JOC *Article*

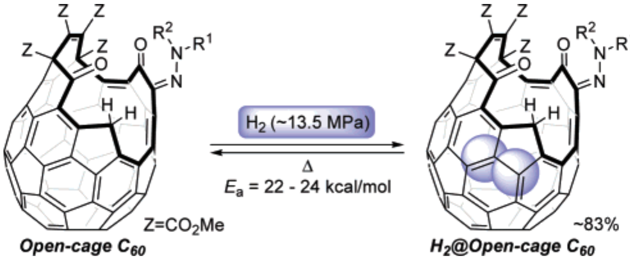
Open-Cage Fullerene Derivatives Suitable for the Encapsulation of a Hydrogen Molecule

Sho-ichi Iwamatsu,*,† Shizuaki Murata,†,‡ Yukihiro Andoh,§ Masayuki Minoura,§
Kaoru Kobayashi,‖ Naomi Mizorogi,‖ and Shigeru Nagase‖

Graduate School of Environmental Studies and School of Informatics and Sciences, Nagoya University, Nagoya 464-8601, Japan, Department of Theoretical Molecular Science, Institute for Molecular Science, Okazaki 444-8585, Japan, and CREST, Japan Science and Technology Agency (JST)

iwmt@urban.env.nagoya-u.ac.jp

Received February 8, 2005



The encapsulation of molecular hydrogen into an open-cage fullerene having a 16-membered ring orifice has been investigated. It is achieved by the pressurization of H_2 at 0.6−13.5 MPa to afford endohedral hydrogen complexes of open-cage fullerenes in up to 83% yield. The efficiency of encapsulation is dominantly dependent on both H_2 pressure and temperature. Hydrogen molecules inside the C_{60} cage are observed in the range of −7.3 to −7.5 ppm in ^{1}H NMR spectra, and the formations of hydrogen complexes are further confirmed by mass spectrometry. The trapped hydrogen is released by heating. The activation energy barriers for this process are determined to be 22−24 kcal/mol. The DSC measurement of the endohedral H_2 complex reveals that the escape of H_2 from the C_{60} cage corresponds to an exothermic process, indicating that encapsulated H_2 destabilizes the fullerene.

Introduction

The inside sphere of fullerene is large enough to enclose atoms and small molecules. For example, the interior of the most abundant C_{60} is approximately 3.5 Å in diameter. From the structural and physical aspects, a variety of endohedral complexes, having metal fragments, noble gases, and atoms inside the cages, have been synthesized and characterized in the past decade.[1−6] Generally, endohedral metallofullerenes are prepared by the evaporation of graphite/metal oxide or carbide composites.[1−4] On the other hand, noble gases and atomic nitrogen can be encapsulated into the pristine fullerene under forced high-pressure conditions or plasma reactions.[5,6] However,

---

[†] Graduate School of Environmental Studies, Nagoya University.
[‡] CREST, Japan Science and Technology Agency (JST).
[§] School of Informatics and Sciences, Nagoya University.
[‖] Institute for Molecular Science.

(1) (a) *Fullerenes: Chemistry, Physics, and Technology*; Kadish, K. M., Ruoff, R. S., Eds.: John Wiley & Sons: New York, 2000; pp 357−436. (b) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.: Kluwer Academic Publisher: Dordrecht, 2002.

(2) (a) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2131−2142. (b) Shinohara, H. Endohedral metallofullerenes: Structures and electronic properties. In *Advances in Metal and Semiconductor Clusters*; Duncan, M. A., Ed.; JAI Press: 1998; Vol. 4, pp 205−226. (c) Liu, S.; Sun, S. *J. Organomet. Chem.* **2000**, *599*, 74−86.

(3) Recent examples ($C_2M_2@C_n$): (a) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 397. (b) Inoue, T.; Tomiyama, T.; Sugai, T.; Shinohara, H. *Chem. Phys. Lett.* **2003**, *382*, 226.

(4) Recent examples ($M_3N@C_n$): (a) Olmstead, M. H.; de Bettencourt-Dias, A.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 1223. (b) Olmstead, M. M.; Lee, H. M.; Duchamp, J. C.; Stevenson, S.; Marciu, D.; Dorn, H. C.; Balch, A. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 900 and references therein.

(5) Selected examples (rare gas complexes): (a) Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693. (b) DiCamillo, B. A.; Hettich, R. L.; Guiochon, G.; Compton, R. N.; Saunders, M.; Jiménez-Vázquez, H. A.; Khong, A.; Cross, R. J. *J. Phys. Chem.* **1996**, *100*, 9197. (c) Yamamoto, K.; Saunders, M.; Khong, A.; Cross, R. J.; Grayson, M.; Gross, M. L.; Benedetto, A. F.; Weisman, R. B. *J. Am. Chem. Soc.* **1999**, *121*, 1591. (d) Syamala, M. S.; Cross, R. J.; Saunders: M. *J. Am. Chem. Soc.* **2002**, *124*, 6216.

