

## Research



**Cite this article:** Murata Y, Chuang S-C, Tanabe F, Murata M, Komatsu K. 2013 Recognition of hydrogen isotopomers by an open-cage fullerene. *Phil Trans R Soc A* 371: 20110629.  
<http://dx.doi.org/10.1098/rsta.2011.0629>

One contribution of 13 to a Theo Murphy Meeting Issue 'Nanolaboratories: physics and chemistry of small-molecule endofullerenes'.

### Subject Areas:

supramolecular chemistry

### Keywords:

open-cage fullerene, hydrogen, isotopomer, encapsulation, escape, kinetics

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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 H<sub>2</sub>/HD/D<sub>2</sub> with the open-cage fullerene and comparison of their relative molecular sizes through kinetic-isotope-release experiments. We took advantage of isotope H<sub>2</sub>/D<sub>2</sub> exchange that generated an equilibrium mixture of H<sub>2</sub>/HD/D<sub>2</sub> 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. D<sub>2</sub> molecule generally binds stronger than H<sub>2</sub> because of its heavier mass; however, the affinity for H<sub>2</sub> becomes larger than D<sub>2</sub> at lower temperature, when size effect becomes dominant. We further investigated the kinetics of H<sub>2</sub>/HD/D<sub>2</sub> release from open-cage fullerene, proving their relative escaping rates. D<sub>2</sub> was found to be the smallest and H<sub>2</sub> the largest molecule. This notion has not only supported the observed inversion of relative binding affinities between H<sub>2</sub> and D<sub>2</sub>, 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.

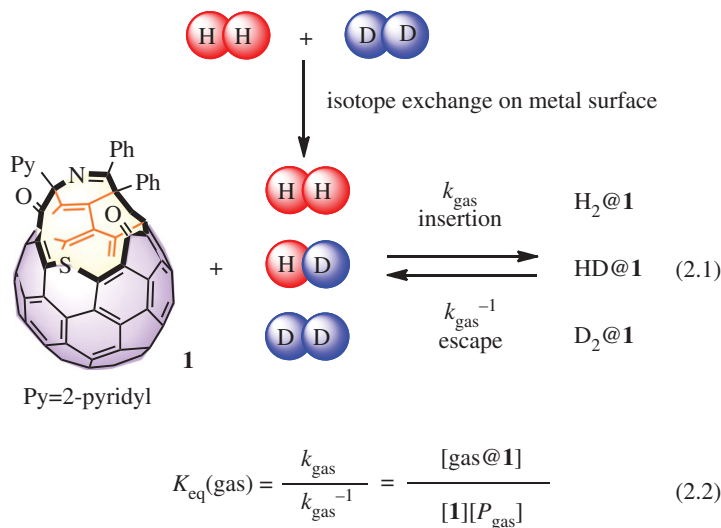
## 2. Results and discussion

Recently, we reported insertion of a H<sub>2</sub> 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. H<sub>2</sub>, HD and D<sub>2</sub>, 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 <sup>1</sup>H NMR spectrum of **1** recorded after treatment with H<sub>2</sub> contaminated with D<sub>2</sub> (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*<sub>4</sub>). This signal is slightly upfield shifted when compared with the encapsulated H<sub>2</sub> signal (–7.24 ppm) in **1** as shown in figure 1.

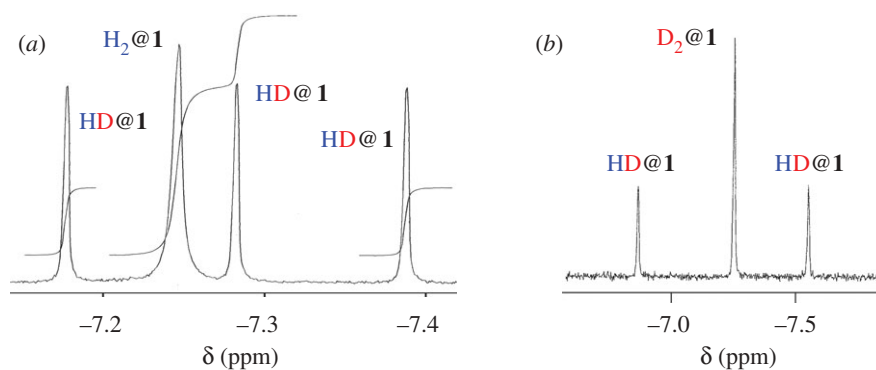
We soon found that HD is formed through H<sub>2</sub>/D<sub>2</sub> exchange by catalytic action on the hot surface of the inner wall of the autoclave [18]. No signal corresponding to HD@**1** was observed in a control experiment when the interior surface of the autoclave was deactivated by silicon grease. Practically, the partial pressures of H<sub>2</sub>, HD and D<sub>2</sub> were analysed by <sup>1</sup>H and <sup>2</sup>H NMR spectra of the gas sample in CDCl<sub>3</sub> 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 H<sub>2</sub> and HD in <sup>1</sup>H NMR; 4.71 ( $J = 42.5$  Hz) and 4.67 ppm for HD and D<sub>2</sub> in <sup>2</sup>H NMR, respectively. The encapsulated ratios of three isotopomers inside **1** were also analysed by <sup>1</sup>H or <sup>2</sup>H NMR spectra using their solutions in *o*-dichlorobenzene-*d*<sub>4</sub>. These peaks were observed at –7.21 ( $J = 41.7$  Hz) and –7.25 ppm for HD@**1** and D<sub>2</sub>@**1** in <sup>2</sup>H NMR, respectively (figure 1). By analysis of relative integrals, we determined the equilibrium constants  $K_{\text{eq}}$  (gas) for insertion/release of these gases into/from open-cage fullerene **1** defined by equation (2.2), where  $P_{\text{gas}}$  denotes partial pressure of H<sub>2</sub>, HD and D<sub>2</sub>, 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% H<sub>2</sub>@**1**, 24% HD@**1** and 52% D<sub>2</sub>@**1** (entry 3), as well as 45% H<sub>2</sub>@**1**, 28% HD@**1** and 4.2% D<sub>2</sub>@**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 H<sub>2</sub>, HD and D<sub>2</sub>, 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 H<sub>2</sub> and D<sub>2</sub>, 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 H<sub>2</sub> or D<sub>2</sub> 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<sup>δ-</sup> – H<sup>δ+</sup>. DH- $\pi$  interaction might be the origin of stronger binding affinity with the  $\pi$ -system of the carbon cage when compared with apolar H<sub>2</sub> and D<sub>2</sub>, similar to CH- $\pi$  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)  $^1\text{H}$  (400 MHz) and (b)  $^2\text{H}$  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)	$P_{\text{tot}}$ (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 ( $K_{\text{H}_2}/K_{\text{HD}}/K_{\text{D}_2}$ , $10^{-3} \text{ atm}^{-1}$ )
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  $k_{\text{H}_2}^{-1}$ ,  $k_{\text{HD}}^{-1}$  and  $k_{\text{D}_2}^{-1}$  ( $10^{-3} \text{ s}^{-1}$ ) for the isotopomers of hydrogen to escape from **1**.

