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Ab Initio Investigation of Hydrogenation of C_{60}

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Ab initio molecular orbital theory was used to examine the hydrogenation of a C_{60} molecule. The 1,2 addition of the 6,6 bond is an energetically favorable adsorption site in one-hydrogen-molecule adsorption. We found that the averaged C−H bond energy is maximized in the $C_{60}H_{36}$ molecule. Calculation of the Gibbs free energy of the $C_{60} + 30\ H_2 \rightarrow C_{60}H_{60}$ reaction showed that this reaction becomes endothermic above 220 K. Moreover, the C−H bond energy associated with the increasing number of six-membered rings found to decrease by calculating the averaged C−H bond energies of five fully hydrogenated fullerenes: $C_{20}H_{20}$, $C_{36}H_{36}$, $C_{60}H_{60}$, $C_{70}H_{70}$, and $C_{90}H_{90}$.

Introduction

Hydrogenation of fullerenes is a basic reaction used to modify fullerenes chemically. Identification of the molecular structure of $C_{60}H_{36}$, which has been the highest hydrogen-covered isomer of C_{60} observed in experiments,[1,2] has especially been an important topic for both experimental[3] and theoretical[4−6] studies of fullerenes. Moreover, hydrogen adsorption on carbon materials (graphite, graphite nanofibers,[7] and carbon nanotubes) has recently aroused a great deal of interest as a promising hydrogen-storage medium for fuel cells. Hydrogen adsorption on carbon nanotubes has been intensively studied experimentally[8,9] and theoretically.[10−12] There are two possibilities of hydrogen adsorption on carbon materials: one is physisorption of atomic or molecular hydrogen; the other is chemisorption of hydrogen atoms by forming C−H bonds. Thus, hydrogenation of fullerenes might become a useful technique for hydrogen storage for fuel cells.

As stated, the highest hydrogen-covered isomer of C_{60} that has been currently identified is $C_{60}H_{36}$. This result seems to indicate that the C−H bond energy decreases at high hydrogen coverage. $C_{20}H_{20}$ (dodecahedrane) was synthesized by Paquette and co-workers in 1982,[13] whereas a fully hydrogenated C_{60} (i.e., $C_{60}H_{60}$) has not been synthesized. According to Euler's rule, the skeletal structure of C_{20} is comprised of 12 five-membered rings, and that of C_{60} is comprised of 12 five-membered rings and 20 six-membered rings. Thus, we can also expect that C−H bond energy decreases as the number of six-membered rings in fullerenes increases.

In the current work, hydrogenation of a C_{60} molecule was investigated by using ab initio molecular orbital theory. To examine the C−H bond energy versus hydrogen coverage, three representative coverages (low, medium, and high) were considered: under low coverage, one H atom or one H_2 molecule is added to a C_{60} molecule; $C_{60}H_{36}$ corresponds to medium coverage, and $C_{60}H_{60}$ corresponds to high coverage. We found that the Gibbs energy change of $C_{60} + 30\ H_2 \rightarrow C_{60}H_{60}$ becomes endothermic above 220 K. Three hypothetical decompositions of a $C_{60}H_{60}$ molecule were examined: $C_{60}H_{60} \rightarrow C_{58}H_{58} + C_2H_2$, $C_{60}H_{60} \rightarrow C_{54}H_{54} + C_6H_6$, and $C_{60}H_{60} \rightarrow C_{46}H_{46} + C_{14}H_{14}$. We found that the decomposition into $C_{46}H_{46}$ is exothermic, while the other two decompositions are endothermic. Moreover, the decrease of the C−H bond energy concerning the increasing number of six-membered rings was investigated by comparing the C−H bond energies on the $C_{20}H_{20}$, $C_{36}H_{36}$, $C_{60}H_{60}$, $C_{70}H_{70}$, and $C_{90}H_{90}$ molecules.

