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ARTICLE *in* JOURNAL OF PHYSICAL CHEMISTRY LETTERS · MARCH 2011

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Distance-Dependent *para*-H₂ → *ortho*-H₂ Conversion in H₂@C₆₀ Derivatives Covalently Linked to a Nitroxide Radical

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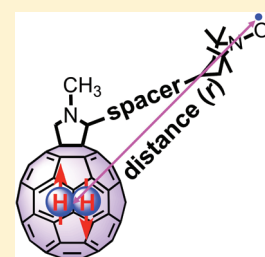
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ABSTRACT: The *ortho*-H₂ → *para*-H₂ conversion in a series of H₂@C₆₀ derivatives covalently linked to a nitroxide radical has been investigated. The resulting conversion rates are in good agreement with the Wigner's theory, modified for intramolecular interaction of H₂ with the paramagnet.

SECTION: Kinetics, Spectroscopy



We recently reported¹ distance-dependent nuclear spin relaxation ($1/T_1$) of a series of H₂@C₆₀ derivatives covalently linked to a nitroxide radical. The results show that T_1 increases with the distance between the encapsulated H₂ and the radical centers (r), and the relaxivity rate constant is proportional to r^{-6} . Another aspect of interest for such H₂@C₆₀ derivatives is the distance dependence of the nitroxide spin catalyzed *para/ortho*-H₂ conversion.^{2,3}

The H₂ molecule exists as two allotropes (*para*-H₂ and *ortho*-H₂).⁴ At room temperature normal (equilibrium) H₂ consists of 75% of *ortho*-H₂ (*o*H₂) and 25% of *para*-H₂ (*p*H₂). When the temperature decreases to 77 K, the composition at equilibrium of *p*H₂ and *o*H₂ is 50%/50%. With adventitious spin catalysts, interconversion of *p*H₂ and *o*H₂ is very slow, typically months or longer. In the presence of a well-defined and selected paramagnetic spin catalyst, the interconversion rate of *p*H₂ and *o*H₂ can be greatly increased. The availability⁵ of a host–guest system, H₂@C₆₀, provides an opportunity to explore the *ortho/para* conversion of H₂ incarcerated in a C₆₀ under well-defined conditions. Oxygen³ has been used as a spin catalyst for *para/ortho*-H₂ interconversion for the H₂@C₆₀ system. The lifetime of *p*H₂ → *o*H₂ conversion at room temperature is ~100 h in an oxygen-saturated solution. The latter time scale is comparable to that for a small molecule of nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), used as a spin catalyst at a concentration of 50 mM.^{3,4}

The spin conversions of *o*H₂ and *p*H₂ with both oxygen and TEMPO as spin catalysts in H₂@C₆₀ are bimolecular processes, that is, the paramagnetic species diffuses, and encounters the H₂@C₆₀ molecule in order to catalyze the conversion. Compared with H₂ gas, an advantage of H₂ encapsulated inside C₆₀ is that one can synthesize a range of H₂@C₆₀ derivatives in which a

paramagnetic spin catalyst is covalently linked to the C₆₀ surface.⁵ Once the nitroxide radical is attached to the H₂@C₆₀ surface, a spin catalyst with a predetermined and relative fixed distance for the intramolecular *para/ortho*-H₂ conversion is realized. Through available synthetic methods, one can readily systematically vary the distance between encapsulated H₂ and the attached nitroxide radical centers. With these nitroxide derivatives of C₆₀, an investigation of distance-dependent conversion of *para/ortho*-H₂ is possible and is the topic of this report.

