Thermal stability of cubane C$_8$H$_8$

M. M. Maslov, D. A. Lobanov, A. I. Podlivaev, and L. A. Openov*

* E-mail: LAOpenov@mephi.ru

Moscow Engineering Physics Institute (State University), 115409 Moscow, Russia

**ABSTRACT**

The reasons for the anomalously high thermal stability of cubane C$_8$H$_8$ and the mechanisms of its decomposition are studied by numerically simulating the dynamics of this metastable cluster at $T = 1050 - 2000$ K using a tight-binding potential. The decomposition activation energy is found from the temperature dependence of the cubane lifetime obtained from the numerical experiment; this energy is fairly high, $E_a = 1.9 \pm 0.1$ eV. The decomposition products are, as a rule, either C$_6$H$_6$ and C$_2$H$_2$ molecules or the isomer C$_8$H$_8$ with a lower energy.
Cubane C₈H₈ (Fig. 1) discovered in 1964 [1] is of great interest from both the fundamental and practical standpoints. In this cluster, the carbon atoms are in cube vertices; i.e., the angles between the C-C covalent bonds are 90° rather than 109.5° as in carbon compounds with a tetrahedral atomic arrangement and sp³ hybridization of the atomic orbitals. Such large bending of the C-C-C bonds is energetically unfavorable. However, hydrogen atoms arranged on the main diagonals of the cube stabilize this atomic configuration (Fig. 1), corresponding to a local rather than global minimum of the potential energy as a function of the atomic coordinates. Although cubane is a metastable cluster, its high stability is demonstrated by the experimental fact that the cubane molecules not only retain their structure at temperatures significantly higher than room temperature but also can form a molecular crystal, namely, solid cubane s-C₈H₈, with a melting temperature near 400 K [2]. The formation heat of cubane is relatively large, 6.5 eV/C₈H₈ [3] (such energy is released, e.g., when solid cubane transforms into graphite layers and H₂ molecules). High energy content of cubane makes it a promising material for fuel elements, and the possibility of replacing the hydrogen atoms with various functional groups (such as CH₃ in methylcubane [4]) opens the way to the synthesis of new compounds with unique properties.

A wide application of cubane is hampered by the absence of cheap methods for its mass production [5]. In our opinion, detailed studies of the mechanisms and products of cubane decomposition may suggest a direction of searching for new methods of its production.

In this case, it is interesting to consider a possible reversal of the chemical reaction (e.g., under heating in the presence of appropriate catalysts lowering the barrier of the reverse reaction). A certain analogy may be drawn with fullerene C₆₀: its decomposition
is preceded by a series of Stone-Wales transformations, which result in the formation of "surface" defects and, eventually, a C$_2$ dimer is separated; on the other hand, annealing of these defects leads (through the same transformations) to the formation of a fullerene from a strongly distorted spherical cluster C$_{60}$ (see [6, 7] and references therein). There are only a few experimental studies of cubane decomposition (see, e.g., [8, 9]), and those experiments were performed only over narrow temperature [8] and lifetime [9] ranges. As for theory, many theoretical studies employed the same schematic potential-energy surface of cubane and its isomers [8], while, to the best of our knowledge, the cubane dynamics before the instant of transition to another isomer has been studied only at very high temperatures and for a very short time ($\sim 1$ ps) corresponding to only several tens of cluster oscillation periods [10].

The main aim of this work is to numerically simulate the cubane dynamics over a wide temperature range and determine the cubane decomposition activation energy, products of its decomposition, and the types of isomers forming at the stage of evolution preceding the decomposition. We calculated the energies of various atomic configurations within a nonorthogonal tight-binding model that was proposed for hydrocarbon compounds in [11] and modified in [12] using a criterion of more exact correspondence between the theoretical and experimental values of the binding energies and interatomic distances in various C$_n$H$_m$ molecules. The model is a reasonable compromise between more rigorous ab initio approaches and extremely simplified classical potentials of interatomic interaction. In this model, the bond lengths in cubane are calculated to be $l_{C-C} = 1.570$ Å and $l_{C-H} = 1.082$ Å, which are close to experimental values 1.571 and 1.097 Å, respectively [13]. The calculated binding energy of the atoms in cubane $E_b = [8E(C) + 8E(H) - E(C_8H_8)]/16 =$
4.42 eV/atom likewise agrees with the experimental value 4.47 eV/atom [13]. The ratio of the energies of the carbon and hydrogen subsystems in the heat-insulated cubane calculated in this model coincides with the theoretical value [14].

