

Research



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Recognition of hydrogen isotopomers by an open-cage fullerene

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We present our study on the recognition of hydrogen isotopes by an open-cage fullerene through determination of binding affinity of isotopes H₂/HD/D₂ with the open-cage fullerene and comparison of their relative molecular sizes through kinetic-isotope-release experiments. We took advantage of isotope H₂/D₂ exchange that generated an equilibrium mixture of H₂/HD/D₂ in a stainless steel autoclave to conduct high-pressure hydrogen insertion into an open-cage fullerene. The equilibrium constants of three isotopes with the open-cage fullerene were determined at various pressures and temperatures. Our results show a higher equilibrium constant for HD into open-cage fullerene than the other two isotopomers, which is consistent with its dipolar nature. D₂ molecule generally binds stronger than H₂ because of its heavier mass; however, the affinity for H₂ becomes larger than D₂ at lower temperature, when size effect becomes dominant. We further investigated the kinetics of H₂/HD/D₂ release from open-cage fullerene, proving their relative escaping rates. D₂ was found to be the smallest and H₂ the largest molecule. This notion has not only supported the observed inversion of relative binding affinities between H₂ and D₂, but also demonstrated that comparison of size difference of single molecules through non-covalent kinetic-isotope effect was applicable.

1. Introduction

Molecular recognition is one of the most prevailing topics in supramolecular chemistry [1–3]. It is only recently that molecular recognition of gases by non-covalent interactions has attracted some interest [4–6]. Among discovered molecular chambers, open-cage fullerenes are unique molecular containers that can retain small gas atom(s) or molecule(s) inside the carbon cages [7–11]. In parallel to the recognition of isotopomers of *p*-xylene by a molecular capsule in solution [12,13], these carbon-rich host systems may permit the study of the recognition of isotopic gas molecules in the gas–solid interface [14]. Here, we report recognition of isotopomers of hydrogen molecules by an open-cage fullerene and the studies of kinetic-isotope effects among them.

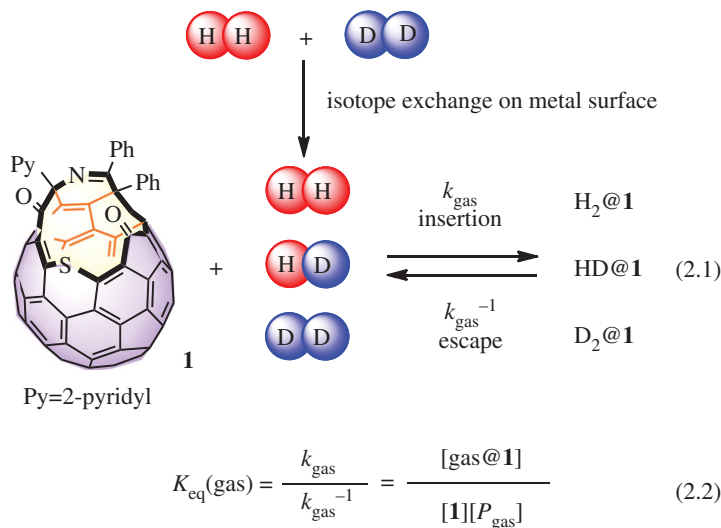
2. Results and discussion

Recently, we reported insertion of a H₂ molecule [15] and a He atom [16] inside open-cage fullerene **1** through its 13-membered-ring orifice [17]. We further extended this work to relative incorporation ratios of isotopomers of hydrogen in **1**, i.e. H₂, HD and D₂, and their rates of escape from **1** (scheme 1). The investigation was initiated from a naive result where encapsulation of a HD molecule inside **1** was achieved without HD as the starting gas component in our routine experiment of hydrogen gas insertion (equation (2.1)). In the ¹H NMR spectrum of **1** recorded after treatment with H₂ contaminated with D₂ (total pressure of 840 atm) at 200°C for 8 h in an autoclave, we observed a triplet with equal intensity centred at –7.28 ppm ($J = 41.6$ Hz, *o*-dichlorobenzene-*d*₄). This signal is slightly upfield shifted when compared with the encapsulated H₂ signal (–7.24 ppm) in **1** as shown in figure 1.

