Can H₂ Inside C₆₀ Communicate with the Outside World?

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The recent synthesis[1] of $H_2@C_{60}$ and $D_2@C_{60}$ has provided photochemists with an opportunity to investigate whether the simplest molecule, H_2, incarcerated inside a fullerene, can communicate with the electronically excited walls of its fullerene container and with excited molecules in the "outside world".[2] We report investigations comparing the photophysical characteristics of triplet C_{60} and triplet $H_2@C_{60}$ and the quenching of singlet molecular oxygen, $^1O_2$ by C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$. For comparison, the quenching of $^1O_2$ by H_2 and D_2 in solution is reported for the first time. Although the interactions of hydrogen with the walls of triplet C_{60} were found to be too weak to be determined by either triplet−triplet absorption or EPR spectroscopy, we report a significant interaction between singlet molecular oxygen ($^1O_2$) and the incarcerated guest H_2 and D_2. Importantly, the $^1O_2$ can sense the difference between incarcerated H_2 and D_2. The rate constants for quenching of $^1O_2$ by $H_2@C_{60}$ and $D_2@C_{60}$ are found to be somewhat larger than those for the quenching of $^1O_2$ by H_2 and D_2.

The interaction of incarcerated H_2 and D_2 with the walls of triplet fullerene was examined by laser flash photolysis, employing pulses from a Nd:YAG laser (532 nm, ∼5 ns pulse width). C_{60} shows a triplet−triplet absorption centered at 747 nm, which was utilized to determine the triplet lifetimes of C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$ in benzene solutions. No differences in the triplet lifetimes were observed within our experimental error ($\tau = 110 \pm 8 \mu s$; for further details see Supporting Information). Thus, the interaction of incarcerated H_2 and D_2 with the paramagnetic walls of the triplet fullerene is too weak to be determined by triplet lifetime measurements.

The magnitude of the interaction of incarcerated H_2 and D_2 with the triplet fullerene was also examined by time-resolved EPR (TREPR). TREPR spectra and transient decay kinetics of C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$ were studied in benzene, toluene, and methylcyclohexane at 285 K. No differences in the spectra and transient decay kinetics of $^3C_{60}$, $H_2@^3C_{60}$, and $D_2@^3C_{60}$ were found.

Although there was no measurable interaction of incarcerated H_2 or D_2 with the triplet walls of C_{60}, we searched for an interaction with the incarcerated H_2 and D_2 with an external electronically excited molecule, singlet molecular oxygen, $^1O_2$.

Large differences in the quenching of $^1O_2$ by H−X and D−X bonds are well-known.[3] To the best of our knowledge, there are no reports of the rate constants for quenching of $^1O_2$ by H_2 or D_2 in solution, although a large isotope effect is found in the gas phase.[4] It was therefore of interest to determine the quenching rate constants of $^1O_2$ by H_2 and D_2 in solution and to compare these rate constants with those for $H_2@C_{60}$ and $D_2@C_{60}$ in solution.

The absolute quenching rate constants of $^1O_2$ by $H_2@C_{60}$ and $D_2@C_{60}$ were determined using a time-resolved method, employing the host, C_{60}, which is known to be an efficient $^1O_2$ sensitizer.[5]
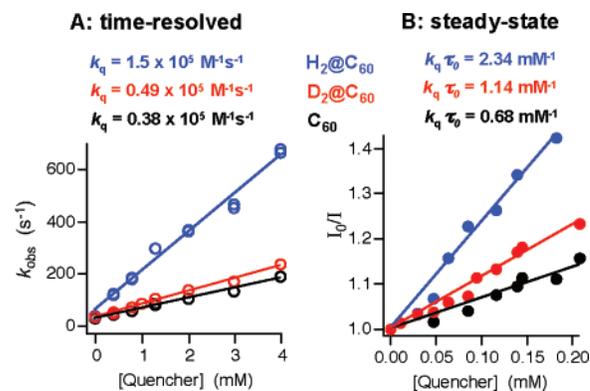
Figure 1. Quenching of $^1O_2$ by C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$. (A) Dependence of the pseudo-first-order rate constant of the decay of $^1O_2$ phosphorescence at 1270 nm on the C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$ concentration (0.004 to 4 mM) after laser excitation (532 nm) of air saturated CS_2 solutions. (B) Stern−Volmer plot of singlet oxygen quenching by C_{60}, $H_2@C_{60}$, and $D_2@C_{60}$ in air saturated CCl_4 at 22 °C; [**1**] = 0.2 mM.