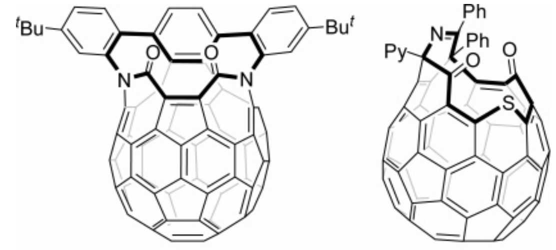
(6) Selected examples ($N@C_{60}$): (a) Murphy, A. T.; Pawlik, T.; Weidinger, A.; Hohne, M.; Alcala, R. Spaeth, J. M. *Phys. Rev. Lett.* **1996**, *77*, 1075. (b) Kobayashi, K.; Nagase, S.; Dinse, K. P. *Chem. Phys. Lett.* **2003**, *377*, 93 and references therein.

10.1021/jo050251w CCC: $30.25

impractical preparation of these complexes—low yields, poor control of the cage size, heavy task of purification, and the limited number of substrates suitable for the encapsulation—has remained a fundamental problem, as has the limited commercial sample supply to common research fields.

To overcome these problems, the "molecular surgery approach" was proposed soon after discovery of the chemical cage-scission reaction of C_{60}.[7−9] It consists of three key steps as follows: (i) opening a hole on the empty fullerene cage, (ii) insertion of the objective material into the cage through the orifice, and (iii) restoration of the broken sphere to yield the desired endohedral complex.[7] Since the proposal of this innovative concept, open-cage fullerene derivatives have drawn much attention as a key intermediate of the endohedral complexes.[10−14] From a different perspective, however, these derivatives can trap and release a molecule in a reversible manner, unlike formal endohedral complexes. This property promises molecular storage and sensing as potential applications. In addition, these compounds are hardly accessible from general chemical sources, only from the combination of fullerene and well-defined organic synthesis. Therefore, the open-cage derivative itself has now become the synthetic target, not just an intermediate toward endohedral fullerenes.

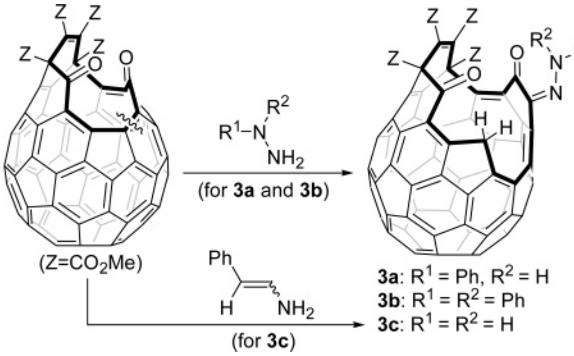
In 2001, Rubin et al., the original inventor of the above concept, synthesized the open-cage bislactam derivative **1** (Figure 1) and proved that it is surely possible to insert a small atom (helium) and a molecule (hydrogen) into the C_{60} cage through the orifice.[10b] Although yields of He@**1** and H_2@**1** were less than 5%, Komatsu et al. subsequently succeeded in the preparation of a new derivative (**2**) that has an orifice larger than that of **1** and achieved the first quantitative encapsulation of H_2.[11b] Furthermore, quite recently, they finally achieved the complete closure of the orifice of H_2@**2**, leading to the first chemical synthesis of $H_2@C_{60}$ from the empty C_{60}.[11g] However, these successful results required high temperature (400 °C for H_2@**1**) and/or high pressure (80 MPa for H_2@**2**) even for these smallest gases. A much larger orifice is necessary to achieve efficient encapsulation under mild conditions, as well as to apply this methodology to bigger elements and molecules.



1 **2**

FIGURE 1. Molecular structures of the open-cage C_{60} derivatives **1** and **2**.

SCHEME 1. Preparation of Open-Cage C_{60} Derivatives 3a−c



Recently, we have succeeded in the syntheses of new open-cage derivatives (**3a−c**) by regioselective carbon−carbon bond scission of the open-cage diketone derivative of C_{60} (Scheme 1).[12−14] The orifice in **3** is larger than that of **1** or **2**. In addition, compared with the rigid orifices of **1** and **2**, that of series **3** contains an sp^3 methylene carbon along the rim, and its flexibility might act positively on the molecular encapsulation. Herein, we describe the encapsulation of hydrogen molecule into **3**.

