Simple Simultaneous Encapsulation of Both Single H Atoms and Single D Atoms in Octasilsesquioxane, Double Four-Ring Cages Using a Deuterated Organic Solvent

Yuki Hayashino,[†] Toshiyuki Isobe,[‡] and Yoshihisa Matsuda*,[†]

Department of Chemistry, Graduate School of Sciences, Kyushu University, Higashi-ku, Fukuoka, 812-8581, Japan, and Graduate School of Social and Cultural Studies, Kyushu University, Chuo-ku, Fukuoka, 810-8560, Japan

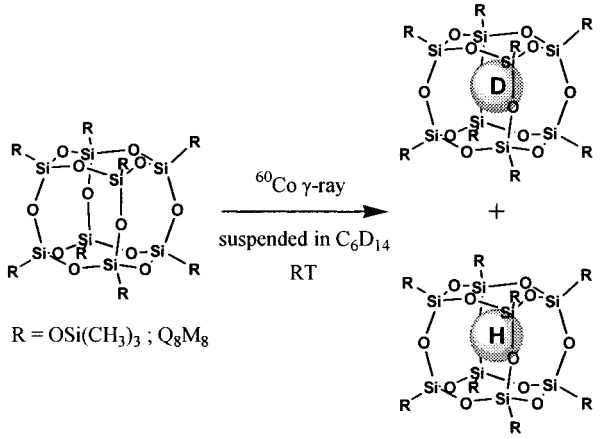
Received July 18, 2000

The irradiation of solid substances using ^{60}Co γ-rays generates H atoms, a process that has been studied physicochemically through electron spin resonance (ESR) spectroscopy.[1] We have trapped a H atom inside a silicate cage with the double four-ring (D4R) structure of octasilsesquioxane, Q_8M_8 ($[(CH_3)_3SiO]_8Si_8O_{12}$), following ^{60}Co γ-ray irradiation of crystalline Q_8M_8.[2] The H atom is difficult to trap in solid materials at ambient temperature because of both a high reactivity and a small size. The H atom becomes stably encapsulated at room temperature and remains inside the D4R structure for months. Päch and Stösser have reported similar phenomena utilizing h_{72}-Q_8M_8 and d_{72}-Q_8M_8 as well as other derivatives of the D4R silicate cage.[3] They synthesized deuterated silsesquioxanes such as DT_8 and d_{72}-Q_8M_8 to serve as the D source. We are interested in the results of their γ-ray irradiation of $EtT_8/C_6D_{12}/I_2$ experiments. This group also recently reported ESR data on D atoms in deuterated Q_8M_8 and EtT_8 cages.[4] H and D atoms can be conveniently generated by pulse radiolysis of H_2O and D_2O, respectively.[5] Liquid-phase and gas-phase radiolyses of alkanes and olefins also yield H and D atoms.[1a] ESR experiments on single H or D atoms may have applications resulting from the sensitivity of hyperfine coupling constant to environmental conditions.[4,5] In addition, as the signal intensity of the trapped H atom is sensitive to the local paramagnetic environment,[2] these techniques may be applicable to magnetic sensing technology.

Previous research on stably encapsulated single H atoms, utilizing γ-ray irradiation in trapping reactive hydrogen atoms inside Q_8M_8 crystals,[2] has not completely elucidated this encapsulation behavior in organic solvents. We have adopted *n*-hexane and *n*-hexane-d_{14} as an organic solvent for our experiments. To investigate the influence of the solvent, several γ-ray irradiation specimens adding *n*-hexane or deuterated *n*-hexane to Q_8M_8 crystals were prepared. After irradiation, ESR detected the presence of the encapsulated atoms; the spin concentration was determined using TEMPO and Mn^{2+}/MgO as the primary and secondary standards, respectively.[6] Following irradiation of Q_8M_8 crystals suspended in deuterated *n*-hexane (*n*-hexane-d_{14}) at room temperature or of a frozen Q_8M_8 solution in *n*-hexane-d_{14} at 77 K, we observed both single H atoms and single D atoms on an ESR spectrum simultaneously (Scheme 1).