TABLE 1: Averaged C−H Bond Energy (in eV) of $C_{60}H_n$ (n = 1,2) by Using B3LYP/6-31G(d,p) Model Chemistry

molecule	adsorption type	bond energy (eV)
$C_{60}H$	(a) H atom addition	2.13
$C_{60}H_2$	(b) 1,2 addition (5,6 bond)	2.43
	(c) 1,2 addition (6,6 bond)	2.86
	(d) 1,3 addition	1.93
	(e) 1,3 addition	1.95
	(f) 1,4 addition	2.69

Computational Method

We used the hybrid density-functional theory using the B3LYP functional[14−16] with the 6-31G(d,p) basis set (except for calculating the vibrational frequency of C_{60}, $C_{60}H_{60}$, and H_2 molecules and the contribution to the Gibbs energy from molecular vibration). All molecular geometries were fully optimized by using the B3LYP/6-31G(d,p) model chemistry. Vibrational frequencies and contribution to the Gibbs energy from molecular vibration were calculated by using HF/6-31G(d,p) model chemistry under the above B3LYP/6-31G(d,p) optimized geometries. All calculations were performed by the Gaussian 98 program.[17]

Results and Discussion

C-H Bond Energy at Low Hydrogen Coverage. First, the addition of one H atom or one H_2 molecule to a C_{60} molecule was examined. Regarding the latter addition, we confined our examination to 1,2 and 1,3 additions (Figure 1). The averaged C−H bond energies are listed in Table 1. The averaged bond energy is defined as

$$\frac{1}{n}\{E(C_{60}) + nE(H) - E(C_{60}H_n)\}$$

where $E(X)$ means the total energy of species X. These bond energies are significantly smaller than the C−H bond energy of methane (4.47 eV). The reactant (C_{60}) is stabilized by the π

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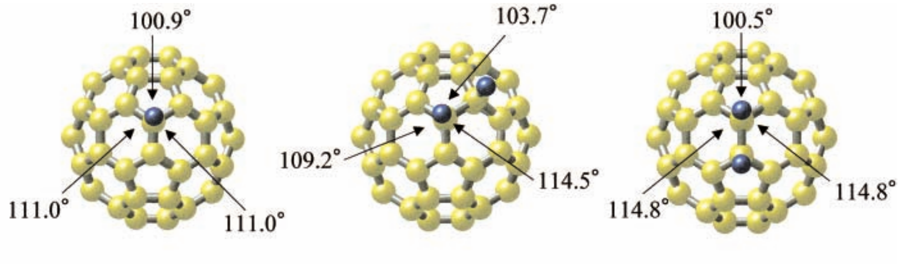
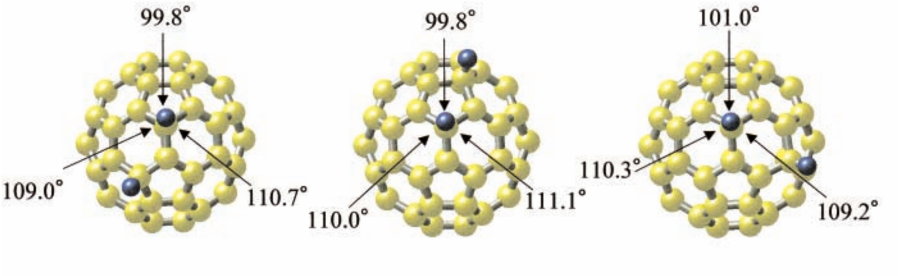
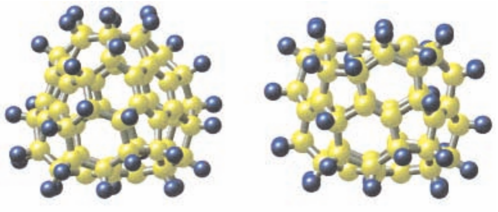


(a) H atom addition (b) 1,2 addition (5,6 bond) (c) 1,2 addition (6,6 bond)

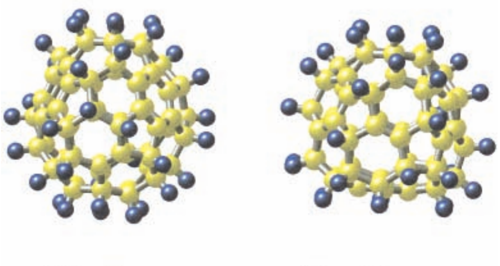


(d) 1,3 addition (e) 1,3 addition (f) 1,4 addition

Figure 1. Optimized geometry (by using B3LYP/6-31G(d,p) model chemistry) of one-hydrogen-atom adsorption (a) and one-hydrogen-molecule adsorption (b−f). Blue and yellow balls stand for H and C atoms, respectively.



