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Density functional investigation on the cycloreversion of cyclobutane radical cation: new reaction mechanism

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Abstract

The cycloreversion of cyclobutane radical cation (**1** $c\text{-C}_4\text{H}_8^+$) has been investigated in detail at the UB3LYP/6-31++G(d,p) level of theory. The ‘rotating’ mechanism of cycloreversion via the ‘tightly bound’ intermediate of tetramethylene radical cation (**2** $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$) has been revealed for the first time. It is shown that both the present ‘rotating’ mechanism and the previous ‘shifting’ one via the ‘loosely bound’ complex (**3** $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{H}_4^+$) may compete intensively with each other for this reaction, leading to the low-lying isomers (**4** $c\text{-CH}_2\text{CH}_2\text{CH-CH}_3^+$ and **5** $\text{CH}_3\text{CH}_2\text{CHCH}_2^+$) in low temperature but to the dissociation products **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ in high temperature above 600 K. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Electron transfer catalysis is an efficient method for the catalysis of symmetry-forbidden or slow pericyclic reactions [1]. The cycloaddition of ethylenes to form cyclobutanes was the first class of pericyclic reaction recognized as catalyzed by electron transfer [2,3], opening new synthetic pathways in organic chemistry. On the other hand, the electron-transfer-catalyzed [2 + 2] cyclorever-

sion of cyclobutanes has important biological implications in splitting the cyclobutane-type pyrimidine dimers in UV damaged DNA [4–6], and may have potential applications for photochemical energy storage [7].

The radical cation [2 + 2] cycloreversions of a number of model systems [8,9] and parent cyclobutane radical cation ($c\text{-C}_4\text{H}_8^+$) [10,11] have been studied experimentally and been postulated to proceed through an intermediate of tetramethylene radical cation [12,13]. The [2 + 2] cycloreversions of several substituted cyclobutane radical cations such as the quadricyclane [14,15] and the pagodane [16,17] radical cations have also attracted considerable theoretical interest. Some early computational investigations [18–20] have been performed

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on the parent $C_4H_8^+$ hypersurface with main attentions on the structures of $c\text{-}C_4H_8^+$ and product complex $C_2H_4 \cdot C_2H_4^+$, without conclusive evidence for or against on the tetramethylene radical cation ($CH_2CH_2CH_2CH_2^+$) intermediate. More recently, the [2 + 2] cycloreversion of $c\text{-}C_4H_8^+$ by shifting two ethylene fragments relative to each other has been revealed by two correlated ab initio calculations [21,22], not involving the postulated tetramethylene radical cation intermediate. However, no such ‘shifting’ mechanism has been found in theoretical studies on some substituted cyclobutane radical cations of quadricyclane [14,15], pagodane [16,17] and uracil dimer [23].

In this Letter, the cycloreversion of the simplest parent system of cyclobutane radical cation ($c\text{-}C_4H_8^+$) has been investigated in detail at the UB3LYP/6-31++G(d,p) level of theory. To our surprise, a new ‘rotating’ mechanism involving the proposed ‘tightly bound’ tetramethylene radical cation ($CH_2CH_2CH_2CH_2^+$) intermediate is found in addition to the previous ‘shifting’ one for the $c\text{-}C_4H_8^+$ system.

2. Computational methods

The GAUSSIAN’98 program package is used to perform all calculations [24]. The relevant structures are fully optimized at the unrestricted density functional UB3LYP/6-31++G(d,p) level (labeled as B3LYP) [25], followed by harmonic frequency calculations to verify whether they are minima with all real frequencies or transition states with only one imaginary frequency. Intrinsic reaction coordinate (IRC) [26] calculations are further carried out to confirm that the transition states connect the right minima. The atomic charges and spin densities are also calculated according to the Mulliken population analysis. This computationally efficient, gradient-corrected and hybrid density functional method has been shown to yield accurate molecule structures and energetics for a large number of open-shell organic systems including radical cations [22,27,28] comparable with some QCISD(T) results [22], without encountering the problems associated with spin contamination that are notorious for UHF and UMP2 calculations

[29]. Indeed, the degree of spin contamination in our B3LYP calculations is very small, as reflected by the $\langle S^2 \rangle$ values within the range 0.75–0.77 (compared with the expected value of 0.75) of all radical cations. Unless otherwise specified, the B3LYP geometries and relative energies (in kcal/mol) including zero-point energies are used in the following discussions.