	H <sub>2</sub> @1	HD@1	D <sub>2</sub> @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 <sub>2</sub> @1	HD@1	D <sub>2</sub> @1
$E_a$ (kcal mol <sup>-1</sup> )	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
$\Delta G^\ddagger$ (kcal mol <sup>-1</sup> )	35.8 ± 0.8	35.5 ± 0.5	35.4 ± 0.7
$\Delta H^\ddagger$ (kcal mol <sup>-1</sup> )	33.4 ± 0.8	32.7 ± 0.5	32.3 ± 0.7
$\Delta S^\ddagger$ (cal mol <sup>-1</sup> K <sup>-1</sup> )	-8.0 ± 2.6	-9.6 ± 1.6	-10.3 ± 2.1

literature [21]. In the temperature range above 170°C, D<sub>2</sub> showed slightly stronger binding affinity than H<sub>2</sub> presumably due to quantum effect [13].

The relative molecular sizes of H<sub>2</sub>, HD and D<sub>2</sub> 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 H<sub>2</sub>, 0.7498 Å for HD and 0.7484 Å for D<sub>2</sub>) [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% H<sub>2</sub>@**1** and 20% HD@**1**) and (24% HD@**1** and 52% D<sub>2</sub>@**1**). One of the datasets using <sup>1</sup>H NMR measurements gave results of escaping rates of H<sub>2</sub> and HD, while the other using <sup>2</sup>H NMR measurements provided escaping rates of HD and D<sub>2</sub>, 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 H<sub>2</sub>, HD and D<sub>2</sub> 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 D<sub>2</sub> < HD < H<sub>2</sub>, in accordance with their relative internuclear distances [20].

On the basis of the Arrhenius plot, the kinetic ( $E_a$ ,  $A$ ) and thermodynamic data ( $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ ) 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<sup>-1</sup> for H<sub>2</sub>, HD and D<sub>2</sub>, 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 H<sub>2</sub>, HD and D<sub>2</sub>, respectively, although the error limit is still too large to discuss in detail. The heavier D<sub>2</sub> might have slower translational velocity towards the transition state. Despite the supposition that D<sub>2</sub> 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  $\Delta S^\ddagger$ . The smallest isotopomer D<sub>2</sub> is less restricted for motion inside **1** and

thus loses more degrees of freedom at the transition state; consequently, a more negative value of  $\Delta S^\ddagger$  ( $-10.3 \pm 2.1$  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  $\text{H}_2/\text{D}_2$  mixtures [22]. The equilibrium constants for encapsulation of the isotopomers were determined to be higher for dipolar HD than apolar  $\text{H}_2$  and  $\text{D}_2$ . 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  $27.5 \text{ cm}^3$ , 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  $30.0 \text{ cm}^3$ . Dow Corning silicon grease (low vapour pressure and thermally stable from  $-40^\circ\text{C}$  to  $260^\circ\text{C}$ ) 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  $\text{D}_2$  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  $\text{H}_2$  to a total pressure of 460 atm using a hydraulic pump. The autoclave was heated at  $130^\circ\text{C}$  in the heating oven for 6 h. After this premixing period, the temperature was elevated to desired temperature ( $160$ – $200^\circ\text{C}$ ) 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  $\text{N}_2$  temperature) and warmed to room temperature for  $^1\text{H}$  (400 MHz) and  $^2\text{D}$  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  $^1\text{H}$  and  $^2\text{D}$  NMR. Other experiments with variable ratio of  $\text{D}_2/\text{H}_2$  were performed in a similar manner by changing the starting pressure of  $\text{D}_2$  gas.

**Funding statement.** This research was supported by the MEXT project of Integrated Research on Chemical Synthesis and Grants-in-Aids for Scientific Research on Innovative Areas (no. 20108003, ‘pi-Space’) and for Scientific Research (A) (no. 23241032).

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