Chart 1 shows a series of H₂@C₆₀ nitroxide derivatives (1–7) with a 2-fold variation in the distance between the encapsulated H₂ and the nitroxide radical centers.¹ A structurally similar diamagnetic H₂@C₆₀ derivative (**D1**) was used as a control compound to provide benchmark data.² The *p*H₂ → *o*H₂ conversion at room temperature was examined by monitoring the change of the ¹H NMR spectrum and the resulting conversion rates are analyzed by a modification of Wigner's theory.⁶

The synthesis of 1–7 and **D1** has been previously reported.^{1,2} From molecular modeling calculations, the distance between encapsulated H₂ and the nitroxide radical centers increases monotonically from 1 to 6.¹ The derivative 7 is similar in structure to 4, but has a biradical attached to the C₆₀ surface. In this report, a mixture of isotopomers of H₂ and HD were encapsulated in the C₆₀ derivatives, so that the ¹H NMR signal of the HD is an internal standard.^{2,3}

The conversion of *o*H₂ → *p*H₂ of 1–7 and **D1** was performed at 77 K with liquid oxygen as the spin catalyst following the procedures described before.^{2,3} Once the 50%/50% ratio of

Received: February 9, 2011

Accepted: March 8, 2011

Published: March 11, 2011

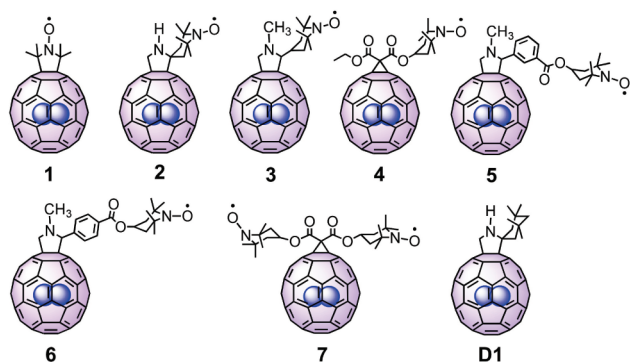
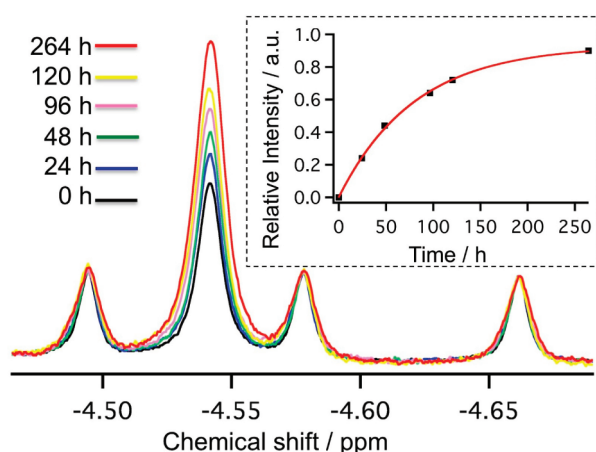
Chart 1. Structures of H₂@C₆₀ derivatives 1–7 and D1^a^aBlue balls indicate a mixture of encapsulated H₂ and HD.

Figure 1. ¹H NMR spectra of **6** in 1,2-dichlorobenzene-*d*₄ (the forward time dependence of the increase of the ¹H NMR signal of an air-saturated sample after forward conversion at 77 K). The signal at −4.53 ppm corresponds to ¹H of the *ortho*-H₂. The remaining triplet of signals corresponds to the ¹H signal of ¹H²H (HD). Inset indicates *para*-H₂ to *ortho*-H₂ conversion profile.

ortho/para-H₂ was reached, the conversion of *p*H₂ → *o*H₂ at room temperature was monitored by ¹H NMR of *o*H₂ (*p*H₂ is NMR silent) in 1,2-dichlorobenzene-*d*₄ solutions. A typical intensity increase of the *o*H₂ peak of ¹H NMR spectra with time is shown in Figure 1. The inset indicates the time-dependent profile, which was fitted to an exponential equation to extract the conversion lifetime.

From these NMR studies, the lifetimes for the *p*H₂ to *o*H₂ conversion were obtained. The resulting conversion lifetimes of *p*H₂ → *o*H₂ of **3**–**7** and **D1** are listed in Figure 2 (also see Table 1). The power of the spin catalysis is revealed by the observation that the conversion rates of **1** and **2** are too fast to be monitored by ¹H NMR, i.e., within the time of the workup of the samples (~15 min), *para/ortho*-H₂ has reached room temperature equilibrium (75% of *o*H₂/25% of *p*H₂) in minutes rather than many hours.² The conversion lifetimes of **3**–**6** increase with the computed distance between the encapsulated H₂ and the nitroxide radical centers. Furthermore, the conversion lifetime of the biradical derivative **7** is about half of its monoradical counterpart **4**, which is consistent with the biradical acting as a pair of spin 1/2 catalyst systems.