We studied the thermal stability of cubane C₈H₈ by the molecular-dynamics method. At the initial instant of time, random velocities and displacements are given to each of the atoms in such a manner that the momentum and the angular momentum of the whole cluster are equal to zero. Then, the forces are calculated acting on the atoms. The classical Newton equations of motion are numerically integrated using the velocity Verlet method. The time step was \( t_0 = 2.72 \cdot 10^{-16} \) s. In the course of the simulation, the total energy of cubane (the sum of the potential and kinetic energies) remained unchanged, which corresponds to a microcanonical ensemble (the system is not in a thermal equilibrium with the surroundings [15-18]). In this case, the "dynamic temperature" \( T \) is a measure of the energy of relative motion of the atoms and is calculated from the formula [19, 20] 

\[
\langle E_{\text{kin}} \rangle = \frac{1}{2} k_B T (3n - 6),
\]

where \( \langle E_{\text{kin}} \rangle \) is the time-averaged kinetic energy of the cluster, \( k_B \) is the Boltzmann constant, and \( n = 16 \) is the number of atoms in cubane. It should be noted that the velocity Verlet algorithm is conservative with respect to the momentum and the angular momentum [21] and the relative change in the total energy of cubane does not exceed \( 10^{-4} \) for at least \( 2 \cdot 10^9 \) molecular-dynamic steps, which corresponds to a time of \( \sim 1 \mu s \).

We studied the cubane evolution for \( \approx 50 \) various sets of initial velocities and displacements of the atoms corresponding to temperatures \( T = 1050 - 2000 \) K. It turned out that, during its decomposition, cubane is most often (in \( \approx 80\% \) of events) transformed to the isomer cyclooctatetraene (COT) (Fig. 2a) with a lower potential energy (a higher binding
energy \( E_b = 4.82 \text{ eV/atom} \). The cubane decomposition into a benzene \( \text{C}_6\text{H}_6 \) molecule \( (E_b = 4.82 \text{ eV/atom}) \) and an acetylene \( \text{C}_2\text{H}_2 \) molecule \( (E_b = 4.54 \text{ eV/atom}) \) occurs more rarely (in \( \approx 20\% \) of events) (Fig. 2b). We also observed several times the formation of styrene and some other isomers of \( \text{C}_8\text{H}_8 \). Almost without exception, upon decomposition, cubane is transformed first into the isomer syn-tricyclooctadiene (STCO) with \( E_b = 4.47 \text{ eV/atom} \) (Fig. 3a), which is quickly transformed (in a time of 0.1 - 1 ps) into either COT or isomer bicyclooctatriene (BCT) with \( E_b = 4.65 \text{ eV/atom} \) (Fig. 3b). BCT, in turn, transforms into COT or decomposes into benzene and acetylene (BEN + A) molecules. We have never observed reverse transitions, such as STCO \( \rightarrow \) cubane, COT \( \rightarrow \) STCO, and BCT \( \rightarrow \) STCO, whereas sometimes COT is transformed into BCT with subsequent decomposition BCT \( \rightarrow \) BEN + A.

As the temperature \( T \) decreases from \( \approx 2000 \) to \( \approx 1000 \text{ K} \), the cubane lifetime \( \tau \) increases by six orders of magnitude, from \( \sim 1 \text{ ps} \) to \( \sim 1 \mu\text{s} \) (Fig. 4). Since the decomposition of metastable clusters is an inherently probabilistic process, the lifetime \( \tau \) exhibits a dispersion at a given temperature \( T \). Nevertheless, it is seen from Fig. 4 that the results of the numerical simulation are described by the common Arrhenius formula

\[
\tau^{-1}(T) = A \cdot \exp \left[ -\frac{E_a}{k_B T} \right].
\]

According to this formula, the dependence of \( \ln(\tau) \) on \( 1/T \) is a straight line, whose slope determines the activation energy \( E_a = (1.9 \pm 0.1) \text{ eV} \) and its intersection point with the ordinate axis determines the frequency factor \( A = 10^{16.03\pm0.36} \text{ s}^{-1} \). It is remarkable that the values of \( E_a \) and \( A \) agree well with the experimental values \( E_a = (1.87 \pm 0.04) \text{ eV} \) and \( A = 10^{14.68\pm0.44} \text{ s}^{-1} \) obtained when studying cubane pyrolysis in a very narrow range \( T = (230 \div 260) \text{ °C} \) [8], which is far apart from the temperature range studied in this
paper. The small (on the logarithmic scale) difference in the frequency factors is likely
due to the temperature dependence of $A$ (we note that the value of $A$ for cubane is almost
four orders of magnitude smaller than that for fullerene $C_{60}$ [7]).