(a) T (b) D_{3d}



(c) C_3 (d) C_3

Figure 2. Optimized geometry (by using B3LYP/6-31G(d,p) model chemistry) of $C_{60}H_{36}$ isomers. Blue and yellow balls stand for H and C atoms, respectively.

electron conjugation; on the other hand, the products $C_{60}H_n$ ($n = 1,2$) are a little unstabilized by the disturbance of the π electron conjugation due to the hydrogen addition, which results in smaller exothermicity in $C_{60}H_n$. We found that the 1,2 addition of the 6,6 bond is the most favorable adsorption site. The averaged C−H bond energies of the 1,2 additions are larger than that of the $C_{60}H$ molecule, whereas the averaged C−H bond energies of the 1,3 additions are smaller than that of the $C_{60}H$ molecule. Although by the addition of hydrogens the bond angle of the five-membered ring becomes similar (about 110°, shown in Figure 1) in both the 1,2 and 1,3 additions, the bond angles of the six-membered ring significantly differ (about 114° in 1,2 additions and 110° in 1,3 additions). Thus, the back bonds of hydrogen-adsorbed carbon atoms in the 1,2 additions have more s-character than those in the 1,3 additions. Therefore, the 1,2 additions do not much disturb the π electron conjugation of C_{60}, so the 1,2 additions are energetically more favorable than the 1,3 additions. We also confirmed that the 1,4 addition (Figure 1f) is less (more) stable than the 1,2 addition of the 6,6 (5,6) bond.

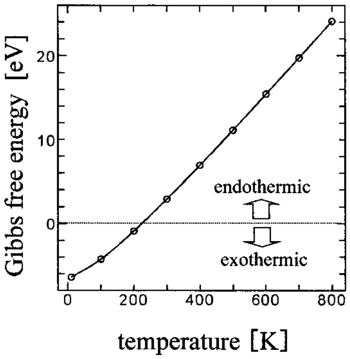


Figure 3. Gibbs energy change of the reaction: $C_{60} + 30\ H_2 \rightarrow C_{60}H_{60}$.

TABLE 2: Averaged C−H Bond Energy (in eV) of $C_{60}H_{36}$ by Using B3LYP/6-31G(d,p) Model Chemistry

symmmetry	bond energy (eV)
(a) T	2.94
(b) D_{3d}	2.90
(c) C_3	2.88
(d) C_3	2.84

C-H Bond Energy under Medium Hydrogen Coverage. Clare and Kepert examined the structures and stability of 63 isomers of $C_{60}H_{36}$ by using a semiempirical AM1 Hamiltonian.[4] We calculated isomers (D_{3d}, T, and two C_3's; Figure 2) that were the four most stable isomers in their calculation. The averaged C−H bond energies are listed in Table 2. Contrary to their semiempirical calculation, we found that an isomer which has T symmetry is more stable than that which has D_{3d} symmetry, and our result is consistent with the previous ab intio calculation by Bühl et al.[5] The averaged C−H bond energy of $C_{60}H_{36}$ (T symmetry: 2.94 eV) is slightly larger than that of $C_{60}H_2$ (6,6 bond: 2.86 eV). Moreover, the averaged C−H bond energy of $C_{60}H_{36}$ (T symmetry: 2.94 eV) is significantly larger

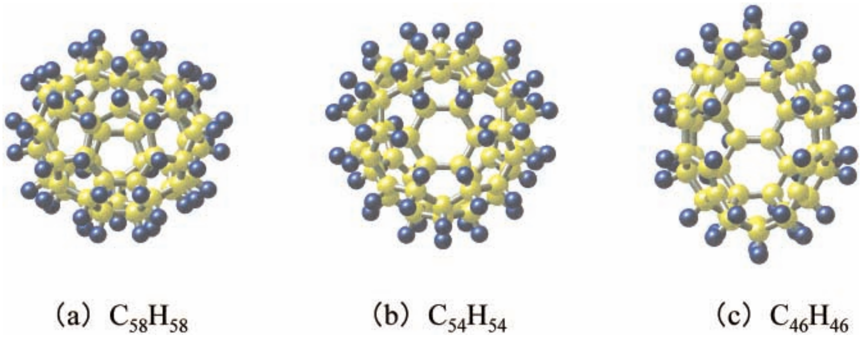

(a) $C_{58}H_{58}$ (b) $C_{54}H_{54}$ (c) $C_{46}H_{46}$

Figure 4. Optimized geometry (by using B3LYP/6-31G(d,p) model chemistry) of $C_{58}H_{58}$, $C_{54}H_{54}$, and $C_{46}H_{46}$ molecules. Blue and yellow balls stand for H and C atoms, respectively.