The rate constant *k*_{po} (Table 1) for catalysis caused by the paramagnetic spin catalyst was calculated from the observed rate

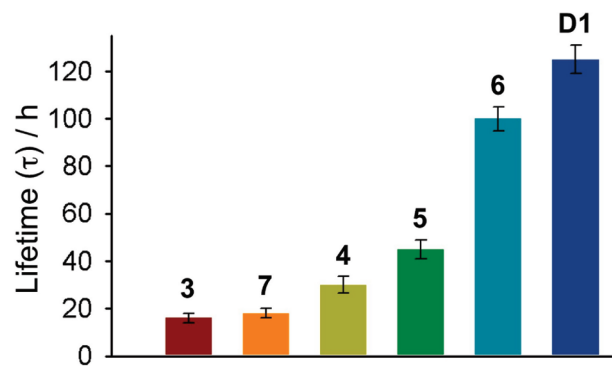


Figure 2. Lifetimes (τ) of *para*-H₂→*ortho*-H₂ conversion of H₂@C₆₀ nitroxide derivatives.

Table 1. Lifetimes and Rate Constants of *para*-H₂→*ortho*-H₂ Conversion of H₂@C₆₀ Nitroxide Derivatives, and Distances between H₂ and the Nitroxide Radical Centers

H ₂ @C ₆₀ nitroxides	conversion lifetimes (h)	<i>k</i> _{po} (s ^{−1}) × 10 ⁶	distances <i>r</i> (Å) ^a
3	16 ± 2	11 ± 2	9.4
4	30 ± 2	5.2 ± 0.5	10.7
5	45 ± 4	2.9 ± 0.2	12.0
6	100 ± 5	0.41 ± 0.11	13.6
7	18 ± 3.5		
D1	125 ± 6		

^aDistances were deduced from relaxivity measurement.¹

constant (1/ τ) by subtracting the rate constant observed for the diamagnetic species (**D1**) (1/ τ_d) and multiplying by 3/4 to adjust for the contribution, *k*_{op}, from the reverse rate.⁷

Quantitative analysis of the conversion rates has been carried out using Wigner's theory^{6,7} of homogeneous bimolecular catalysis of *para*→*ortho* conversion via the field gradient across the H₂ molecule produced by a magnetic moment, μ , at fixed distance, *r*, from the H₂ center of mass. In the present case, however, the H₂ and paramagnet remain permanently in contact, and the physical theory resembles the *ortho*→*para* conversion of H₂ physisorbed on surfaces, which has been extensively developed.⁸ For simplicity we will assume that only the lowest *para* (*J* = 0) and *ortho* (*J* = 1) states are involved in the conversion process, which accounts for about 80% of the molecules at room temperature.

In this approximation, the probability at time *t* of a transition to the *ortho* state by a molecule initially in the *para* state may be written in conventional notation as^{9a}

$$P_{p \rightarrow o}(t) = 3 \left(\frac{\mu_0}{4\pi} \right)^2 [\gamma_p^2 g^2 \mu_B^2 S(S+1) r^{-6}] \left(\frac{r_0}{r} \right)^2 \left[\frac{\sin(\omega_{op} t/2)}{(\omega_{op}/2)} \right]^2 \quad (1)$$

The first-order rate coefficient for conversion of *para*- to *ortho*-H₂, *k*_{po}, may then be obtained⁷ by taking the time derivative of eq 1 and averaging over a distribution of times during which the coherence expressed in eq 1 is maintained. The result is^{9b}