We soon found that HD is formed through H₂/D₂ exchange by catalytic action on the hot surface of the inner wall of the autoclave [18]. No signal corresponding to HD@**1** was observed in a control experiment when the interior surface of the autoclave was deactivated by silicon grease. Practically, the partial pressures of H₂, HD and D₂ were analysed by ¹H and ²H NMR spectra of the gas sample in CDCl₃ prepared by transferring the resulting gas mixture to a pressure-resistant NMR tube. The signals of three isotopomers were observed at 4.63 and 4.59 ppm ($J = 42.3$ Hz) for H₂ and HD in ¹H NMR; 4.71 ($J = 42.5$ Hz) and 4.67 ppm for HD and D₂ in ²H NMR, respectively. The encapsulated ratios of three isotopomers inside **1** were also analysed by ¹H or ²H NMR spectra using their solutions in *o*-dichlorobenzene-*d*₄. These peaks were observed at –7.21 ($J = 41.7$ Hz) and –7.25 ppm for HD@**1** and D₂@**1** in ²H NMR, respectively (figure 1). By analysis of relative integrals, we determined the equilibrium constants K_{eq} (gas) for insertion/release of these gases into/from open-cage fullerene **1** defined by equation (2.2), where P_{gas} denotes partial pressure of H₂, HD and D₂, and [gas@**1**]/[**1**] represents the encapsulation ratio of the gas molecule inside **1**.

Total encapsulation ratios more than 70% were observed under the conditions summarized in table 1. At temperatures of 190°C and 200°C (entries 1–6), the reaction periods of 0.5 and 1 day, respectively, were found to be enough to reach post-equilibrium period. We used empty **1** (entry 2) and two other independent mixtures containing 2.8% H₂@**1**, 24% HD@**1** and 52% D₂@**1** (entry 3), as well as 45% H₂@**1**, 28% HD@**1** and 4.2% D₂@**1** (entry 4) as starting materials under the same high-pressure conditions for control experiments.

In these experiments (entries 2–4), all materials produced similar encapsulation ratios of H₂, HD and D₂, which supported that insertion/escape of the three isotopomers is reversible. In all these entries, especially at higher temperature, HD always displayed higher affinity inside **1** than H₂ and D₂, which is most probably due to its dipolar nature. The dipole moment of HD was reported experimentally as $(8.0\text{--}9.8) \times 10^{-4}$ D [19], whereas such dipolar nature was never seen in H₂ or D₂ composed of two identical nuclei. Because the electron cloud tends to locate near the D nucleus in a HD molecule [20], we can represent the molecule as D^{δ-} – H^{δ+}. DH- π interaction might be the origin of stronger binding affinity with the π -system of the carbon cage when compared with apolar H₂ and D₂, similar to CH- π interaction seen frequently in the



Scheme 1. Encapsulation and release of hydrogen isotopomers into and from open-cage fullerene **1**. (Online version in colour.)

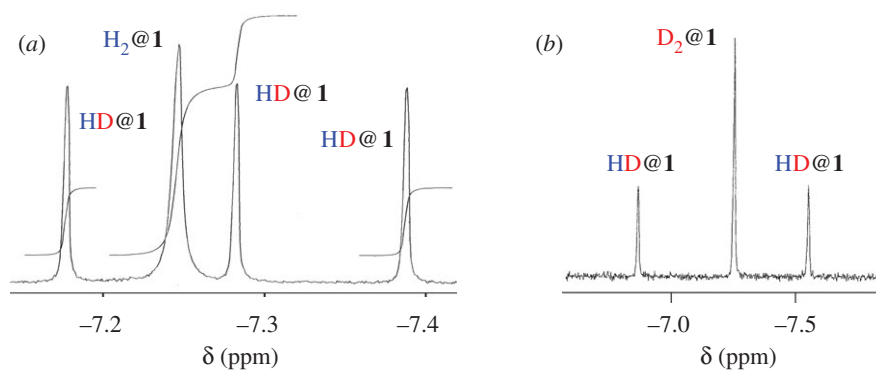


Figure 1. (a) ^1H (400 MHz) and (b) ^2H NMR (60.7 MHz) spectra (*o*-dichlorobenzene- d_4) of the region for encapsulated hydrogen molecule inside open-cage fullerene **1**. (Online version in colour.)

