Numerical simulation of Platonic hydrocarbons and fullerenes

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Abstract. Thermal stability of small cage clusters known as Platonic hydrocarbons (tetrahedrane, cubane) was studied over a wide temperature range using tight-binding molecular dynamics simulation. Activation energies and frequency factors in the Arrhenius equation were obtained for these clusters. Ab initio calculations using HF, and B3LYP methods with 6-31G* basis set were performed on C_{20}, C_{36} and C_{60} fullerenes to compute the lowest energy barriers preventing their decomposition. Possible decomposition products were also analyzed in detail.

1. Introduction

Since the discovery of C_{60} fullerene in 1985 [1] cage-like carbon clusters have been widely studied both theoretically and experimentally. The fact that C_{60} is the smallest fullerene, that obeys the isolated pentagon rule [2], probably explains why it can be synthesized in large amounts [3]. The smallest possible C_{20} fullerene (see figure 1(a)) was synthesized and experimentally identified in 2000 [4], carbon atoms in its shell are arranged in the network of pentagons only. Fullerenes C_{36} (see figure 1(b)) attracts a special fundamental interest [5]. It occupies an intermediate position between C_{20} and C_{60} fullerenes and possesses uncommon physicochemical properties. Great attention is focused on the study of the macroscopic crystalline forms based on C_{36} fullerenes similar to C_{60} fullerites [5, 6]. Both C_{20} and C_{36} fullerenes have adjacent pentagons, which makes them more reactive than C_{60}. This fact enables them to form a covalently bound solids with fullerenes playing the role of elemental building blocks [6, 7].

Platonic hydrocarbons are named after Platonic solids (five regular polyhedrons). Tetrahedrane C_{4}H_{4} (see figure 1(c)) is the smallest and most strained hydrocarbon because of its 60-degree bonding angle of carbon atoms. Due to molecule’s high strain it was not synthesized yet, but there exist some of its compounds where hydrogen atoms are substituted by organic groups [8, 9]. Cubane C_{8}H_{8} (see figure 1(d)) [10] is the most rigorously studied cluster among the Platonic hydrocarbons. Since the carbon bond angle of 90° is closer to the equilibrium value for the tetrahedral bond angle of 109.5°, this molecule is less strained than tetrahedrane. After Eaton and Cole synthesized it for the first time in 1964, cubane is widely studied as a promising high-energy fuel and a starting material for novel chemical compounds [11, 12].

Since many practical applications of these molecules depend on their stability, it is important to investigate under what conditions they transit to different structures. Generally when exposed

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to high temperature molecules begin to evolve by repeatedly crossing energy barriers from one
local minimum to another, with rate $\tau^{-1}$ described by the Arrhenius equation:

$$\tau^{-1}(T) = A\exp(-E_a/k_B T),$$

(1)

where $k_B$ is the Boltzmann constant. Two quantities determining the rate are activation
energy $E_a$ and frequency factor $A$. In this paper we report calculations on stability of Platonic
hydrocarbons $C_4H_4$ and $C_8H_8$ and fullerenes $C_{20}$, $C_{36}$ and $C_{60}$. We found the lowest energy
transition states of fullerenes binding the initial cluster with the next isomer and simulated
thermal dissociation of Platonic hydrocarbons over a wide temperature range, allowing us to
find frequency factors and activation energies.

2. Computational details

Calculations on $C_4H_4$ and $C_8H_8$ were performed with the nonorthogonal tight-binding potential
(NTB) for hydrocarbons [13], for fullerenes NTB and the orthogonal tight-binding potential
(OTB) [14] were used. A molecular dynamics (MD) simulation was performed on hydrocarbons.
During simulation full energy of the system was held constant, and temperature was defined as a mean kinetic energy of the atoms. Tetrahedrane was simulated at about 50 different temperatures evenly distributed across the range of 1050-2000 K. In computations on cubane the system was sampled at about 50 different temperatures evenly distributed across the range of 1050-2000 K. In this study we used Newton method to optimize geometries of the first transition states. Fullerenes were also treated using the HF and DFT methods with 6-31G* basis set. At DFT level B3LYP functional was used.