Result and Discussion

Molecular Structure of 3. Preparation and characterization of the compounds **3a−c** have been described in previous literature (Scheme 1).[13a,c] To evaluate the size of the orifice, geometry optimization of **3c** was carried out at the B3LYP/3-21G level.[15] Top views of the optimized structure are shown by both stick and space-filling models in Figure 2a. The corresponding space-filling models of **1** and **2** are given in Figure 2b and 2c,

---

(7) (a) Rubin, Y. *Chem. Eur. J.* **1997**, *3*, 1009−1016. (b) Rubin, Y. *Top. Curr. Chem.* **1999**, *199*, 67−91. (c) Rubin, Y.; Diederich, F. From fullerenes to novel carbon allotropes: Exciting prospects for organic synthesis. In *Stimulaing Concepts in Chemistry*; Vögtle, F., Stoddart, J. F., Shibasaki, M., Eds.; Wiley-VCH: Weinheim, 2000; pp 163−186.

(8) (a) Hummelen, J. C.; Prato, M.; Wudl, F. *J. Am. Chem. Soc.* **1995**, *117*, 7, 7003. (b) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554.

(9) (a) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 1869. (b) Al-Matar, H.; Abdul-Sada, A. K.; Avent, A. G.; Taylor, R. *Org. Lett.* **2001**, *3*, 1669.

(10) (a) Schick, G.; Jarrosson, T.; Rubin, Y. *Angew. Chem., Int. Ed.* **1999**, *38*, 2360. (b) Rubin, Y.; Jarrosson, T.; Wang, G.-W.; Bartberger, M. D.; Houk, K. N.; Schick, G.; Saunders: M.; Cross, R. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543. (c) Irle, S.; Rubin, Y.; Morokuma, K. *J. Phys. Chem. A* **2002**, *106*, 680. (d) Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2001**, *40*, 2973.

(11) (a) Murata, Y.; Murata, M.; Komatsu, K. *Chem. Eur. J.* **2003**, *9*, 1600. (b) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152. (c) Carravetta, M.; Murata, Y.; Murata, M.; Heinmaa, I.; Stern, R.; Tontcheva, A.; Samoson, A.; Rubin, Y.; Komatsu, K.; Levitt, M. H. *J. Am. Chem. Soc.* **2004**, *126*, 4092. (d) Yoshimoto, S.; Tsutsumi, E.; Honda, Y.; Murata, Y.; Murata, M.; Komatsu, K.; Ito, O.; Itaya, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 3044. (e) Vougioukalakis, G. C.; Prassides, K.; Orfanopoulos, M. *Org. Lett.* **2004**, *6*, 1245. (f) Stanisky, C. M.; Cross, R. J.; Saunders: M.; Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2005**, *127*, 299. (g) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238.

(12) (a) Inoue, H.; Yamaguchi, H.; Iwamatsu S.-i.; Uozaki, T.; Suzuki, T.; Akasaka, T.; Nagase, S.; Murata, S. *Tetrahedron Lett.* **2001**, *42*, 895. (b) Murata Y.; Komatsu K. *Chem. Lett.* **2001**, *30*, 896. (c) Murata, Y.; Murata, M.; Komatsu, K. *J. Org. Chem.* **2001**, *66*, 8187.

(13) (a) Iwamatsu, S.-i.; Ono, F.; Murata, S. *Chem. Commun.* **2003**, 1268. (b) Iwamatsu, S.-i.; Ono, F.; Murata, S. *Chem. Lett.* **2003**, *32*, 614. (c) Iwamatsu, S.-i.; Kuwayama, T.; Kobayashi, K.; Nagase, S.; Murata, S. *Synthesis* **2004**, 2962. (d) Vougioukalakis, G. C.; Prassides, K.; Campanera, J. M.; Heggie, M. I.; Orfanopoulos, M. *J. Org. Chem.* **2004**, *69*, 4524. (e) Chen, Z.-X.; Wang, G.-W. *J. Org. Chem.* **2005**, *70*, 2380.

(14) (a) Iwamatsu, S.-i.; Uozaki, T.; Kobayashi, K.; Suyong, R.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668. (b) Iwamatsu, S.-i.; Murata, S. *Tetrahedron Lett.* **2004**, *45*, 6391.

(15) *Gaussian 03*, Revision C.2.; Gaussian, Inc.: Pittsburgh, PA, 2003.