Table 1 details the amount of *n*-hexane or *n*-hexane-d_{14} utilized, the states of each specimen, the irradiation conditions, and the results of ESR measurements. We did not obtain any H atom

Scheme 1



encapsulation for the solution state entries, 6−8. Small differences in the amount of *n*-hexane present (0.2 mL) had a profound effect upon encapsulation behavior, as seen by the comparison of entries 5 (suspension state) and 6 (solution state), likely resulting from the solubility of Q_8M_8 in *n*-hexane. We detected the ESR spectra of H atoms for entries 3−5 (suspension states); the spin concentration displayed that the value determined was lower than the solvent free, crystalline specimen (entry 1). We did not observe a significant difference in spin concentration between the two frozen solutions (entries 12 and 13) and a crystalline specimen (entry 2), following γ-irradiation at 77 K. Therefore, the encapsulation behavior does not appear to correlate with the amount of solvent added in frozen solution.

We obtained more informative results for the irradiation of Q_8M_8 suspensions using the deuterated solvent, *n*-hexane-d_{14}. Under these conditions, we detected both single H atoms and single D atoms simultaneously on an ESR spectrum (entries 9−11 in Table 1 and Figure 1a). Each room temperature ESR spectrum displayed a hyperfine doublet for the H atom ($I = {}^1/_2$) and a triplet resulting from the D atom ($I = 1$). The calculated g value and the hyperfine splitting constant, A, of atomic hydrogen were 2.0028 and 1415.02 MHz, respectively. For atomic deuterium, g is equal to 2.0029 and A is equal to 217.6 MHz. Although Q_8M_8 crystals were recrystallized with *n*-hexane-d_{14} and then γ-irradiated, only H signals were observed; D signals were not detected

* Corresponding author. Fax: +81-92-642-2570. E-mail address: matsuscc@mbox.nc.kyushu-u.ac.jp.
[†] Graduate School of Sciences.
[‡] Graduate School of Social and Cultural Studies.

(1) For example, see: (a) Hasegawa, A. *CRC Handbook of Radiation Chemistry*: CRC Press: Boca Raton, 1991; Chapter X. (b) Ogoh, K.; Takaki, S.; Yamanaka, C.; Ikeya M.; Ito, E. *J. Phys. Chem. Jpn.* **1996**, *65*, 844−847.
(2) Sasamori, R.; Okaue, Y.; Isobe, T.; Matsuda, Y. *Science* **1994**, *265*, 1691−1693.
(3) Päch, M.; Stösser, R. *J. Phys. Chem. A* **1997**, *101*, 8360−8365.
(4) Dilger, H.; Roduner, E.; Scheuermann, R.; Major, J.; Schefzik, M.; Stösser, R.; Päch, M.; Fleming, D. G. *Physica B* **2000**, *289*−*290*, 482−486.
(5) Roduner, E.; Percival, P. W.; Han, P.; Bartels, D. M. *J. Chem. Phys.* **1995**, *102*, 5989−5997.
(6) For entries 3−13, the crystal was first placed in a vial or an ampule. Following the addition of solvent, the samples were irradiated at either room temperature or 77 K. ESR measurements were performed after allowing the specimen solvent to evaporate slowly on standing. Approximately 25 mg of dried solid sample was transferred into a quartz tube. X-band ESR spectra were measured on a JEOL JES-RE1X at room temperature.

10.1021/ic000803n CCC: $20.00
Published on Web 04/05/2001

Table 1. Experimental Conditions and Encapsulation Behavior for H and D Atoms in Q_8M_8[a] Using *n*-Hexane or Deuterated *n*-Hexane

entry	solvent	amt of solvent, added (mL)	states of specimen	γ-ray irradiation		encapsulation?	spin concn $\times 10^5$ per Q_8M_8 unit	
				temp	dose (kGy)		hydrogen	deuterium
1	*b*	0	crystal	rt	73.5	yes	3.13	*c*
2	*b*	0	crystal	77 K	73.5	yes	2.28	*c*
3	C_6H_{14}	0.1	suspension[d]	rt	73.5	yes	3.08	*c*
4	C_6H_{14}	0.4	suspension[d]	rt	73.5	yes	2.45	*c*
5	C_6H_{14}	0.8	suspension[d]	rt	73.5	yes	2.62	*c*
6	C_6H_{14}	1.0	solution	rt	73.5	no	*c*	*c*
7	C_6H_{14}	2.0	solution	rt	73.5	no	*c*	*c*
8	C_6H_{14}	4.0	solution	rt	73.5	no	*c*	*c*
9	C_6D_{14}	0.1	suspension[d]	rt	120	yes	5.42	0.0751
10	C_6D_{14}	0.4	suspension[d]	rt	120	yes	3.05	0.618
11	C_6D_{14}	0.6	suspension[d]	rt	120	yes	0.991	1.07
12	C_6H_{14}	1.5[e]	frozen soln	77 K	73.5	yes	2.13	*c*
13	C_6H_{14}	1.25[e]	frozen soln	77 K	73.5	yes	2.19	*c*