Table 1. Ratios of isotopomers (applied gas and encapsulated molecule) and equilibrium constants.

entry	temp. (°C)	time (d)	P_{tot} (atm)	partial pressure ratio ($P_{\text{H}_2}/P_{\text{HD}}/P_{\text{D}_2}$, %)	encapsulation ratio ($\text{H}_2@1/\text{HD}@1/\text{D}_2@1/1$, %)	equilibrium constant ($K_{\text{H}_2}/K_{\text{HD}}/K_{\text{D}_2}$, 10^{-3} atm^{-1})
1	200	0.5	655	22/40/38	11/34/28/27	2.9/4.9/4.1
2	190	1	630	27/42/31	15/36/21/28	3.3/5.0/3.9
3	190	1	630	27/42/31	14/34/22/30	2.9/4.3/3.8
4	190	1	630	27/42/31	15/33/22/30	2.9/4.2/3.8
5	190	2.5	645	29/41/30	15/35/22/28	2.8/4.7/4.1
6	190	5	650	16/43/41	10/32/28/30	3.2/3.7/3.4
7	180	2.5	640	21/42/37	12/36/27/25	3.6/5.3/4.6
8	170	6.5	640	22/47/31	15/36/24/25	4.4/4.9/4.8
9	160	16.5	635	18/46/36	13/36/27/24	5.1/5.2/4.9

Table 2. First-order rate constants $k_{\text{H}_2}^{-1}$, k_{HD}^{-1} and $k_{\text{D}_2}^{-1}$ (10^{-3} s^{-1}) for the isotopomers of hydrogen to escape from **1**.

	H ₂ @1	HD@1	D ₂ @1
150°C	1.03 ± 0.08	1.14 ± 0.02	1.19 ± 0.12
160°C	2.42 ± 0.20	2.92 ± 0.13	3.25 ± 0.17
170°C	6.74 ± 0.23	7.27 ± 0.74	7.46 ± 0.75
180°C	14.9 ± 1.0	15.6 ± 0.3	16.7 ± 1.0
190°C	34.2 ± 1.2	35.8 ± 0.6	36.2 ± 1.5

Table 3. Kinetic and thermodynamic data for the isotopomers of hydrogen to escape from **1**.

	H ₂ @1	HD@1	D ₂ @1
E_a (kcal mol ⁻¹)	34.5 ± 0.8	33.5 ± 0.5	33.2 ± 0.7
log A	11.8 ± 0.6	11.3 ± 0.3	11.1 ± 0.5
ΔG^\ddagger (kcal mol ⁻¹)	35.8 ± 0.8	35.5 ± 0.5	35.4 ± 0.7
ΔH^\ddagger (kcal mol ⁻¹)	33.4 ± 0.8	32.7 ± 0.5	32.3 ± 0.7
ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	-8.0 ± 2.6	-9.6 ± 1.6	-10.3 ± 2.1

literature [21]. In the temperature range above 170°C, D₂ showed slightly stronger binding affinity than H₂ presumably due to quantum effect [13].

The relative molecular sizes of H₂, HD and D₂ are significant in this study. Although we could infer their relative sizes from the internuclear lengths of the three isotopomers, they differ only in a small extent (0.7511 Å for H₂, 0.7498 Å for HD and 0.7484 Å for D₂) [20]. Therefore, we studied kinetic-isotope effect on the rates of hydrogen escape from open-cage fullerene **1** to find consistency with their known physical parameters.

The first-order kinetic data were obtained by carrying out competition experiments using two sets of mixtures of isotopomers@**1** inside sealed NMR tubes: (48% H₂@**1** and 20% HD@**1**) and (24% HD@**1** and 52% D₂@**1**). One of the datasets using ¹H NMR measurements gave results of escaping rates of H₂ and HD, while the other using ²H NMR measurements provided escaping rates of HD and D₂, both taken at five temperatures (150°C, 160°C, 170°C, 180°C and 190°C).

From these two datasets, first-order rate constants for release of H₂, HD and D₂ from **1** were obtained and are summarized in table 2. First-order rate constants observed at all temperatures demonstrate that these three isotopomers escaping from **1** follow the order of $k_{\text{D}_2}^{-1} > k_{\text{HD}}^{-1} > k_{\text{H}_2}^{-1}$. Since no correlation with polarity was observed, these kinetic results indicated that the van der Waals sizes of the three isotopomers would be the dominant factor influencing their relative release rates, which are in the order of D₂ < HD < H₂, in accordance with their relative internuclear distances [20].