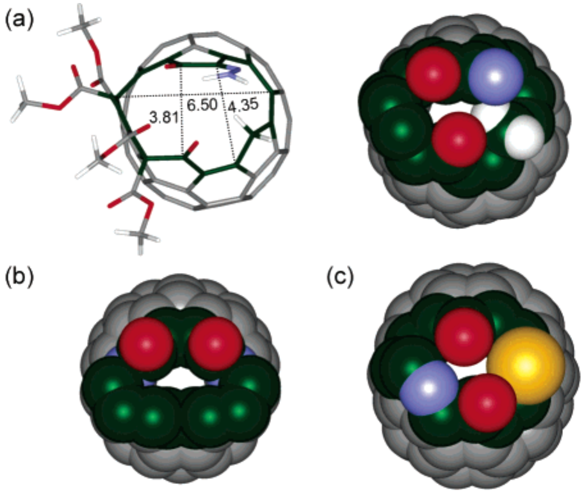


FIGURE 2. (a) Top views of the stick and space-filling models of **3c** (B3LYP/3-21G). Selected interatom distances are shown in Å. (b, c) Top views of the space-filling models of **1** and **2**.[10b,11b] Carbon atoms of C_{60} located in the bottom and functional groups are partly omitted for clarity. The center white layers correspond to the orifices in space-filling models.

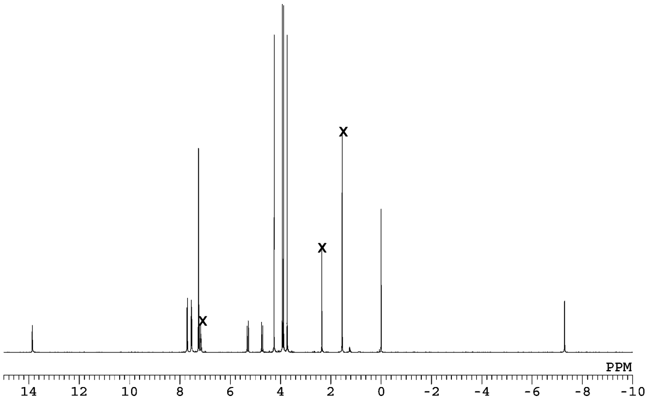


FIGURE 3. ^{1}H NMR spectrum of H_2@**3a** in $CDCl_3$ (after 4 h pressurization of H_2 at 13.5 MPa/100 °C); "×" indicates residual toluene in the starting material **3a** and water in $CDCl_3$.

respectively, for comparison.[10b,11b] The series **3** has an elliptical orifice consisting of a 16-membered ring, and the size was estimated to be 6.5 Å along the major axis and 3.8 Å along the minor axis. The opening seen in the space-filling model appears only slightly larger than, or comparable to, those of **1** and **2**. However, considering the flexibility of the orifice derived from the sp^3 methylene carbon it contains, the effective size of the orifice in **3** might be much larger than those of **1** and **2**.

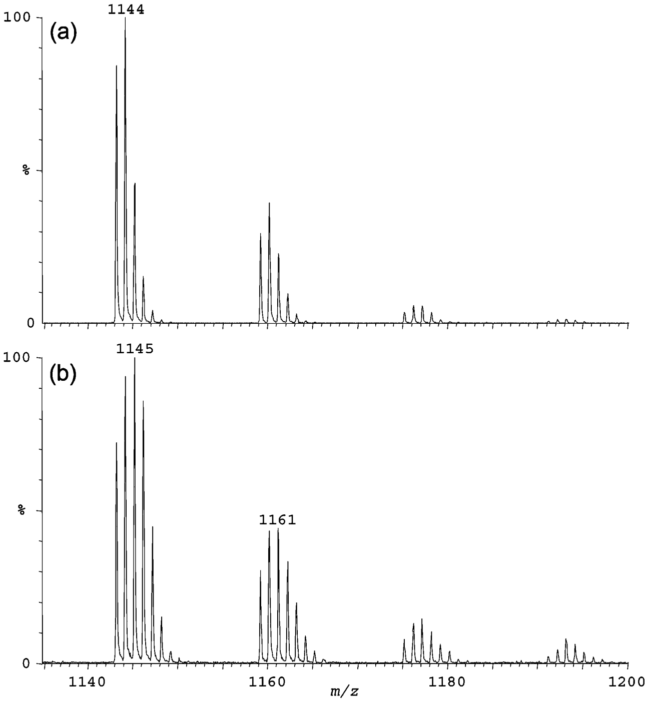


FIGURE 4. Electrospray mass spectra (negative) of (a) the empty **3a** and (b) H_2@**3a**.