than that of $C_{60}H$ (2.13 eV). $C_{60}H_{36}$ is the highest hydrogen-covered isomer that has been detected to date.[1,2] Thus, we expect that the averaged C−H bond energy is maximized in $C_{60}H_{36}$. We also calculated the averaged C−H bond energies of $C_{60}H_{12}$ (S_6 symmetry: 2.51 eV), $C_{60}H_{24}$ (T symmetry: 2.81 eV), $C_{60}H_{48}$ (S_6 symmetry: 2.82 eV), and $C_{60}H_{60}$ (I_h symmetry: 2.61 eV) by using B3LYP/6-31G(d,p) model chemistry. The structure of $C_{60}H_{24}$ (T symmetry) was assumed to be complementary to $C_{60}H_{36}$ (T symmetry); that is, the sites where hydrogen atoms adsorb on $C_{60}H_{36}$ are not adsorbed on $C_{60}H_{24}$. The structure of $C_{60}H_{12}$ was also assumed to be complementary to $C_{60}H_{48}$. Although these hydrogenated C_{60} molecules may not be the most stable isomers, the averaged C−H bond energy seems to be maximized in $C_{60}H_{36}$. Yoshida et al. showed that the strain energy of $C_{60}H_n$ ($n = 32-42$) is minimized at $n = 36$.[18] Our result is consistent with their finding.

Thermodynamic Stability of the $C_{60}H_{60}$ Molecule. As a further hydrogenation process of $C_{60}H_{36}$, the reaction of $C_{60}H_{36}$ (T symmetry) + 12 $H_2 \rightarrow C_{60}H_{60}$ (I_h symmetry) was studied. We found that this reaction is exothermic with an energy of 7.60 eV. The reaction, however, could be unfavorable thermodynamically if Gibbs free energy of the reaction becomes endothermic. Since the calculation of the vibrational frequency of $C_{60}H_{36}$ (T symmetry) was much more computationally demanding than that of $C_{60}H_{60}$ (I_h symmetry), we calculated the Gibbs energy change of C_{60} (I_h symmetry) + 30 $H_2 \rightarrow C_{60}H_{60}$ (I_h symmetry) instead at 10 K and in the range 100−800 K at increments of 100 K. A conventional scale factor (0.8929) was used to calculate the contribution to the Gibbs energy from molecular vibration. The result is shown in Figure 3, which shows that although Gibbs-free-energy change of the reaction is exothermic at low temperature, it becomes endothermic above 220 K.

The main IR active frequency of the C−H stretching mode of $C_{60}H_{60}$ is at 3172 cm^{-1} (T_{1u} symmetry). On the other hand, the main Raman active frequencies of C−H stretching mode of the $C_{60}H_{60}$ are at 3157 cm^{-1} (H_g symmetry) and at 3183 cm^{-1} (A_g symmetry). These frequencies were not scaled.

Since $C_{60}H_{60}$ is not thermodynamically stable above 220 K, we next considered three hypothetical decompositions of a $C_{60}H_{60}$ molecule: $C_{60}H_{60} \rightarrow C_{58}H_{58} + C_2H_2$, $C_{60}H_{60} \rightarrow C_{54}H_{54} + C_6H_6$, and $C_{60}H_{60} \rightarrow C_{46}H_{46} + C_{14}H_{14}$. We obtained the optimized geometries of the $C_{58}H_{58}$, $C_{54}H_{54}$, and $C_{46}H_{46}$ molecules from the initial geometries generated from the optimized geometries of $C_{60}H_{60}$ by subtracting the C_2H_2, C_6H_6, and $C_{14}H_{14}$ fragments, respectively. The optimized geometries of these molecules are shown in Figure 4. Although there are two inequivalent bonds in C_{60} (the 6,6-bond and the 5,6-bond), the two optimized geometries of $C_{58}H_{58}$ with a seven-membered ring are almost identical. We found that the decompositions $C_{60}H_{60} \rightarrow C_{58}H_{58} + C_2H_2$ and $C_{60}H_{60} \rightarrow C_{54}H_{54} + C_6H_6$ are endothermic at energies of 1.29 and 5.81 eV, respectively, whereas the decomposition of $C_{60}H_{60} \rightarrow C_{46}H_{46} + C_{14}H_{14}$ is exothermic at energy of 6.52 eV. The fact that the decomposition into $C_{46}H_{46}$ is exothermic might be due to the large relaxation of the molecular geometry of $C_{46}H_{46}$ (Figure 4).