On the basis of the Arrhenius plot, the kinetic (E_a , A) and thermodynamic data (ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger) at 25°C for escape of the three isotopomers from **1** are summarized in table 3. The activation barriers E_a are 34.5 ± 0.8, 33.5 ± 0.5 and 33.2 ± 0.7 kcal mol⁻¹ for H₂, HD and D₂, respectively, parallel to their relative sizes. Furthermore, the relative mass of the three isotopomers could be also reflected from the transmission frequency values log A , which are 11.8 ± 0.6, 11.3 ± 0.3 and 11.1 ± 0.5 for H₂, HD and D₂, respectively, although the error limit is still too large to discuss in detail. The heavier D₂ might have slower translational velocity towards the transition state. Despite the supposition that D₂ moves slower towards the orifice, it exhibits the highest escaping rate, presumably due to its smaller size exerting less friction while passing through the opening. The relative size of the isotopomers could be further reflected from the value of entropy of activation ΔS^\ddagger . The smallest isotopomer D₂ is less restricted for motion inside **1** and

thus loses more degrees of freedom at the transition state; consequently, a more negative value of ΔS^\ddagger (-10.3 ± 2.1 e.u.) was observed.

3. Concluding remarks

In summary, we have observed significant differences in encapsulation of hydrogen isotopomers by open-cage fullerene **1** at high temperatures, initiated by isotope hydrogen exchange that took place in the autoclave. This exchange reaction allows for preparation of various ratios of $\text{H}_2/\text{HD}/\text{D}_2$ inside an open-cage fullerene starting from various ratios of H_2/D_2 mixtures [22]. The equilibrium constants for encapsulation of the isotopomers were determined to be higher for dipolar HD than apolar H_2 and D_2 . Their molecular sizes, $\text{H}_2 > \text{HD} > \text{D}_2$, were directly distinguished from measurement of the escaping rates from **1**. Overall, this work has initiated a scarce prototype of molecular recognition on isotope gases in a type of solid–gas interphase system.

4. Experimental

(a) Material and methods

The 13-membered-ring open-cage fullerene **1** was synthesized based on a reported procedure [17]. Hydrogen (99.9%) was purchased from Kyoto Teisan K.K. (Japan) and deuterium (99.9%) gas from ISOTEC company (OH, USA) and used as received. The home-made high-pressure autoclave (1990) uses stainless steel 304 (JIS standard) that contains 18.0% chromium, 8.0% nickel, 2.0% Mn, 1.0% silicon, 0.08% carbon and Fe as the rest for its balancing composition. The internal volume of the cylindrical autoclave is estimated to be 27.5 cm^3 , with an internal radius of 0.81 cm and depth of 13.1 cm. The total internal volume of the autoclave including cap and pressure gauge is 30.0 cm^3 . Dow Corning silicon grease (low vapour pressure and thermally stable from -40°C to 260°C) is applied to the inner part of the autoclave for deactivating the metal surface.

(b) Typical procedure for the insertion of isotopomers of hydrogen

The insertion experiment of hydrogen isotopomers was conducted by introducing D_2 inside the autoclave, in which *ca* 30 mg of open-cage fullerene **1** was placed, to a pressure of 230 atm at room temperature. The autoclave was then filled with H_2 to a total pressure of 460 atm using a hydraulic pump. The autoclave was heated at 130°C in the heating oven for 6 h. After this premixing period, the temperature was elevated to desired temperature (160 – 200°C) for variable length of time. After the autoclave was cooled to room temperature, the gas mixture was introduced to a J-Young valve NMR tube to about 2.0 atm (liquid N_2 temperature) and warmed to room temperature for ^1H (400 MHz) and ^2D NMR (60.7 MHz) analyses. Finally, the high-pressure hydrogen gas was released and solid sample dissolved in *o*-dichlorobenzene- d_4 was analysed by ^1H and ^2D NMR. Other experiments with variable ratio of D_2/H_2 were performed in a similar manner by changing the starting pressure of D_2 gas.

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References

1. Cram DJ, Cram JM. 1994 *Container molecules and their guests*. Cambridge, UK: The Royal Society of Chemistry.
2. Lehn J-M. 1995 *Supramolecular chemistry: concepts and perspectives*. Weinheim, Germany: VCH.
3. Steed JW, Atwood JL. 2009 *Supramolecular chemistry*, 2nd edn. Chichester, UK: Wiley.
4. Matsuda R *et al.* 2005 Highly controlled acetylene accommodation in a metal–organic microporous material. *Nature* **436**, 238–241. (doi:10.1038/nature03852)