Extrapolation of the $\tau(T)$ curve to the range $T < 1000$ K (which is inaccessible in
direct numerical calculations because of extremely long simulation time) permits one to
compare the results of the simulation with the experimental values of $\tau$ obtained in [9]
for several temperatures in the range $T = 373 \div 973$ K. As seen from Fig. 4, here also
there is agreement between theory and experiment. Thus, Eq. (1) with the values of
$E_a$ and $A$ found can be used to determine the cubane lifetime (or, in any case, to make
order-of-magnitude estimates) at both very high and comparatively low temperatures. In
particular, Eq. (1) gives $\tau \sim 10^{16}$ s at room temperature and $\tau \sim 10^8$ s at the melting
temperature of solid cubane $T_m \approx 400$ K (at which, on melting, only weak van der Waals
bonds between $C_8H_8$ clusters are broken, whereas the clusters themselves retain their
structure and the energy stored in them). The lifetime decreases to $\tau \sim 1$ s only on
heating to $T \approx 600$. Pyrolysis experiments [9] give $\tau \approx 10$ ms at $T = 573$ K and $\tau \approx 2$
ms at $T = 673$ K (Fig. 4).

Note that, when analyzing the $\tau(T)$ dependence, we used Eq. (1) without a thermal-
reservoir finite-size correction [22, 23]. This correction reduces to replacing $T$ by $T −
E_a/2C$ in the exponent of Eq. (1), where $C$ is the microcanonical heat capacity of the
cluster. With $C = k_B(3n − 6)$, where $n = 16$ is the number of atoms in cubane, the
closest fit between the modified Arrhenius formula and the numerical-simulation data is
achieved at $E_a = (1.41 \pm 0.07)$ eV, which differs substantially from the experimental value
[8] and, as we will see below, is lower than the height $U$ of the minimum energy barrier
to the cubane decomposition. The reason for this difference is unclear, since earlier the inclusion of this correction allowed us to describe the experimental data on the fullerene $C_{60}$ fragmentation [7]. Unlike fullerenes $C_{20}$ and $C_{60}$, cubane consists of unlike atoms and the kinetic energy is nonuniformly distributed between the hydrogen and carbon subsystems in the thermally insulated cubane [14]. This is likely to increase the effective heat capacity of cubane during its decomposition, and the finite-size correction becomes insubstantial. However, this problem requires additional studies.

Let us find the height $U$ of the minimum energy barrier to cubane decomposition. Figure 5 presents calculated energies of various isomers of cubane, decomposition products, and saddle points on the potential energy hypersurface as functions of the atomic coordinates (the details of the calculation procedure can be found in [15, 24, 25]). It is seen that the quantity $U$ is determined by the barrier to the transformation of cubane into STCO isomer, which completely agrees with the molecular-dynamics simulation data. According to our calculations, $U = 1.59$ eV, which agrees with both the decomposition activation energy $E_a = (1.9 \pm 0.1)$ eV (which we found from analyzing the numerical simulation data) and the experimental value $E_a = (1.87 \pm 0.04)$ eV [8]. As we might expect, the quantity $U$ is somewhat smaller than $E_a$, since in experiments (including numerical one) cubane can decompose along paths with higher energy barriers. The fact that the barrier to the BCT $\rightarrow$ COT transition is lower in height than that to decomposition of BCT into benzene and acetylene molecules explains why COT is a much more frequent product of the cubane decomposition in numerical simulations.

We also calculated the quantity $U$ by the Hartree-Fock (HF) method without and with inclusion of the Moller-Plesset second-order correction (MP2) and by the density
functional method with the B3LYP exchange-correlation functional. All the calculations are performed in the 6-31G* basis set. We found that $U = 3.95, 3.09, \text{ and } 3.19 \text{ eV}$, respectively. These values are much higher than the experimental value of $E_a$ [8] (despite the fact that, as noted above, the inequality $U < E_a$ must take place). Thus, the results obtained in the tight-binding model agree much better with the experimental data than the first-principle calculations do. This circumstance is due to the fact that we selected the model parameters based on the requirement of the best agreement between the theoretical and experimental characteristics of the various hydrocarbon molecules [12]. Note that one more decisive advantage of the tight-binding model is the fact that the cluster evolution over a comparatively long time (on an atomic scale) of $t \sim 1 \mu s$ can be simulated (whereas for the ab initio methods $t \sim 1 \text{ ps}$).

The results obtained in this work have allowed us to find the temperature dependence of the lifetime of the metastable cubane $C_8H_8$, which may be useful in analyzing possible applications of cubane $C_8H_8$ and solid cubane s-$C_8H_8$ as fuel elements. It is also interesting to develop new methods for synthesizing cubane based on its known decomposition products.

References

[1] P. E. Eaton and T. W. Cole, Jr., J. Am. Chem. Soc. 86, 962 (1964).

[2] M. A. White, R. E. Wasylishen, P. E. Eaton, Y. Xiong, K. Pramod, and N. Nodari, J. Phys. Chem. 96, 421 (1992).
[3] B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnel, J. L. Margrave, and J. L. Franklin, J. Am. Chem. Soc. 88, 626 (1966).