3. Results and discussions

The B3LYP geometries of five $C_4H_8^+$ isomers **1** $c\text{-}C_4H_8^+$ (C_{2h}), **2** $CH_2CH_2CH_2CH_2^+$ (C_2), **3** $C_2H_4 \cdot C_2H_4^+$ (C_2), **4** $c\text{-}CH_2CH_2CH\text{-}CH_3^+$ (C_1), **5** $CH_3CH_2CHCH_2^+$ (C_1), and the dissociation product **6** C_2H_4 (D_{2h}) + $C_2H_4^+$ (D_2) are depicted in Fig. 1 and those of four transition states **TS1/2** (C_2), **TS1/3** (C_s), **TS2/4** (C_1) and **TS3/5** (C_1) in

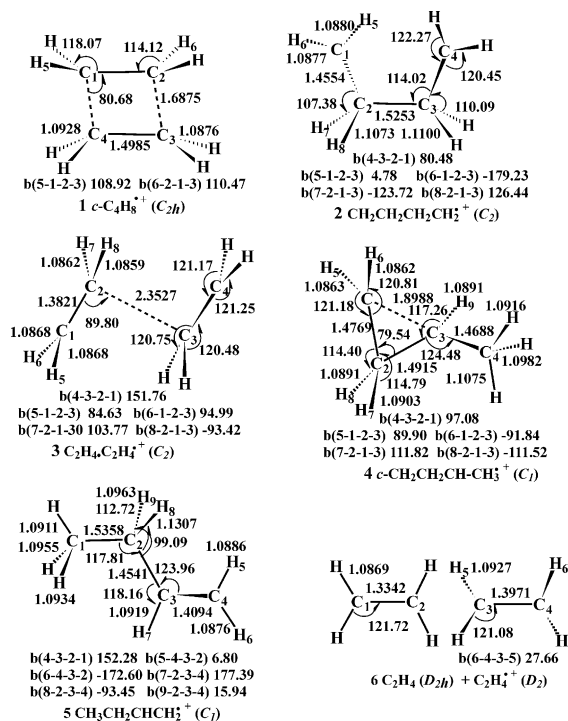


Fig. 1. The geometries of five $C_4H_8^+$ isomers and the dissociation product **6** $C_2H_4 + C_2H_4^+$ calculated at the UB3LYP/6-31++G(d,p) level. Bond lengths are in angstroms and bond angles in degrees.

Fig. 2. Note that **TS1/2** (C_2) is referred to as the C_2 -symmetrized transition state connecting isomers **1** and **2** as revealed by IRC calculations, and so on. The zero-point, total and relative energies (0 K) as well as the standard (298.15 K, 1 atm) entropies (S°) and enthalpies (H°) of all relevant structures are listed in Table 1. By means of the B3LYP relative energies, the schematic potential energy surface (PES) for this cycloreversion reaction is depicted in Fig. 3. For simplicity, the calculated harmonic frequencies are omitted here.

3.1. Relevant structures on the $C_4H_8^+$ PES

In order to verify the reliability of our B3LYP calculations for the $C_4H_8^+$ open-shell system, a comparison with some available theoretical and experimental data is made. Our B3LYP geometries for the cyclic isomer **1** c - $C_4H_8^+$ (C_{2h}) and the ‘loosely bound’ complex **3** $C_2H_4 \cdot C_2H_4^+$ (C_2) in Fig. 1, and the transition state **TS1/3** (C_s) in Fig. 2 related to ‘shifting’ cycloreversion of isomer **1** are very close to the previous QCISD/6-31G(d) values [21,22] generally within 0.05 Å for bond lengths and 2° for bond angles, except for the flexible long C · C distance (B3LYP: 2.353 Å and QCISD: 2.033 Å)