Encapsulation of Hydrogen Molecule into 3. The encapsulation experiment of H_2 into **3** was initially carried out by the simple pressurization of hydrogen gas on a powder **3a** using an ordinary steel autoclave. After the pressurization on **3a** for 4 h at 13.5 MPa with heating at 100 °C, the ^{1}H NMR spectrum of the product solution showed one sharp singlet at δ −7.29 ppm together with signals assigned to the functional groups in **3a** (Figure 3). Generally, atoms and molecules inside the fullerene cage are known to show an upfield shift in NMR because of the magnetic shielding effect by the π-electron shell of the fullerene.[16] The reported chemical shifts of H_2@**1** and H_2@**2** are δ −5.43 ppm and δ −7.25 ppm, respectively.[10b,11b] Thus, we reasonably assigned this signal as that of a hydrogen molecule inside **3a** (H_2@**3a**). Reflecting the existence of H_2 inside the cage, methylene protons of H_2@**3** could be distinguished from those of the empty **3** in the ^{1}H NMR spectrum. However, differences in chemical shifts between them were less than 0.01 ppm for each signal. The formation of the hydrogen complex was further confirmed by electrospray mass spectrometry (negative ion mode). The calculated parent ion peaks $[M]^-$ for the empty **3a** and H_2@**3a** are 1144 and 1146, respectively. As shown in Figure 4b, the spectrum of the product showed significant increases in peak intensities at *m*/*z* = 1145 and 1146. Because of the moderate fraction of H_2@**3a** (62%, discussed later), the product was an inseparable mixture of the empty **3a** and H_2@**3a**. Further, for **3a**, an ion peak at $[M - H]^-$ was also observed with a relatively high peak intensity as shown in Figure 4a. Thus, the observed mass spectrum was in agreement with the corresponding ^{1}H NMR spectrum. On the basis of the comparison of peak intensities at *m*/*z* = 1144 and 1146 coupled with the fraction of H_2@**3a** estimated by ^{1}H NMR, a slight escape of the trapped H_2 molecule might have taken place during the measurement. In IR and UV−vis spectra of H_2@**3a**, there was no detectable difference from those of the empty **3a**. HPLC analysis of the product showed only one peak, and the separation of H_2@**3a** from the empty **3a** was not successful.

The fraction of H_2@**3** can be estimated by comparison of the integral value of the signal assigned to the hydrogen molecule inside the cage with those assigned

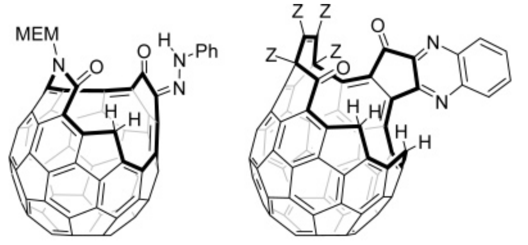
---

[16] (a) Sternfeld, T.; Hoffman, R. E.; Saunders: M.; Cross, R. J.; Syamala, M. S.; Rabinovitz, M. *J. Am. Chem. Soc.* **2002**, *124*, 8786. (b) Sternfeld, T.; Saunders, M.; Cross, R. J.; Rabinovitz, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 3136 and references therein.

TABLE 1. Encapsulation of Hydrogen Gas into 3a−c

					H_2@**3a−c**	
entries	compd	H_2 (initial), MPa	temp, °C	time, h	yield, %	^{1}H NMR, ppm[a]
1	**3a**	13.5 (12.0)	100	1	46	−7.29
2	**3a**	13.5 (12.0)	100	4	62	
3	**3a**	13.5 (12.0)	100	12	62	
4[b]	**3a**	13.5 (12.0)	100	4	72	
5	**3a**	9.5 (8.0)	100	4	52	
6	**3a**	4.5 (4.0)	100	4	38	
7	**3a**	0.6 (0.5)	100	4	7	
8	**3a**	15.0 (12.0)	150	4	61	
9	**3a**	13.0 (12.0)	50	4	16	
10	**3b**	13.5 (12.0)	100	4	58	−7.53
11[b]	**3b**	13.5 (12.0)	100	4	75	
12	**3c**	13.5 (12.0)	100	4	75	−7.34
13[b]	**3c**	13.5 (12.0)	100	4	83	

[a] In $CDCl_3$. [b] Reactions were carried out in 1,1,2,2-tetrachloroethane-d_2.



4 **5**

FIGURE 5. Molecular structures of **4** and **5**.