3. Results

3.1. Thermal stability of the tetrahedrane and cubane molecules

At the beginning we optimized initial molecular geometries. Bond lengths in the tetrahedrane are $l_{C-C} = 1.525$ Å and $l_{C-H} = 1.068$ Å and in cubane are $l_{C-C} = 1.570$ Å and $l_{C-H} = 1.082$ Å. The values for cubane are close to the ones obtained experimentally in [15] ($l_{C-C} = 1.571$ Å and $l_{C-H} = 1.097$ Å). Since tetrahedrane was not synthesized yet, our results can only be compared to the results of previous computations. The lengths computed in [16] at B3LYP/6-31G* level are $l_{C-C} = 1.480$ Å and $l_{C-H} = 1.073$ Å. To access relative stabilities binding energies $E_b$ were calculated:

$$E_b = \frac{n \cdot E(C) + m \cdot E(H) - E(C\text{H}_m)}{n + m},$$

where $E(C\text{H}_m)$ is potential energy of the molecule, $E(C)$ and $E(H)$ are energies of isolated carbon and hydrogen atoms, respectively. Binding energy of tetrahedrane is 3.90 eV/atom and for cubane $E_b$ equals to 4.42 eV/atom (experimental value is 4.47 eV/atom [15]).

We performed an MD simulation to identify the sequence of transitions during thermal decomposition of Platonic hydrocarbons. The tetrahedrane decomposition starts from breaking of two opposite carbon bonds and transition to cyclobutadiene ($E_b = 4.29$ eV/atom). Next follows a fast (<1 ps) “splitting” of cyclobutadiene into two acetylene molecules ($E_b = 4.54$ eV/atom). This increase in $E_b$ shows that stored potential energy of 5.12 eV/molecule is released in the process. The cubane decomposition starts from the transition to syn-tricyclooctadiene ($E_b = 4.47$ eV/atom), which is followed by a fast (0.1-1 ps) transition to cyclooctatetraene ($E_b = 4.73$ eV/atom) or to bicyclooctatriene ($E_b = 4.65$ eV/atom). Finally, bicyclooctatriene transforms into cyclooctatetraene or dissociates to benzene and acetylene ($E_b = 4.75$ eV/atom). The values of mechanical energy released in transition to cyclooctatetraene (4.96 eV/molecule) and in dissociation to benzene and acetylene (5.28 eV/molecule) are very close to that in tetrahedrane. The decomposition in both cases results in lowering the strain by increasing the carbon bond angle.

Direct calculation of the tetrahedrane and cubane lifetimes $\tau$ at different temperatures allowed us to find the values of the activation energies $E_a$ and the frequency factors $A$ by fitting the data to the Arrhenius equation (1). For the tetrahedrane these values are $E_a = 0.7 \pm 0.1$ eV and $A = 10^{14.52 \pm 0.59}$ s$^{-1}$, and for the cubane they are $E_a = 1.9 \pm 0.1$ eV and $A = 10^{16.03 \pm 0.36}$ s$^{-1}$. The values of activation energies and frequency factors can be used to estimate tetrahedrane and cubane lifetimes in the range of high and low temperatures, where experimental data are unavailable.

3.2. The values of energy barriers preventing the dissociation of fullerenes

We addressed the problem of fullerenes’ stability by optimizing geometries and calculating the heights $U$ of the lowest energy transition states bridging ideal fullerene with next energy minimum using both ab initio approaches and tight-binding methods [13, 14]. The detailed results for energy barriers are shown in table 1. Symbols $F_{i}^{N}$ and $S_{i,j}^{N}$ denote the first local minimum and corresponding saddle point, respectively, indices $i$ and $j$ denote the isomer (“0” is the ideal or “undistorted” cluster and “1” is the next minimum ) and $N$ is the number of atoms
Table 1. Potential energy (eV) of the metastable and saddle structures of fullerenes.

| Method | B3LYP/6-31G* | HF/6-31G* | OTB | NTB |
|--------|--------------|----------|-----|-----|
| $F_{20}^{20}$ | 5.86 | 4.00 | 3.83 | 3.02 |
| $S_{20}^{20}$ | 5.98 | 4.40 | 5.00 | 3.29 |
| $F_{36}^{36}$ | -0.15 | -0.83 | -0.33 | -0.14 |
| $S_{36}^{36}$ | 6.30 | 5.73 | 5.74 | 4.52 |
| $F_{60}^{60}$ | 1.31 | 2.01 | 1.42 | 1.33 |
| $S_{60}^{60}$ | 7.37 | 8.58 | 6.48 | 5.23 |

in the molecule. The energies in the table are given relative to the energies of ideal fullerenes i.e. $F_{0}^{20}$, $F_{0}^{36}$ and $F_{0}^{60}$.

4. Concluding remarks
Thermal stability of the tetrahedrane and cubane molecules was analyzed using tight-binding and *ab initio* approaches. Temperature dependencies of their lifetimes were obtained and main products of dissociation were identified. During this process strain is released by increasing bond angles. The problem of fullerenes’ stability was addressed by calculating heights of the lowest energy barriers preventing the decomposition of fullerenes. The obtained results are essential in practical applications of Platonic hydrocarbons, fullerenes and their derivatives.

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