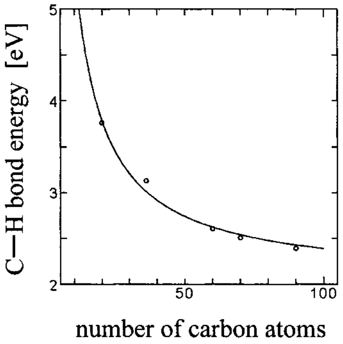


Figure 5. Averaged C−H bond energy (by using B3LYP/6-31G(d,p) model chemistry) of $C_{20}H_{20}$, $C_{36}H_{36}$, $C_{60}H_{60}$, $C_{70}H_{70}$, and $C_{90}H_{90}$ molecules. See text for the explanation of the curve.

Effect of Six-Membered Rings on the C-H Bond Energy. Although, as stated in the Introduction, fully hydrogenated $C_{20}H_{20}$ has been synthesized, $C_{60}H_{60}$ has not. The number of five-membered rings is 12 in both C_{20} and C_{60}. Additionally, C_{60} has 20 six-membered rings. Moreover, comparison of 1,2 and 1,3 additions of $C_{60}H_2$ showed that the C−H bond energy is more affected by the adsorption on a six-membered ring than that on a five-membered ring. These observations suggest that as the number of six-membered ring increases, the averaged C−H bond energy decreases. We examined this hypothesis by calculating the averaged C−H bond energy of five fully hydrogenated fullerenes that have 12 five-membered rings: $C_{20}H_{20}$ (0: I_h symmetry), $C_{36}H_{36}$ (8: D_{6h} symmetry), $C_{60}H_{60}$ (20: I_h symmetry), $C_{70}H_{70}$ (25: D_{5h} symmetry), and $C_{90}H_{90}$ (35: D_{5h} symmetry). The values in parentheses are the number of six-membered rings. Figure 5 shows the averaged C−H bond energy decreases as the number of six-membered rings increases, and this decrease is well fitted by the equation; bond energy = $34.9/n + 2.04$ eV (shown in Figure 5), where n is the number of carbon atoms. The fitted value, 2.04 eV, corresponds to the C−H bond energy on the (5,5) carbon nanotube. We found that this value agrees well with the LDA (2.10 eV) and GGA (1.75 eV) supercell calculations of the hydrogenation of the (5,5) nanotube obtained by Lee and Lee.[12]

Summary

Hydrogenation of a C_{60} molecule was investigated by calculations using ab initio molecular orbital theory. At low coverage, additions of one H atom or one H_2 molecule on a C_{60} molecule were considered in the calculations. We found that 1,2 additions are energetically more favorable than 1,3 additions. At medium coverage, we found that the averaged C−H bond energy of the $C_{60}H_{36}$ molecule is maximized. At high coverage, the $C_{60}H_{60}$ molecule becomes thermodynamically unstable above 220 K. The hypothetical decomposition $C_{60}H_{60} \rightarrow C_{46}H_{46} + C_{14}H_{14}$ was found to be exothermic with an energy of 6.52 eV. Moreover, the C−H bond energy concerning the increasing number of six-membered rings was found to decrease by comparing the averaged C−H bond energies of five fully hydrogenated fullerenes: $C_{20}H_{20}$, $C_{36}H_{36}$, $C_{60}H_{60}$, $C_{70}H_{70}$, and $C_{90}H_{90}$. From these hydrogenated fullerenes, the C−H bond energy on a (5,5) carbon nanotube was estimated to be 2.04 eV.

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