass spectra, the parameters were adjusted so that signal intensity approached saturation, and the data were corrected for coincidence losses. The data are given in Table 1.
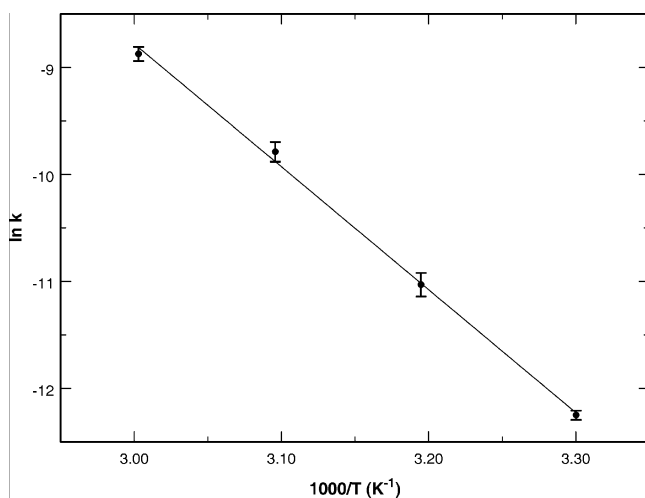
Figure 2. Arrhenius plot of the natural logarithm of the rate constants versus reciprocal temperatures for the rate data acquired by monitoring the rate of escape of ^{3}He from KOCF at 30, 40, 50, and 60 °C. The best fit gives $\ln k = 25.7 - 11\,500K/T$, with $r^2 = 0.998$.

Table 1. Mass Spectral Data for C_{60} and ^{3}He@C_{60}

mass[a]	$I(C_{60})$	$I(^3\text{He@}C_{60})$[b]
720	100.00	100.00
721	64.36	67.17
722	22.27	23.80
723	4.17	7.25
724	1.04	2.91
725	1.11	1.21
726	0.48	0.97

[a] Mass 720 corresponds to C_{60} with all ^{12}C atoms. Mass 723 corresponds to C_{60} with three ^{13}C atoms and to ^{3}He@C_{60} with all ^{12}C atoms. [b] Contains $(100 - x)$% C_{60} and x% ^{3}He@C_{60}.

Table 2. Measured Rate Constants for the Escape of ^{3}He from KOCF

T (°C)	k (10^{-6} s^{-1})	half-life (h)
30	4.78±0.21	40.3
40	16.2±1.8	11.9
50	56.1±5.2	3.4
60	140±9.3	1.4

Comparing the mass spectra for ^{3}He@C_{60} to spectra of empty C_{60} allowed a determination of the fraction of C_{60} molecules in the standard sample that have incorporated an atom of ^{3}He.

Results and Discussion

The kinetics for reaction 1 were monitored at 30, 40, 50, and 60 °C. Table 2 gives the measured rate constants and half-lives.

Figure 2 is an Arrhenius plot of the data. It gives a good linear fit and allows the determination of the Arrhenius activation parameters. The activation energy for reaction 1 was determined to be 22.8 ± 0.7 kcal mol^{-1}. The preexponential factor $10^{11.2 \pm 0.5}$ s^{-1} corresponds to an entropy of activation of -9.3 ± 2.3 cal mol^{-1} K^{-1}.

Table 3 summarizes these results and compares the Arrhenius parameters for the escape of ^{3}He from Rubin's open-cage fullerene (ROCF)[16] and the escape of H_2 from KOCF.[17] We note that the experimental results agree well with the theoretical predictions. More important are the following comparisons. The activation barrier for the escape of ^{3}He from KOCF is lower than the barrier for the escape of H_2, as is the case in ROCF, and the barrier for the escape of ^{3}He from KOCF is also lower

Table 3. Comparison of Theoretical and Experimental Arrhenius Activation Parameters for the Escape of ^{3}He from Rubin's (ROCF) and Komatsu's (KOCF) Compounds

| | activation energy (kcal mol^{-1}) | | | | preexponential factor (s^{-1}) | | entropy of activation (cal mol^{-1} K^{-1}) | |
| | X@ROCF | | X@KOCF | | | | | |
	theory	exp	theory	exp	X@ROCF	X@KOCF	X@ROCF	X@KOCF
^{3}He	24.3[a]	24.6[a]	18.6[b]	22.8	$10^{9.6\,a}$	$10^{11.2}$	-17[a]	-9
H_2	40.0[a]		28.7[b]	34.3[b]		$10^{11.8\,b}$		-7[b]

[a] Reference 16. [b] Reference 17.

than the barrier for ROCF, confirming that KOCF has a larger opening in the cage. It is not immediately clear why there is such a large difference in the preexponential factors between KOCF and ROCF. Both cases are unusual for unimolecular reactions in that three degrees of freedom in the reactants, the motion of the helium atom, are more like translations than a typical vibration. According to the Eyring equation, this should result in a decrease in the preexponential factor from the usual 10^{13} s^{-1}. However, we might expect this decrease in both cases.