$$k_{po} = \Omega^2 d^{-8} J(\omega_{op}, \tau_r) \quad (2)$$

where the angular frequency, $\Omega = 1.0 \times 10^{10}$ rad s^{−1}, the

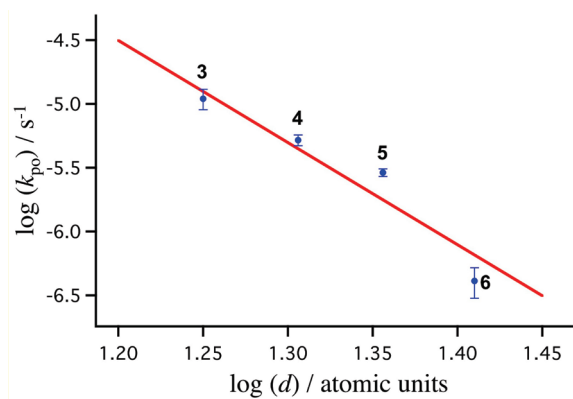


Figure 3. Logarithm profile of the *para*-H₂→*ortho*-H₂ conversion rate constant (k_{po} , s⁻¹) versus distance (d , atomic units) of H₂@C₆₀ nitroxide derivatives. The slope is fixed at -8 , and the best-fit intercept, corresponding to $d = 1$ atomic unit, is $\log(\Omega^2 \langle J(\omega_{op}, \tau_r) \rangle)$ (equals to 5.1) from which $\langle \tau_r \rangle$ has been calculated.

distance, d , between the paramagnet and H₂ is expressed in atomic units (0.529×10^{-10} m), and the spectral density function, $J(\omega_{op}, \tau_r) = \tau_r / (1 + \omega_{op}^2 \tau_r^2)$.

The introduction of $J(\omega_{op}, \tau_r)$ assumes that the evolution of coherent mixing between the *para* state and the *ortho* states, which in Wigner's gas phase theory⁶ or the solution analogue⁷ is limited by the collision lifetime, in our case decreases exponentially with a correlation time, τ_r . A possible mechanism for loss of coherence would be mixing of one of the target *ortho* states with one of the other two $J = 1$ states in an "m-diffusion" process in which the orientation, but not the magnitude, of the angular momentum J is randomly modulated.¹⁰ On the basis of T_1 measurements^{11,12} in H₂@C₆₀ it is expected that $\tau_r \approx 10^{-12}$ s.

Equation 2 leads to the prediction that k_{po} should vary¹³ as d^{-8} and depend on τ_r through the function $J(\omega_{op}, \tau_r)$. If it is assumed that τ_r (and therefore $J(\omega_{op}, \tau_r)$) is insensitive to the nitroxide side chain, a plot of $\log(k_{po})$ versus $\log(d)$ (Figure 3) should be linear with a slope of -8 and an intercept from which an average value of τ_r can be estimated. The $\langle \tau_r \rangle$ obtained, $1.6 \pm 0.5 \times 10^{-12}$ s, is remarkably close to the value of the spin-rotation correlation time for H₂@C₆₀, obtained from T_1 measurements, which ranges from ca. 3–8 ps, depending on the model used for analysis.^{12,13}

The dipole–dipole mechanism analogous to the Wigner theory has also been applied to explain bimolecular relaxation, R_1 , and *para/ortho* conversion of H₂@C₆₀ by TEMPO.^{3,4} The ratio of bimolecular rate constants, R_1/k_{po} , in that case⁴ has the value 1.7×10^6 . The corresponding ratio, $(1/T_{1p})/k_{po}$, for 3–6 ranges from 1.1 to 3.8×10^6 . The similarity of the ratios seems to indicate that the effectiveness of the paramagnet in the two processes is relatively insensitive to the dynamics of the H₂–paramagnet interaction. Interestingly, the ratio of relaxation to bimolecular conversion for solutions of H₂ in toluene catalyzed by TEMPO is 6000 times smaller than that for H₂@C₆₀,⁴ indicating either more effective conversion or less effective relaxation of H₂ in solution.

In conclusion, $p\text{H}_2 \rightarrow o\text{H}_2$ conversion of a series of H₂@C₆₀ derivatives covalently linked to a nitroxide radical has been measured by monitoring their ¹H NMR. The resulting conversion rates are in good agreement with the Wigner's theory, modified for intramolecular interaction of H₂ with the paramagnet.

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ACKNOWLEDGMENT

The authors thank the National Science Foundation for its generous support through Grant CHE 07-17518. We are also grateful to three reviewers for encouraging us to refine our description of the analysis and interpretation of the data.

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