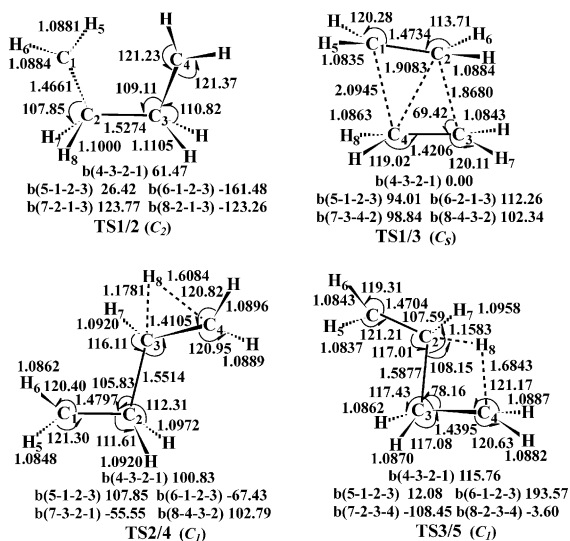


Fig. 2. The geometries of four transition states on the $C_4H_8^+$ potential energy surface calculated at the UB3LYP/6-31++G(d,p) level. Bond lengths are in angstroms and bond angles in degrees.

between two ethylene fragments of complex **3**. Also, our B3LYP geometries for dissociation product **6** C_2H_4 (D_{2h}) + $C_2H_4^+$ (D_2) are in good agreement with the experimental data [30,31], though some large discrepancies (larger than 0.1 Å for bond lengths and 14° for bond angles) between our B3LYP and previous UMP2/6-31G(d) geometries [21] are found for isomer **5** $CH_3CH_2CHCH_2^+$ (C_1) and transition state **TS3/5** (C_1). Moreover, the problems associated with spin contamination in previous UHF and UMP2 calculations have been avoided in our B3LYP calculations for the $C_4H_8^+$ open-shell system. Thus very reliable geometries may be provided by the present B3LYP calculations.

Two new isomers of **2** $CH_2CH_2CH_2CH_2^+$ (C_2) and **4** c - $CH_2CH_2CH-CH_3^+$ (C_1) and two transition states of **TS1/2** (C_2) and **TS2/4** (C_1) are found in our B3LYP calculations for the first time. As shown in Fig. 1, the acyclic isomer **2** possesses a normal C–C single bond of 1.5253 Å between two ethylene fragments, with the dihedral angle of the skeleton of two pyramidal inner carbons and two planar outer carbons to be 80.48° . It is interesting that the ‘tightly bound’ structure **2** is the best candidate for the long postulated [12,13] tetramethylene radical cation intermediate, though there is still no conclusive evidence for or against the involvement of this intermediate in the cycloreversion of substituted cyclobutane radical cations. However, the calculated (**2** → **6**) dissociation energy of 18.4 kcal/mol for the ‘tightly bound’ isomer **2** is even 9.6 kcal/mol smaller than the (**3** → **6**) dissociation energy for the ‘loosely bound’ isomer **3** at the B3LYP level. No transition states are required for the (**2** → **6**) and (**3** → **6**) dissociations. The cyclic methylcyclopropane radical cation **4** possesses two normal C–C single bonds and one long (1.8988 Å) C · C single-electron bond within the propane three-membered-ring, as supported by the dominant spin densities on two carbons with and without methyl-substituent (0.45 and 0.61, respectively) within the long C · C bond. The order of thermodynamic stability of all $C_4H_8^+$ isomers may be listed as follows: **6** (+29.5) < **2** (+11.1) < **3** (+1.5) < **1** (0.0) < **4** (–13.1) < **5** (–14.9).

As shown in Fig. 2, the geometries of transition state **TS1/2** (C_2) are very similar to those of isomer

Table 1

The zero-point vibrational (ZPE), total (TE, without ZPE) and relative (RE, including ZPE) energies as well as the standard (298.15 K, 1 atm) entropies (S°) and enthalpies (H°) of all relevant species calculated at the UB3LYP/6-31++G(d,p) level

Species	ZPVE (hartree)	TE (hartree)	RE (kcal/mol)	S° (kcal/mol)	H° (hartree)
1	0.106498	−156.821786	0.0	72.72	−156.762673
2	0.102747	−156.853877	+11.1	74.84	−156.744190
3	0.104695	−156.871138	+1.5	79.15	−156.758947
4	0.106091	−156.895805	−13.1	71.47	−156.783496
5	0.104867	−156.897561	−14.9	74.27	−156.785754
6	0.099854	−156.821786	+29.5	106.66	−156.713799
TS1/2	0.103501	−156.853138	+12.0	69.08	−156.743729
TS1/3	0.105384	−156.851284	+14.4	72.56	−156.739746
TS2/4	0.102347	−156.849977	+13.3	72.56	−156.741280
TS3/5	0.103864	−156.855600	+10.8	70.60	−156.745757