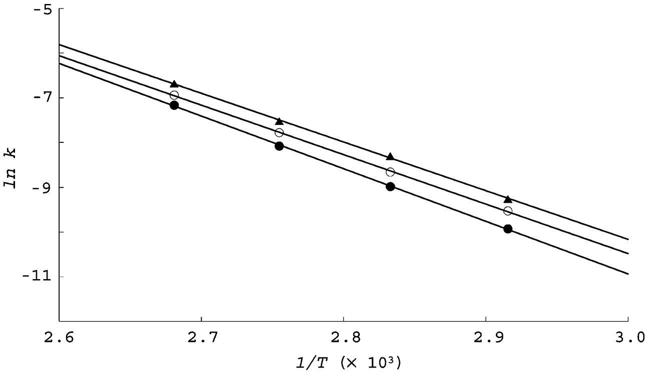


FIGURE 6. Arrhenius plots of the release of hydrogen from H_2@**3a** (●), H_2@**3b** (○), and H_2@**3c** (▲).

SCHEME 2

$$H_2@\mathbf{3a–c} \xrightarrow[100\ °C,\ <1\ h,\ TCE\text{-}d_2]{-H_2} \mathbf{3a–c}$$

TABLE 2. the Kinetic Parameters for the Release of Hydrogen from H$_2$@3a−c

compd	log *A*	E_a, kcal/mol	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, cal/K·mol	$\Delta G^‡$, kcal/mol	ref
H_2@**3a**	10.8 (1)	23.7 (2)	23.0 (2)	−12 (1)	26.4 (4)	
H_2@**3b**	9.9 (3)	22.0 (4)	21.3 (4)	−16 (1)	26.0 (7)	
H_2@**3c**	9.8 (3)	21.7 (4)	21.0 (4)	−16 (1)	25.8 (8)	
H_2@**2**	11.8	34.3	33.4	−7	35.5	11b
He@**2**	11.2	22.8		−9		11f
He@**1**	9.6	24.6		−17		10b

to the functional groups. Table 1 summarizes the results of encapsulation experiments for **3a**−**c**. At 13.5 MPa of H_2 with heating at 100 °C, the fraction of H_2@**3a** reached a constant value after 4 h (62%), and prolonged reaction time did not improve the yield (entries 1−3). The same conditions but with a solution state experiment slightly improved the yield of H_2@**3a** (72%, entry 4). The pressure of H_2 and the reaction temperature dominantly affected yields. The fraction of H_2@**3a** gradually decreased with reducing the pressure of H_2, as expected. It fell to 52%, 38%, and 7%, at 9.5, 4.5, and 0.6 MPa, respectively (entries 5−7). Heating the sample is necessary for efficient encapsulation. Though no improvement was achieved by elevating the reaction temperature to 150 °C, the yield of H_2@**3a** dropped to 16% at 50 °C (entries 8 and 9). Substituents on the nitrogen atom in **3a**−**c** scarcely affected the yield of H_2@**3**. Under the condition identical to that for entry 1, H_2@**3b** and H_2@**3c** were obtained in 58% and 75% yields, respectively (entries 10 and 12). The maximum 83% yield was achieved by pressurization on the 1,1,2,2-tetrachloroethane-d_2 solution of **3c** (entries 11). There was no significant difference in the chemical shifts of trapped H_2 inside **3a**−**c** in ^{1}H NMR. The corresponding signals of H_2@**3b** and H_2@**3c** were observed at δ −7.53 and −7.34 ppm, respectively. Although we also carried out the same experiments using related derivatives **4** and **5** shown in Figure 5,[13b,d,14a] no signal assignable to the endohedral H_2 complex was observed after the pressurization of H_2 at 13.5 MPa/100 °C in each case. The orifice in the former **4** might be too small to pass a hydrogen molecule. On the other hand, we confirmed that the latter **5** can hold one water molecule inside the cage.[14a] This indicates that the orifice in **5** is wide enough for H_2 but too large to suppress the rapid escape of H_2 from the cage. Though we confirmed that the water molecule inside **5** can be removed by heating,[14a] weak interaction between the inside H_2 and the C_{60} cage, which is in contrast to the strong binding affinity of H_2O with **5**, should be pointed out as another reason.