5. Kitaura R *et al.* 2002 Formation of a one-dimensional array of oxygen in a microporous metal-organic solid. *Science* **298**, 2358–2361. (doi:10.1126/science.1078481)
6. Rudkevich DM. 2004 Emerging supramolecular chemistry of gases. *Angew. Chem. Int. Ed.* **43**, 558–571. (doi:10.1002/anie.200300606)
7. Murata Y, Maeda S, Murata M, Komatsu K. 2008 Encapsulation and dynamic behavior of two H₂ molecules in an open-cage C₇₀. *J. Am. Chem. Soc.* **130**, 6702–6703. (doi:10.1021/ja801753m)
8. Xiao Z *et al.* 2007 Synthesis of [59] fullereneones through peroxide-mediated stepwise cleavage of fullerene skeleton bonds and X-ray structures of their water-encapsulated open-cage complexes. *J. Am. Chem. Soc.* **129**, 16 149–16 162. (doi:10.1021/ja0763798)
9. Iwamatsu S, Stanisky CM, Cross RJ, Saunders M, Mizorogi N, Nagase S, Murata S. 2006 Carbon monoxide inside an open-cage fullerene. *Angew. Chem. Int. Ed.* **45**, 5337–5340. (doi:10.1002/anie.200601241)
10. Rubin Y, Jarrosson T, Wang G-W, Bartberger MD, Houk KN, Schick G, Saunders M, Cross RJ. 2001 Insertion of helium and molecular hydrogen through the orifice of an open fullerene. *Angew. Chem. Int. Ed.* **40**, 1543–1546. (doi:10.1002/1521-3773(20010417)40:8<1543::AID-ANIE1543>3.0.CO;2-6)
11. Kurotobi K, Murata Y. 2011 A single molecule of water encapsulated in fullerene C₆₀. *Science* **333**, 613–616. (doi:10.1126/science.1206376)
12. Rechavi D, Scarso A, Rebek Jr J. 2004 Isotopomer encapsulation in a cylindrical molecular capsule: a probe for understanding noncovalent isotope effects on a molecular level. *J. Am. Chem. Soc.* **126**, 7738–7739. (doi:10.1021/ja048366p)
13. Zhao Y-L, Houk KN, Rechavi D, Scarso A, Rebek Jr J. 2004 Equilibrium isotope effects as a probe of nonbonding attractions. *J. Am. Chem. Soc.* **126**, 11 428–11 429. (doi:10.1021/ja0471065)
14. Tanaka H, Knoh H, Yudasaka M, Iijima S, Kaneko K. 2005 Quantum effects on hydrogen isotope adsorption on single-wall carbon nanohorns. *J. Am. Chem. Soc.* **127**, 7511–7516. (doi:10.1021/ja0502573)
15. Murata Y, Murata M, Komatsu K. 2003 100% Encapsulation of a hydrogen molecule into an open-cage fullerene derivative and gas-phase generation of H₂@C₆₀. *J. Am. Chem. Soc.* **125**, 7152–7153. (doi:10.1021/ja0354162)
16. Stanisky CM, Cross RJ, Saunders M, Murata M, Murata Y, Komatsu K. 2005 Helium entry and escape through a chemically opened window in a fullerene. *J. Am. Chem. Soc.* **127**, 299–302. (doi:10.1021/ja045328x)
17. Murata Y, Murata M, Komatsu K. 2003 Synthesis, structure, and properties of novel open-cage fullerenes having heteroatom(s) on the rim of the orifice. *Chem. Eur. J.* **9**, 1600–1609. (doi:10.1002/chem.200390184)
18. Rittenberg D, Bleakney W, Urey HC. 1934 The decomposition of complex molecules at high pressures. *J. Chem. Phys.* **2**, 48–49. (doi:10.1063/1.1749359)
19. Nelson JB, Tabisz GC. 1982 New spectroscopic determination of the dipole moment of HD in the ground vibrational state. *Phys. Rev. Lett.* **48**, 1393–1396. (doi:10.1103/PhysRevLett.48.1393)
20. Tachikawa M, Osamura Y. 2000 Isotope effect of hydrogen and lithium hydride molecules. Application of the dynamic extended molecular orbital method and energy component analysis. *Theor. Chem. Acc.* **104**, 29–39. (doi:10.1007/s002149900086)
21. Tsuzuki S, Fujii A. 2008 Nature and physical origin of CH/π interaction: significant difference from conventional hydrogen bonds. *Phys. Chem. Chem. Phys.* **10**, 2584–2594. (doi:10.1039/B718656H)
22. Turro NJ *et al.* 2008 Demonstration of a chemical transformation inside a fullerene. The reversible conversion of the allotropes of H₂@C₆₀. *J. Am. Chem. Soc.* **130**, 10 506–10 507. (doi:10.1021/ja804311c)