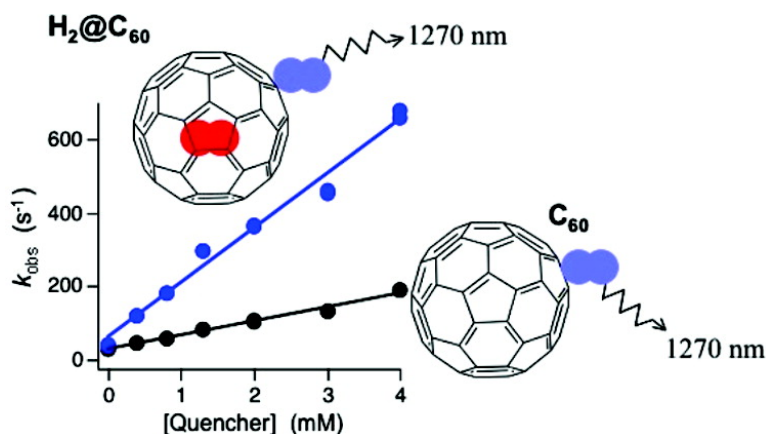


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Can H₂ Inside C₆₀ Communicate with the Outside World?

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The recent synthesis¹ of H₂@C₆₀ and D₂@C₆₀ has provided photochemists with an opportunity to investigate whether the simplest molecule, H₂, 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 C₆₀ and triplet H₂@C₆₀ and the quenching of singlet molecular oxygen, ¹O₂ by C₆₀, H₂@C₆₀, and D₂@C₆₀. For comparison, the quenching of ¹O₂ by H₂ and D₂ in solution is reported for the first time. Although the interactions of hydrogen with the walls of triplet C₆₀ 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 (¹O₂) and the incarcerated guest H₂ and D₂. Importantly, the ¹O₂ can sense the difference between incarcerated H₂ and D₂. The rate constants for quenching of ¹O₂ by H₂@C₆₀ and D₂@C₆₀ are found to be somewhat larger than those for the quenching of ¹O₂ by H₂ and D₂.

The interaction of incarcerated H₂ and D₂ 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). C₆₀ shows a triplet–triplet absorption centered at 747 nm, which was utilized to determine the triplet lifetimes of C₆₀, H₂@C₆₀, and D₂@C₆₀ in benzene solutions. No differences in the triplet lifetimes were observed within our experimental error ($\tau = 110 \pm 8 \mu\text{s}$; for further details see Supporting Information). Thus, the interaction of incarcerated H₂ and D₂ 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 H₂ and D₂ with the triplet fullerene was also examined by time-resolved EPR (TREPR). TREPR spectra and transient decay kinetics of C₆₀, H₂@C₆₀, and D₂@C₆₀ were studied in benzene, toluene, and methylcyclohexane at 285 K. No differences in the spectra and transient decay kinetics of ³C₆₀, H₂@³C₆₀, and D₂@³C₆₀ were found.

Although there was no measurable interaction of incarcerated H₂ or D₂ with the triplet walls of C₆₀, we searched for an interaction with the incarcerated H₂ and D₂ with an external electronically excited molecule, singlet molecular oxygen, ¹O₂.

Large differences in the quenching of ¹O₂ 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 ¹O₂ by H₂ or D₂ 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 ¹O₂ by H₂ and D₂ in solution and to compare these rate constants with those for H₂@C₆₀ and D₂@C₆₀ in solution.

The absolute quenching rate constants of ¹O₂ by H₂@C₆₀ and D₂@C₆₀ were determined using a time-resolved method, employing the host, C₆₀, which is known to be an efficient ¹O₂ sensitizer.⁵

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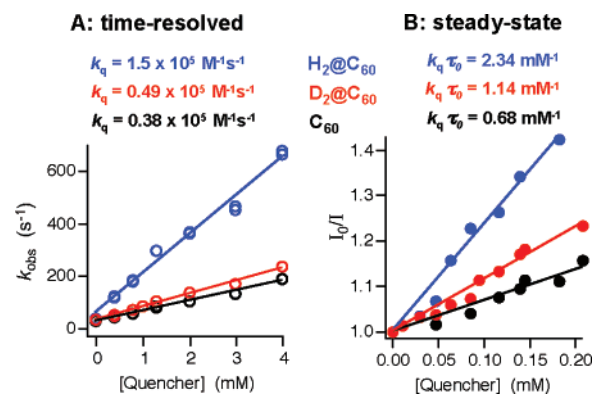


Figure 1. Quenching of ¹O₂ by C₆₀, H₂@C₆₀, and D₂@C₆₀. (A) Dependence of the pseudo-first-order rate constant of the decay of ¹O₂ phosphorescence at 1270 nm on the C₆₀, H₂@C₆₀, and D₂@C₆₀ concentration (0.004 to 4 mM) after laser excitation (532 nm) of air saturated CS₂ solutions. (B) Stern–Volmer plot of singlet oxygen quenching by C₆₀, H₂@C₆₀, and D₂@C₆₀ in air saturated CCl₄ at 22 °C; [I] = 0.2 mM.