[4] P. E. Eaton, J. Li, and S. P. Upadhyaya, J. Org. Chem. 60, 966 (1995).

[5] P. E. Eaton, Angew. Chem., Int. Ed. Engl. 31, 1421 (1992).

[6] A. I. Podlivaev and L. A. Openov, Pisma Zh. Eksp. Teor. Fiz. 81, 656 (2005) [JETP Lett. 81, 533 (2005)].

[7] L. A. Openov and A. I. Podlivaev, Pisma Zh. Eksp. Teor. Fiz. 84, 73 (2006) [JETP Lett. 84, 68 (2006)].

[8] H.-D. Martin, T. Urbanek, P. Pfohler, and R. Walsh, J. Chem. Soc., Chem. Commun., No. 14, 964 (1985).

[9] Z. Li, and S. L. Anderson, J. Phys. Chem. A 107, 1162 (2003).

[10] C. Kililc, T. Yildirim, H. Mehrez, and S. Ciraci, J. Phys. Chem. A 104, 2724 (2000).

[11] J. Zhao and J. P. Lu, Phys. Lett. A 319, 523 (2003).

[12] A. I. Podlivaev, M. M. Maslov, and L. A. Openov, Inzh. Fiz., No. 5, 42 (2007).

[13] http://srdata.nist.gov/ccccdb.

[14] L. A. Openov and A. I. Podlivaev, Fiz. Tverd. Tela (St. Petersburg) 50 1146 (2008) [Phys. Solid State 50, 1195 (2008)].

[15] I. V. Davydov, A. I. Podlivaev, and L. A. Openov, Fiz. Tverd. Tela (St. Petersburg) 47, 751 (2005) [Phys. Solid State 47, 778 (2005)].
[16] L. A. Openov and A. I. Podlivaev, Pisma Zh. Eksp. Teor. Fiz. 84, 217 (2006) [JETP Lett. 84, 190 (2006)].

[17] L. A. Openov, I. V. Davydov, and A. I. Podlivaev, Pisma Zh. Eksp. Teor. Fiz. 85, 418 (2007) [JETP Lett. 85, 339 (2007)].

[18] I. V. Davydov, A. I. Podlivaev, and L. A. Openov, Pisma Zh. Eksp. Teor. Fiz. 87, 447 (2008) [Phys. Solid State 87, 385 (2008)].

[19] C. Xu and G. E. Scuseria, Phys. Rev. Lett. 72, 669 (1994).

[20] J. Jellinek and A. Goldberg, J. Chem. Phys. 113, 2570 (2000).

[21] K. P. Katin, A. I. Podlivaev, and L. A. Openov, Inzh. Fiz., No. 3, 55 (2007).

[22] C. E. Klots, Z. Phys. D: At., Mol. Clusters 20, 105 (1991).

[23] J. V. Andersen, E. Bonderup, and K. Hansen, J. Chem. Phys. 114, 6518 (2001).

[24] A. I. Podlivaev and L. A. Openov, Fiz. Tverd. Tela (St. Petersburg) 48, 2104 (2006) [Phys. Solid State 48, 2226 (2006)].

[25] A. I. Podlivaev and L. A. Openov, Fiz. Tverd. Tela (St. Petersburg) 50, 954 (2008) [Phys. Solid State 50, 996 (2008)].
Fig. 1. Cubane $\text{C}_8\text{H}_8$ (schematic).
Fig. 2. Cubane decomposition products: (a) isomer cyclooctatetraene (COT) and (b) $C_6H_6$ (benzene) and $C_2H_2$ (acetylene) molecules.
Fig. 3. Isomers of C₈H₈ that form at the cubane evolution stage preceding its decomposition: (a) isomer STCO (syn-tricyclooctadiene) and (b) BCT (bicyclooctatriene).
Fig. 4. Logarithm of the lifetime $\tau$ of cubane $\text{C}_8\text{H}_8$ plotted as a function of the reciprocal initial temperature $T^{-1}$: circles are the results of calculations, the solid line is a least-squares linear fit, and triangles are the experimental data from [9]. The arrows indicate the results obtained in [9] at temperatures $T \leq 474$ K and $T \geq 773$ K for which, because of technical problems, only the lower ($\tau > 40$ ms) and upper ($\tau < 0.8$ ms) limitations on $\tau$, respectively, were determined.
Fig. 5. Energies calculated by the tight-binding method for various isomers of cubane C₈H₈, its decomposition products, and saddle points Sᵢ of the potential energy as a function of the atomic coordinates. The cubane energy is taken as a reference point. The lines schematically show the paths of possible transitions. The experimental value of the cubane decomposition activation energy [8] and the values of the minimum barrier to the transformation of cubane into STCO calculated from first principles are also indicated (designations of isomers and ab initio methods are given in text).