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Demonstration of a Chemical Transformation Inside a Fullerene. The Reversible Conversion of the Allotropes of H₂@C₆₀

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The citation of the Nobel Prize awarded to Heisenberg in 1932 stated[1] that he had "created quantum mechanics, the application of which led to the discovery of the allotropic forms of hydrogen". Based on the symmetry requirements of the wave function for hydrogen, Heisenberg deduced that the product of the symmetries of the spin and rotational wave functions must be antisymmetrical, leading to the remarkable conclusion that the antisymmetric spin wave functions could only be associated with symmetrical rotational wave functions and vice versa.[2a] Following this logic, the lowest ($J = 0$) rotational state must possess singlet spin character (spins paired ↑↓, antisymmetric, termed *para* hydrogen, pH_2) and the first excited rotational state must possess triplet spin character (spins parallel ↑↑, symmetric, termed *ortho* hydrogen, oH_2). Since pH_2 and oH_2 are two distinct forms of the same element, hydrogen, they are allotropes. The energy difference[2a] between the lowest states of pH_2 and oH_2 is ca. 120 cm^{-1} (0.34 kcal mol^{-1}). At room temperature the equilibrium distribution of "normal hydrogen", nH_2, is a 25/75 mixture of pH_2 and oH_2. The equilibrium consists[2a] of ~100% pH_2 at 4 K and 50% at 77 K. The interconversion of oH_2 and pH_2 in the gas phase is very slow (weeks or longer) but proceeds at much faster practical rates in the presence of paramagnetic spin catalysts even at very low temperatures.[2b]

The recent availability[3] of $H_2@C_{60}$ provides an opportunity to explore the intriguing possibility of performing chemical transformations of the allotropes of hydrogen incarcerated in a C_{60}. We report the experimental demonstration of the spin catalyzed forward conversion of $oH_2@C_{60}$ to $pH_2@C_{60}$ on a zeolite external surface at 77 K and of the back conversion of $pH_2@C_{60}$ to $oH_2@C_{60}$ in solution at room temperature.

The experimental execution for the spin catalyzed forward and back conversion of the allotropes of $H_2@C_{60}$ must fulfill the following requirements: (1) $H_2@C_{60}$ must be subject to intimate and direct molecular contact with the spin catalyst at 77 K until the 50/50 equilibrium mixture is obtained; (2) The spin catalyst must then be capable of being rapidly removed before the sample is brought from 77 K to room temperature to avoid the back conversion to the 25/75 room temperature equilibrium mixture; (3) An accurate and reliable method must be able to analyze the ratio of the $pH_2@C_{60}/oH_2@C_{60}$ at room temperature to track the back conversion.

Requirement (1) is met by dispersing $H_2@C_{60}$ on the external surface of a zeolite[4] and by employing liquid oxygen as a paramagnetic spin catalyst at 77 K. The dispersion of $H_2@C_{60}$ on the zeolite insures intimate contact of the liquid spin catalyst with the adsorbed $H_2@C_{60}$.
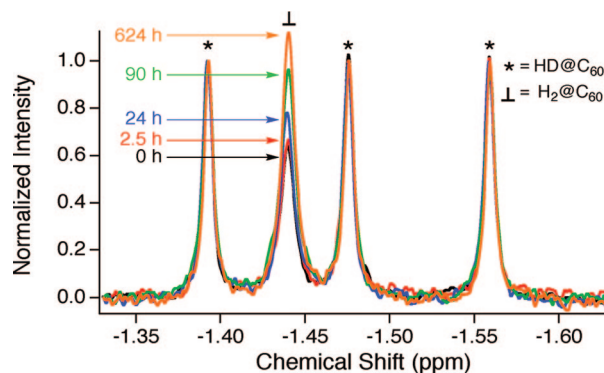

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Figure 1. 500 MHz ¹H NMR spectrum of the isotopomeric mixture of $H_2@C_{60}$, $HD@C_{60}$, and $D_2@C_{60}$ in 1,2-dichlorobenzene-d_4. The ²H NMR spectrum is not shown. The first, third, and fourth peak in the spectrum with increasing field are due to $HD@C_{60}$. The times shown indicate the time dependence of the recovery of the ¹H NMR signal of an O_2 saturated sample after forward conversion at 77 K.