Release of the Hydrogen Molecule from H$_2$@3. It is known that helium and hydrogen incorporated in **1** and **2** are released from the cage by heating.[10b,11b] Although H_2@**3** is storable more than a few months in solid state at −30 °C, in solution, gradual leak of H_2 from H_2@**3** was observed even at room temperature. At 100 °C, all incorporated H_2 in **3** was completely ejected within 1 h (Scheme 2). According to the reported experiments by Rubin and Komatsu,[10b,11b] time course NMR experiments were done for H_2@**3a**−**c** at 70, 80, 90, and 100 °C. The rate of escape of the trapped H_2 followed first-order kinetics, and the Arrehnius plot gave a linear fit as shown in Figure 6. The pre-expotential factor (*A*) values were in the range of 9.8−10.8, and the activation energies for the escape of H_2 from H_2@**3a**, H_2@**3b**, and H_2@**3c** were estimated as 23.7, 22.0, and 21.7 kcal/mol, respectively (Table 2). The activation parameters for H_2@**3a** at 25 °C were determined to be $\Delta H^‡ = 23.0$ kcal/mol, $\Delta S^‡ = -11.5$ cal/K·mol, and $\Delta G^‡ = 26.4$ kcal/mol. To support these experimental results, the corresponding transition-state structure for H_2@**3c** was optimized at the B3LYP/3-21G level by using the QST3 option.[15] The result was verified by the frequency calculation, and the energy was computed from this geometry using the 6-31G(d,p) basis set. The TS has one imaginary frequency of 224i cm^{-1}, and the structure is shown in Figure 7. The predicted activation energy for the escape of H_2 from **3c** was 19.8 kcal/

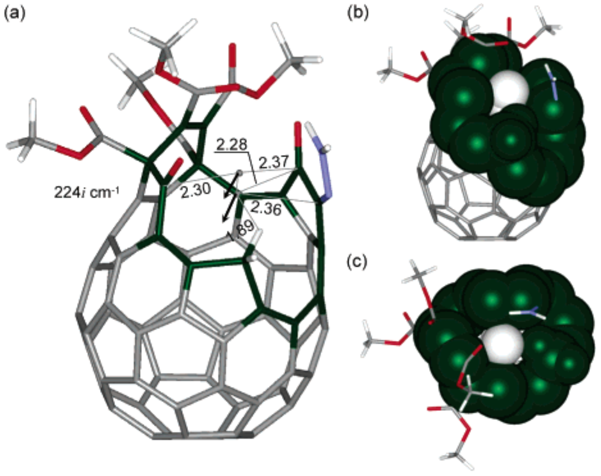


FIGURE 7. (a) The B3LYP/3-21G transition structure of the hydrogen insertion into **3c**. Selected interatom distances are given in Å. Displacement vectors are shown by arrows. (b, c) Space-filling models. For clarity, only the hydrogen molecule and the orifice moiety are described in the space-filling representation.

TABLE 3. Calculated Relative Energies (kcal/mol) for the Encapsulation/Release of H_2 into/from 3c and Related Compounds

compd	energy barrier to insertion	energy barrier to escape	destabilization by H_2 or He	ref
H_2@**3c**	21.3	19.8	+1.5	
H_2@**2**	30.1	28.7	+1.4	11b
H_2@**1**	41.4	40.0	+1.4	10b
H_2@C_{60}			+1.2, +2.3	17a, 17f
He@**2**	18.9	18.6	+0.3	11f
He@**1**	24.5	24.3	+0.2	10b

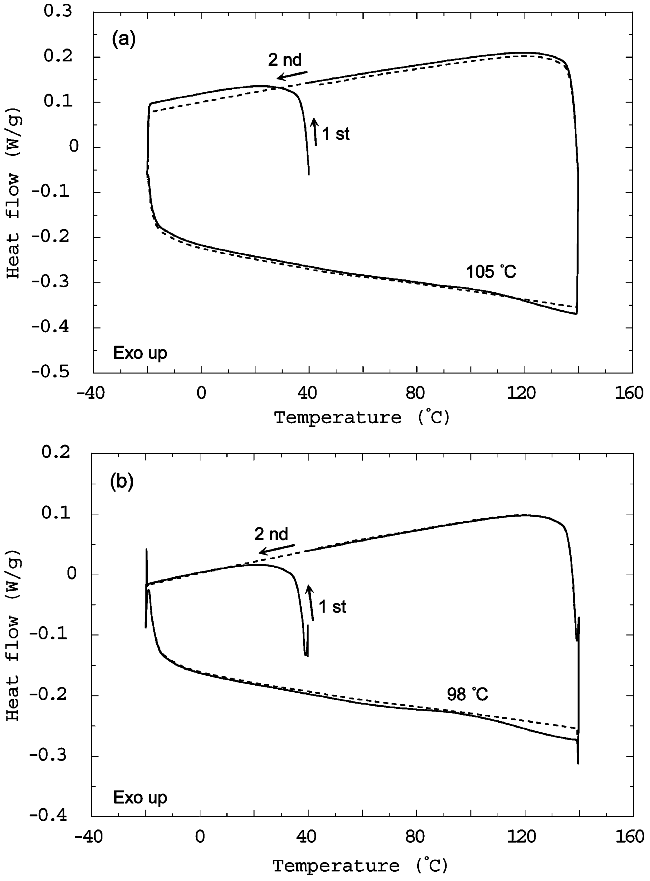


FIGURE 8. DSC charts of (a) H_2@**3a** and (b) H_2@**3b**. The initial and second cycles are shown as plain and dotted lines, respectively (ramp: 10 °C/min, hold temperature for 10 min at −20 °C and at 140 °C).