[a] Preparations of entries 1 and 3−11 were performed with 40 mg of Q_8M_8. Preparations of entries 2, 12, and 13 were performed with 50, 60, and 25 mg of Q_8M_8, respectively. [b] The sample was irradiated in the solid phase without solvent. [c] Not detected. [d] Crystals remain in solvent. [e] The concentrations of entries 12 and 13 were the same as those of entries 6 and 7, respectively.

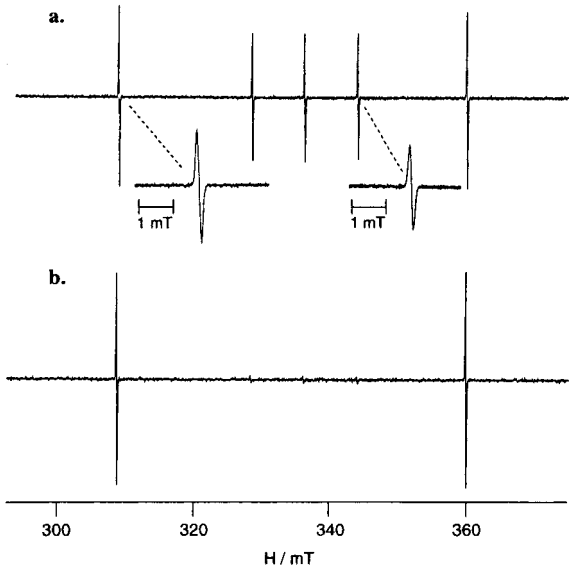


Figure 1. ESR spectra at room temperature for γ-irradiated Q_8M_8. Irradiation specimens: **(**a**)** Q_8M_8 suspension in C_6D_{14} (entry 11, room temperature irradiation) or **(b)** frozen Q_8M_8 solution in C_6D_{14} (the precise data were not shown in Table 1 for 77 K irradiation).

by room temperature ESR. D atoms are not likely to be exchanged with H in the Q_8M_8 structure prior to the γ-irradiation of the samples. These results suggest that the encapsulated H atoms and D atoms must be derived from either substituents attached to the D4R cage or the deuterated solvent, respectively. The H atom spin concentration decreased as the amount of *n*-hexane-d_{14} increased; in contrast, the spin concentration of the D atom increased with increasing *n*-hexane-d_{14}. This decrease in spin concentration [entries 3−5 (suspension states)] suggests that the encapsulation of H atoms, generated from the cage substituents, decreases with increasing *n*-hexane. Intense hydrogen signals and weak deuterium signals, however, were detected in an ESR spectrum for a γ-irradiated, frozen Q_8M_8 solution of *n*-hexane-d_{14} (Figure 1b).

The ESR spectra (Figure 1) indicate that the encapsulation of hydrogen or deuterium may differ greatly depending on the temperature of γ-irradiation, performed either at room temperature for suspension samples or 77 K for frozen solutions. It will be necessary to examine other organic solvents; we hope to evaluate encapsulation mechanisms in later reports. Herein, we communicate a simple and convenient method for the simultaneous encapsulation of single H atoms and D atoms in the different D4R cages of Q_8M_8 without the laborious synthesis of d_{72}-Q_8M_8. This method will be very useful in the relevant field and may prove to be a potential pathway for the encapsulation of atomic tritium without irradiation.[7]

Acknowledgment. We would like to thank Dr. T. Okai and Mr. K. Matsumoto of the Institute for Irradiation and Analysis of Quantum Radiation, Kyushu University, for their valuable technical assistance in performing γ-ray irradiation.

IC000803N

(7) Lambe, J. *Phys. Rev.* **1960**, *120*, 1208−1211.