Requirement (2) is met by evaporating the liquid oxygen *in vacuo* under controlled conditions such that the temperature does not rise substantially until sufficient oxygen has been removed to prevent catalysis of the back reaction as the temperature is raised to room temperature. Requirement (3) is met by dissolving the $pH_2@C_{60}$ enriched sample in a suitable solvent and monitoring the ¹H NMR spectrum of the residual $oH_2@C_{60}$. The chemical shift of H_2 in liquids is ~4 ppm, whereas that of $H_2@C_{60}$ and $HD@C_{60}$ are shifted to ~ −1.5 ppm, simplifying the quantitative analysis of the data by isolating cleanly the ¹H signals of the endofullerenes. The sample used in the study reported here was a mixture of isotopomers containing 7.5% $H_2@C_{60}$, 31% $HD@C_{60}$, 40% $D_2@C_{60}$, and 21% of empty C_{60}. The ¹H NMR signals of $oH_2@C_{60}$ and $HD@C_{60}$ are clearly resolved at room temperature (Figure 1). Since the nuclear spin and rotational states of HD are not subject to the same symmetry restrictions as those of H_2 and D_2, it is possible to employ $HD@C_{60}$ as an internal standard whose intensity is not affected by the spin catalysis. The transformations $oH_2@C_{60} \rightarrow pH_2@C_{60}$ and $pH_2@C_{60} \rightarrow oH_2@C_{60}$ have been demonstrated experimentally as follows.

In a typical experiment, 2 mg of the mixture of $H_2@C_{60}$ isotopomers in cyclohexane were dispersed on 1 g of NaY zeolite at room temperature using the following procedure to form a mixture of the supramolecular complexes [$H_2@C_{60}$]@NaY + [$HD@C_{60}$]@NaY + [$D_2@C_{60}$]@NaY + C_{60}@NaY. The mixture of isotopomers was dissolved in 1 mL of CS_2 and then diluted with 35 mL of cyclohexane. The zeolite was added to the solutions and stirred for 2 h, after which the solvent was evaporated under vacuum. The sample was immersed in liquid oxygen at 77 K for
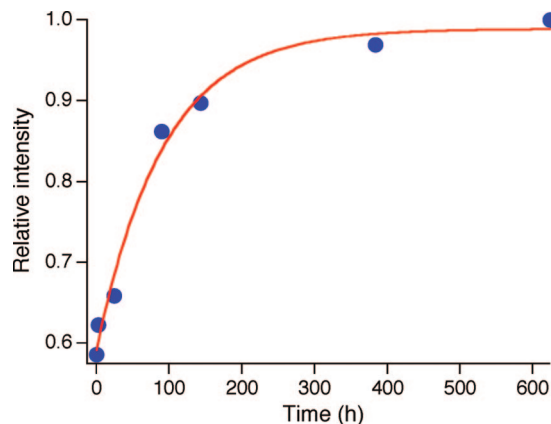
Figure 2. Time dependence of the $pH_2@C_{60}$ to $oH_2@C_{60}$ conversion in a 1,2-dichlorobenzene-d_4 oxygen saturated solution at room temperature.

30 min and then the oxygen was rapidly removed under vacuum, leaving the solid complexes at room temperature. The $H_2@C_{60}$ isotopomers were extracted from the zeolite complex with CS_2, and the solid zeolite was separated by centrifugation. The CS_2 was then removed under vacuum leaving a solid sample of the endofullerenes. The solid was redissolved in 1,2-dichlorobenzene-d_4, the solution was purged with argon, and the sealed sample was analyzed by ^1H NMR spectroscopy. The results of the NMR analysis are shown in Figure 1.

Figure 1 shows the ^1H NMR signals of a sample of the endofullerenes after treatment with the spin catalyst as a function of time. A salient difference in Figure 1 is the significant initial reduction in the signal of $oH_2@C_{60}$ relative to that of $HD@C_{60}$ as expected, since low temperature favors pH_2. The ratio of the $H_2@C_{60}$ and $HD@C_{60}$ signals at 624 h is experimentally undistinguishable to that of the original $H_2@C_{60}$ and $HD@C_{60}$ before conversion.