mol (Table 3), which is in good agreement with the experimental value (21.7 kcal/mol, Table 2). As summarized in Tables 2 and 3, compared with corresponding values of H_2@**1** (40.0 kcal/mol by theory) and H_2@**2** (34.3 kcal/mol by experiments, 28.7 kcal/mol by theory), activation energies for the escape of H_2 from H_2@**3a**−**c** are lower by 9 kcal/mol or more, proving the large orifices of **3a**−**c**.

Contained H_2: Stabilize or Destabilize the Fullerene Cage? In regard to the stabilization effect as well as the interaction between the fullerene cage and hydrogen molecule inside, DFT calculations for our system predicted that the contained H_2 destabilizes the fullerene cage. As given in Table 3, the calculated relative energy of H_2@**3c** to H_2+**3c** was +1.5 kcal/mol. This trend is in accordance with the corresponding data for H_2@**1** and H_2@**2** (Table 3).[10b,11b] A pioneering theoretical work for H_2@C_{60} also predicted that the encapsulated H_2 destabilizes the C_{60} cage at about 1.2 kcal/mol.[17a,f] On the other side, Patchkovskii and Thiel carried out counterpoise-corrected MP2 calculations for the series of endohedral noble gas complexes of C_{60} (He, Ne, Ar, Kr, and Xe), and concluded that (1) there is no destabilization effect and (2) the DFT calculation underestimates exothermicity of the encapsulation into C_{60}.[17c] On the basis of these reports, Rubin remarked in his article that encapsulations of He and H_2 into the open-cage fullerene are expected to be thermoneutral or slightly exothermic.[10b] To confirm this problem experimentally, we carried out the differential scanning calorimetry (DSC) measurement of H_2@**3a**. The heating/cooling process was recycled in the range from −20 to 140 °C, and the same measurement was applied to the empty **3a** for comparison. As shown in Figure 8a, in the first cycle, an exothermic curve (0.9 kcal/mol) was observed with a peak top at 105 °C. The corresponding curve could not be detected in the second heating process or the blank measurement using empty **3a**. The observed curve was small but reproducible, and the same result was also obtained for H_2@**3b** (Figure 8b). In addition, the temperature range of the peak is in good agreement with the escape of H_2 monitored by variable temperature ^{1}H NMR measurements described above. Thus, we assigned this exothermic signal to the escape of H_2 from H_2@**3**. Although quantitative discussion is difficult because both observed and expected values are too small compared to the precision of the DSC measurement, in consideration of the fraction of H_2@**3a**, the escape of H_2 might be an exothermic process at about 1−2 kcal/mol. This result conversely suggests that the

---

[17] (a) Cioslowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4139. (b) Williams, C. I.; Whitehead, M. A.; Pang, L. *J. Phys. Chem.* **1993**, *97*, 11652. (c) Patchkovski, S.; Thiel, W. *J. Chem. Phys.* **1997**, *106*, 1796. (d) Bühl, M.; Patchkovskii, S.; Thiel, W. *Chem. Phys. Lett.* **1997**, *275*, 14. (e) Patchkovskii, S.; Yurchenko, S. N. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4152. (f) Hu, Y. H.; Ruckenstein, E. *Chem. Phys. Lett.* **2004**, *390*, 472.

encapsulation of H_2 is endothermic and the encapsulated hydrogen destabilizes the fullerene.

Conclusion

In summary, we report the encapsulation of a hydrogen molecule into the open-cage C_{60} derivative having a 16-membered ring orifice. The wide orifice allows the facile formation of the endohedral hydrogen complex using ordinary equipment. Studies on endohedral open-cage fullerene derivatives, especially the encapsulation of bigger atoms and molecules, are now underway.

Acknowledgment. We thank Dr. Y. Sakamoto, Prof. T. Suzuki (Institute for Molecular Science), and Prof. I. Matsuda (Nagoya University) for valuable discussions. This research was partly supported by Grant in Aids for Scientific Research and by the "Nanotechnology Support Project" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. Parts of the calculations were carried out at the Center of the Institute for Molecular Science.

Supporting Information Available: Experimental procedures, data of kinetics, copies of spectra (^1H NMR, MS, DSC), and molecular modeling coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

JO050251W