CS_2 was selected as solvent based on the relatively long lifetime of $^1O_2$ ($\tau = 79$ ms)[6] and high solubility of C_{60} in CS_2 (7.9 mg/mL).[7] The $^1O_2$ quenching was monitored by its characteristic phosphorescence at 1270 nm.[6] $^1O_2$ phosphorescence decay traces after laser excitation (532 nm) were recorded at different concentrations of $H_2@C_{60}$ (or $D_2@C_{60}$ and C_{60}). The plot of the pseudo-first-order decay rate constants vs the quencher concentration yielded the absolute rate constants k_q (Figure 1A; $k_q(H_2@C_{60}) = 1.5 \times 10^5$ M^{-1} $s^{-1} > k_q(D_2@C_{60}) = 0.49 \times 10^5$ M^{-1} $s^{-1} > k_q(C_{60}) = 0.38 \times 10^5$ M^{-1} s^{-1}).

An independent chemiluminescence method was used to verify the trends of k_q. The thermal decomposition of 1,4-dimethylnaphthalene-1,4-endoperoxide (**1**) produces $^1O_2$ cleanly and in good yield.[8] For these experiments CCl_4 was selected as a solvent because of its lower volatility compared to CS_2 in addition to the relatively long lifetime of $^1O_2$ in CCl_4 (τ ∼130 ms)[6] and the acceptable solubility of C_{60} in CCl_4 (0.32 mg/mL).[7] The chemiluminescence emission of $^1O_2$ at 1270 nm produced by thermolysis of **1** was utilized to determine Stern−Volmer quenching constants.[8a] The time scale of the measurements for each concentration of quencher (∼5 min) was small relative to the half-life of **1** at 25 °C (∼5 h). The Stern−Volmer data for quenching of chemiluminescence produced by thermolysis of **1** by $H_2@C_{60}$, $D_2@C_{60}$, and C_{60}, are shown in Figure 1B.

From the relative slopes of the Stern−Volmer plots in Figure 1B, it is clear that the rate constant for quenching of $^1O_2$ by $H_2@C_{60}$ is considerably larger than the rate constant for quenching of $^1O_2$ by $D_2@C_{60}$ and that both endo fullerenes are better quenchers than the empty fullerene.

An explanation of these results can be deduced from the observation that $^1O_2$ undergoes vibrationally assisted intersystem

Table 1. Singlet Oxygen Quenching Rate Constant

	k_q [M^{-1} s^{-1}][a]	solvent	lit. k_q [M^{-1} s^{-1}]
C_{60}	3.8×10^4	CS_2	$(6.2 \pm 1.2) \times 10^{4}$ [c]
$H_2@C_{60}$	1.5×10^5	CS_2	---
$D_2@C_{60}$	4.9×10^4	CS_2	---
H_2	8.1×10^4	CCl_4	$(2.2 \pm 0.3) \times 10^{4}$ [d]
D_2	2.4×10^3	CCl_4	$(2.6 \pm 1.3) \times 10^{3}$ [d]

[a] Estimated to have error limits of $\pm 15\%$. [b] Reference 10. [c] Reference 11. [d] Quenching rate constant for gas phase (ref 4).

crossing[3,9] to $^3O_2$, *e.g.*, the lifetime of $^1O_2$ in C_6D_6 (681 μs) is $\sim$20 times longer than the lifetime of $^1O_2$ in C_6H_6 (30 μs).[6] The higher frequency of a C−H vibration compared to a C−D vibration is an important factor which makes C_6H_6 a much better quencher than C_6D_6.