The ^1H NMR signal of the argon purged $pH_2@C_{60}/oH_2@C_{60}$ mixture was found to increase very slowly over the course of 1 month at room temperature, yielding an estimated half-life of ca. 7.5 days for a return to equilibrium. This result demonstrates that pH_2 in the C_{60} cage is substantially more "magnetically isolated" than dissolved H_2 itself under the same conditions in the absence of paramagnetic catalysts.[5] To obtain a more readily measurable rate of back conversion to the equilibrium mixture at room temperature, the spin catalysts oxygen and nitroxides were added to independent samples (Figure 1). Even in the presence of these spin catalysts, however, the back conversion of $pH_2@C_{60} \rightarrow oH_2@C_{60}$ is slow compared to the catalyzed rates for solutions of pH_2. It was found that an oxygen saturated solution of the enriched sample underwent back conversion (Figure 2) with a lifetime of ca. 100 h, corresponding to a value of the second-order rate constant for catalysis, k_{O_2}, of ca. 5×10^{-4} M^{-1} s^{-1}, based on an estimate of the solubility of oxygen in aromatic solvents. The rate constant for the nitroxide spin catalyzed back reaction (Figure 3) was found to be 4×10^{-5} M^{-1} s^{-1}. These rates may be compared with those for catalysis of the conversion reaction for solutions of pH_2: 2×10^{-1} M^{-1} s^{-1} (O_2 in H_2O),[6a] 6×10^{-3} M^{-1} s^{-1} (Cu^{2+} complex in H_2O),[6b] and 8×10^{-2} M^{-1} s^{-1} (nitroxide in $CDCl_3$).[6c]

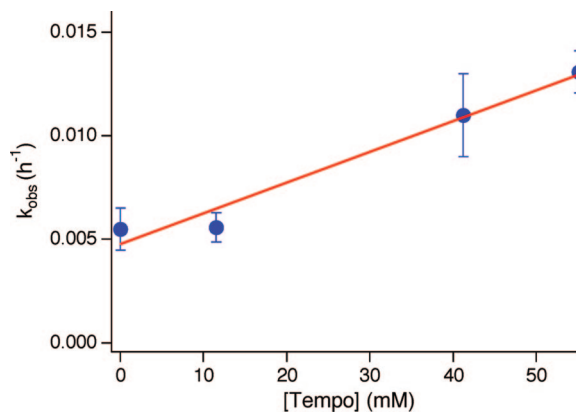**Figure 3.** Rate for the $pH_2@C_{60} \rightarrow oH_2@C_{60}$ conversion in the presence of various concentrations of the nitroxide Tempo at room temperature.

In conclusion, we have demonstrated the efficient conversion of one allotrope of hydrogen into another when both are incarcerated in the interior space of a C_{60} molecule dispersed on a zeolite surface. The conversion of $oH_2@C_{60}$ to $pH_2@C_{60}$ reaches equilibrium in less than 0.5 h when the sample is immersed in liquid oxygen at 77 K. Rapid removal of the oxygen provides a sample of enriched $pH_2@C_{60}$ that is stable for many days in the absence of paramagnetic catalysts. Thus, enriched $pH_2@C_{60}$, which is nonvolatile, readily soluble in common solvents, or adsorbed on surfaces, can be viewed as a more versatile probe than pH_2 for investigating subtle magnetic effects in condensed media or on surfaces. Understanding such phenomena has important applications to the liquefaction and storage of liquid hydrogen[7] and the production and chemical or medical uses of nuclear polarization.[8]

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(5) Aroulanda, C.; Starovoytova, L.; Canet, D. *J. Phys. Chem. A* **2007**, *111*, 10615–10624; half-lives for pH_2-oH_2 conversion in deuterated solvents are reported to be 10−15 h at room temperature in the absence of a catalyst. The conventional mechanism for the conversion of oH_2 and pH_2 requires the development of an inhomogeneous magnetic field that causes the two nuclear spins to become nonequivalent and undergo nuclear spin singlet−triplet transitions through dipole−dipole coupling. The conversion of $oH_2@C_{60}$ and $pH_2@C_{60}$ in the presence of oxygen and nitroxides can be understood in terms of this mechanism. However, in the present case, an alternative mechanism in which a collision of oxygen or nitroxide with $oH_2@C_{60}$ or $pH_2@C_{60}$ forms a weak complex with a significant lifetime, enhancing the time scale of the inhomogeneous magnetic field, cannot be ruled out.
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