CS₂ was selected as solvent based on the relatively long lifetime of ¹O₂ ($\tau = 79 \text{ ms}$)⁶ and high solubility of C₆₀ in CS₂ (7.9 mg/mL).⁷ The ¹O₂ quenching was monitored by its characteristic phosphorescence at 1270 nm.⁶ ¹O₂ phosphorescence decay traces after laser excitation (532 nm) were recorded at different concentrations of H₂@C₆₀ (or D₂@C₆₀ and C₆₀). The plot of the pseudo-first-order decay rate constants vs the quencher concentration yielded the absolute rate constants k_q (Figure 1A; $k_q(\text{H}_2@\text{C}_{60}) = 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} > k_q(\text{D}_2@\text{C}_{60}) = 0.49 \times 10^5 \text{ M}^{-1} \text{ s}^{-1} > k_q(\text{C}_{60}) = 0.38 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).

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 ¹O₂ cleanly and in good yield.⁸ For these experiments CCl₄ was selected as a solvent because of its lower volatility compared to CS₂ in addition to the relatively long lifetime of ¹O₂ in CCl₄ ($\tau \sim 130 \text{ ms}$)⁶ and the acceptable solubility of C₆₀ in CCl₄ (0.32 mg/mL).⁷ The chemiluminescence emission of ¹O₂ 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 H₂@C₆₀, D₂@C₆₀, and C₆₀, 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 ¹O₂ by H₂@C₆₀ is considerably larger than the rate constant for quenching of ¹O₂ by D₂@C₆₀ and that both endo fullerenes are better quenchers than the empty fullerene.

An explanation of these results can be deduced from the observation that ¹O₂ 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 ³O₂, e.g., the lifetime of ¹O₂ in C₆D₆ (681 μs) is ~20 times longer than the lifetime of ¹O₂ in C₆H₆ (30 μs).⁶ The higher frequency of a C–H vibration compared to a C–D vibration is an important factor which makes C₆H₆ a much better quencher than C₆D₆.

The rate constants for quenching of ¹O₂ by H₂ and D₂ 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 ¹O₂ by H₂ and D₂ were determined in a CCl₄ solution (Supporting Information, Figure S2). A CCl₄ solution of **1** was bubbled with dried Ar to eliminate any traces of dissolved O₂. 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 ¹O₂ lifetime was measured using methylcyclohexene as standard^{8b} assuming $k_q = 3.3 \times 10^5$ M⁻¹ s⁻¹. Mixtures of N₂ and H₂ (or D₂) gas were bubbled into the sample solution to produce varying concentrations of H₂ (or D₂). The concentration of dissolved H₂ and D₂ in CCl₄ was determined quantitatively by NMR spectroscopy employing 1,2,4-trichlorobenzene as standard (6.4 mM). The area for the H₂ signal at 3.8 ppm (relative to TMS) was integrated relative to the area for the signal for 1,2,4-trichlorobenzene. For a H₂ saturated CCl₄ solution a value of 3.32 mM was obtained which compared favorably with that from the literature (3.34 mM). For D₂ a value of 5.67 mM was found for a saturated CCl₄ solution. The resulting rate constants (Table 1) were found to be $k_q(\text{H}_2) = 8.1 \times 10^4$ M⁻¹ s⁻¹ and $k_q(\text{D}_2) = 2.4 \times 10^3$ M⁻¹ s⁻¹, which are significantly lower than the values for quenching of ¹O₂ by H₂@C₆₀ and D₂@C₆₀, 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, H₂ (and D₂). The effectiveness of H₂@C₆₀ versus H₂ as a quencher of (paramagnetic) ¹O₂ 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 C₆₀ and ¹O₂ has been studied previously,¹⁵ and it is reported that C₆₀ and triplet molecular oxygen (³O₂) form

a weak complex.¹⁶ It is well-established that ¹O₂ forms exciplexes with many organic molecules.¹⁷ It is plausible that ¹O₂ 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 ¹O₂ and the incarcerated H₂ to interact for a considerable period of time. In contrast, collisions between ¹O₂ and H₂ are probably very short-lived, since exciplex formation is unlikely and H₂ possesses an unusually high diffusion in solution (O₂ has a diffusion coefficient of 3.82×10^{-5} cm² s⁻¹ in CCl₄ compared to 9.75×10^{-5} cm² s⁻¹ of H₂).¹⁸ Both rates are large compared to the rate of diffusion of C₆₀ [$(1.4 \pm 0.3) \times 10^{-5}$ cm² s⁻¹ in dichloromethane].¹⁹

In conclusion, we report the first example of a significant electron and vibrational interaction of incarcerated guests in fullerenes (H₂@C₆₀) with an external electronically excited molecule (¹O₂). 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 ¹O₂ 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 ¹O₂ and H₂ (or D₂) and the time of interaction of the guests with the triplet state of the fullerene.

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Supporting Information Available: Laser flash photolysis, TREPR and experiments to determine k_q of H₂ and D₂ in solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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