The rate constants for quenching of $^1O_2$ by H_2 and D_2 have been measured in the gas phase as 2.2×10^4 M^{-1} s^{-1} and 2.6×10^3 M^{-1} s^{-1}, respectively.[4] Employing the chemiluminescence method as described above, the rate constants for quenching of $^1O_2$ by H_2 and D_2 were determined in a CCl_4 solution (Supporting Information, Figure S2). A CCl_4 solution of **1** was bubbled with dried Ar to eliminate any traces of dissolved O_2. The resulting value of I_0 was assigned to zero quencher concentration. In order to extract rate constants from the slopes of Figure S2 (Supporting Information) ($k_q\tau$ values), a value of τ is required. A value of $\tau = 21$ ms for the $^1O_2$ lifetime was measured using methylcyclohexene as standard[8b] assuming $k_q = 3.3 \times 10^5$ M^{-1} s^{-1}. Mixtures of N_2 and H_2 (or D_2) gas were bubbled into the sample solution to produce varying concentrations of H_2 (or D_2). The concentration of dissolved H_2 and D_2 in CCl_4 was determined quantitatively by NMR spectroscopy employing 1,2,4-trichlorobenzene as standard (6.4 mM). The area for the H_2 signal at 3.8 ppm (relative to TMS) was integrated relative to the area for the signal for 1,2,4-trichlorobenzene. For a H_2 saturated CCl_4 solution a value of 3.32 mM was obtained which compared favorably with that from the literature (3.34 mM). For D_2 a value of 5.67 mM was found for a saturated CCl_4 solution. The resulting rate constants (Table 1) were found to be $k_q(H_2) = 8.1 \times 10^4$ M^{-1} s^{-1} and $k_q(D_2) = 2.4 \times 10^3$ M^{-1} s^{-1}, which are significantly lower than the values for quenching of $^1O_2$ by $H_2@C_{60}$ and $D_2@C_{60}$, respectively.

The results in Table 1 represent a unique example of an incarcerated guest having a significantly *larger* rate constant for quenching than the unincarcerated guest. It is expected and generally found that the molecular wall of the host provides an electronic barrier that "protects" the guest and reduces the effectiveness of the guest as a quencher of excited molecules "in the outside world".[12] For example, room-temperature phosphorescence in air saturated solutions can be observed for some organic molecules encapsulated in cyclodextrins.[13] The triplet state of the complexed guest molecule is protected by the cyclodextrin from oxygen quenching. The uniqueness of the contrasting results of Table 1 may be related to the uniqueness of the incarcerated guest molecule, H_2 (and D_2). The effectiveness of $H_2@C_{60}$ *versus* H_2 as a quencher of (paramagnetic) $^1O_2$ may be related to the mechanism of paramagnetic nuclear relaxation which considers an important feature of the effectiveness (rate constant) of relaxation to be the "residence time" of the relaxant in the vicinity (outer sphere or inner sphere) of the relaxee.[14]

Interaction between C_{60} and $^1O_2$ has been studied previously,[15] and it is reported that C_{60} and triplet molecular oxygen ($^3O_2$) form

a weak complex.[16] It is well-established that $^1O_2$ forms exciplexes with many organic molecules.[17] It is plausible that $^1O_2$ forms an exciplex with the outer surface of fullerenes. The exciplex is expected to possess a significant lifetime compared to an ordinary collision complex and provides an opportunity for $^1O_2$ and the incarcerated H_2 to interact for a considerable period of time. In contrast, collisions between $^1O_2$ and H_2 are probably very short-lived, since exciplex formation is unlikely and H_2 possesses an unusually high diffusion in solution (O_2 has a diffusion coefficient of 3.82×10^{-5} cm^2 s^{-1} in CCl_4 compared to 9.75×10^{-5} cm^2 s^{-1} of H_2).[18] Both rates are large compared to the rate of diffusion of C_{60} $[(1.4 \pm 0.3) \times 10^{-5}$ cm^2 s^{-1} in dichloromethane].[19]

In conclusion, we report the first example of a significant electron and vibrational interaction of incarcerated guests in fullerenes ($H_2@C_{60}$) with an external electronically excited molecule ($^1O_2$). This reactivity feature is unprecedented in guest host systems. It is speculated that the unique behavior can be attributed to a long-lived exciplex between $^1O_2$ and fullerenes, which allows for a long duration of contact and an electronic-vibrational interaction that is effective because it is integrated over a long time; this long interaction time through a fullerene wall is more effective than the brief time of interaction in the collisions of $^1O_2$ and H_2 (or D_2) and the time of interaction of the guests with the triplet state of the fullerene.

Supporting Information Available: Laser flash photolysis, TREPR and experiments to determine k_q of H_2 and D_2 in solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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