Since it is possible to put a measurable amount of ^{3}He into KOCF at low pressures on a vacuum line, we can measure the equilibrium constant for the incorporation. There is a complication, however. The measurement of the rate of escape requires only the relative amount of ^{3}He@KOCF. To determine the equilibrium constant, on the other hand, it is necessary to measure the absolute concentration of ^{3}He@KOCF. This requires knowledge of the incorporation fraction of our internal standard, ^{3}He@C_{60}, as well as the pressure of ^{3}He and the concentration of KOCF. The incorporation fraction of the standard, calibrated sample of ^{3}He-labeled C_{60} was determined by LDI-TOF mass spectrometry. The measurement is difficult because the incorporation fraction is only about 1% and because the mass peaks for ^{3}He@C_{60} with varying numbers of ^{13}C atoms overlap those of the empty C_{60}. The spectrum can easily be distorted by saturating the electron multiplier and counting electronics. After application of a small correction for coincidence losses, the spectra for ^{3}He@C_{60} and empty C_{60} were compared to determine that the fraction of the C_{60} cages that have incorporated a helium atom was 0.015 ± 0.005.

The equilibrium constant for the incorporation of helium inside C_{60} has long been of interest to us in determining to what extent our high-pressure method approaches equilibrium. Before now, we have never been able to prepare a sample at equilibrium. There are various ways to calculate the equilibrium constant, but ultimately, one has to know the energy of He@C_{60} as a function of the position of the helium atom in the C_{60} cage. This calculation is difficult because the interaction is largely due to the van der Waals attraction, and, therefore, depends strongly on electron correlation. Patchkovskii and Thiel[19] have performed an MP2 calculation using a very large basis set to obtain an equilibrium constant of 6.4×10^{-4} atm^{-1}. Because the binding energy is quite small, 2.0 kcal/mol,[19] the equilibrium constant varies only slightly with temperature. Since a helium atom does not interact strongly with the C_{60} cage, the equilibrium constant for ^{3}He@KOCF should be close to that for ^{3}He@C_{60}.

The measured equilibrium constants are given in Table 4. We estimate an overall uncertainty of 40% in K_{eq}. The largest

(19) Patchkovskii, S.; Thiel, W. *J. Chem. Phys.* **1997**, *106*, 1796.

Table 4. Measured Equilibrium Constants for ^{3}He Incorporation in KOCF

run	T (°C)	p (atm)	K_{eq} (10^{-4} atm^{-1})
1	60	1.218	3.4
2	60	1.985	2.7
3	50	1.986	3.1

contribution (30%) is due to the calibration of the measurement of the incorporation fraction of the standard sample of ^{3}He@C$_{60}$. This error does not contribute to the comparison of different runs, since the same standard is used in all cases. The uncertainty in the NMR intensities is estimated at 25%. The values at 50 and 60 °C are the same within the experimental error. It is reasonable to refer to the pressure of ^{3}He even in solution, since at equilibrium, the chemical potential of the dissolved helium is equal to that of the gas-phase helium. Since the fullerene is rigid and the helium is inside, the equilibrium constant should be relatively insensitive to whether it is in solution, the gas phase, or the solid phase. The experimental equilibrium constants are smaller than those calculated by Patchkovskii and Thiel by a factor of 2. This is rather good agreement considering the large experimental uncertainties, particularly the calibration of the standard sample of ^{3}He@C$_{60}$, and the high sensitivity of the theoretical results to the basis set and method used.

We have measured the rate and the activation energy for ^{3}He escaping from a chemically opened fullerene. We also obtained the equilibrium constant. Since the equilibrium constant is the ratio of the forward and reverse rate constants, we also get the rate for ^{3}He entering KOCF. Our measurement of the equilibrium constant shows that it is relatively insensitive to temperature, in agreement with the theoretical calculation, which shows a very small binding energy. This means that the barrier for entrance is nearly equal to the barrier for exit, 22.8 kcal/mol. Our results are also consistent with the earlier measurements on Rubin's compound. This has a smaller hole than Komatsu's compound, and therefore the activation energy for escape is larger. Presumably, making a larger hole will lead to a further decrease in the activation energy.