2 except for the smaller dihedral angle of 61.47° of carbon skeleton. This transition state is related to the ‘rotating’ cycloreversion of isomer **1** $c\text{-C}_4\text{H}_8^+$ around one C–C bond leading to the acyclic isomer **2**, as revealed by our IRC calculations. The (**1** → **2**) ‘rotating’ cycloreversion barrier is even 2.4 kcal/mol lower than the previous ‘shifting’ (**1** → **3**) one via transition state **TS1/3**. Transition state **TS2/4** (C_1) is shown to correspond to the 1,2-H-shift of isomer **2** leading to the low-lying isomer **4**. According to the schematic PES in Fig. 3, we can know that isomer **2** is rather unstable towards isomerization into **1** and **4** with the respective (**2** → **1**) and (**2** → **4**) barriers of only 0.9 and 2.2

kcal/mol. The low kinetic stability of isomer **2** should explain why it is difficult to be observed in experiments. On the other hand, isomers **1** and **3** show better kinetic stabilities of 12.0 and 9.3 kcal/mol towards isomerization, respectively.

3.2. Mechanism of cycloreversion

According to the PES in Fig. 3, we can obtain four possible pathways for the cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$ (with the relative energies in kcal/mol of all relevant species in parentheses) as follows:

Path 1: **1** (0.0) → **TS1/2** (+12.0) → **2** (+11.1) → **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ (+29.5)

Path 2: **1** (0.0) → **TS1/2** (+12.0) → **2** (+11.1) → **TS2/4** (+13.3) → **4** (−13.1)

Path 3: **1** (0.0) → **TS1/3** (+14.4) → **3** (+1.5) → **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ (+29.5)

Path 4: **1** (0.0) → **TS1/3** (+14.4) → **3** (+1.5) → **TS3/5** (+10.8) → **5** (−14.9)

We first consider **Path 1** and **Path 2** related to the ‘rotating’ cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$ with the same initial (**1** → **2**) barrier of 12.0 kcal/mol. From the common intermediate **2**, the direct cleavage of the C–C single bond between two ethylene fragments needs 18.4 kcal/mol to produce the final dissociation products **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ as shown in **Path 1**, while the 1,2-H-shift via **TS2/4** can lead to the low-lying isomer **4** over the (**2** → **4**) barrier of only 2.2 kcal/mol. Thus, **Path 2** should be both kinetically and thermodynamically more favorable than **Path 1**. It should be pointed out that such ‘rotating’ pathways have closely resembled the

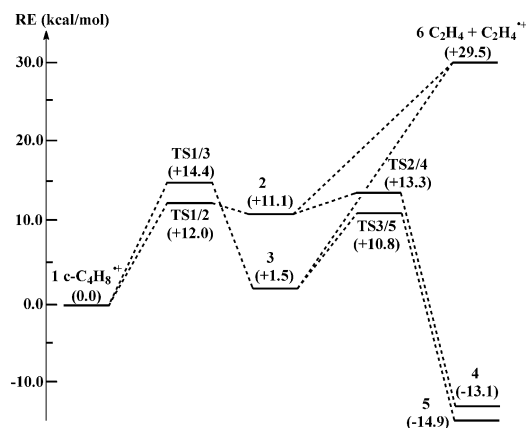


Fig. 3. The schematic potential energy surface for the cycloreversion of cyclobutane radical cation ($c\text{-C}_4\text{H}_8^+$) based on the UB3LYP/6-31++G(d,p) relative energies (in kcal/mol) including the zero-point energies.

stepwise biradical pathways for the cycloreversion of neutral cyclobutane [32,33]. We consider further **Path 3** and **Path 4** related to the ‘shifting’ cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$ with the same initial (**1** \rightarrow **3**) barrier of 14.4 kcal/mol. From the common intermediate **3**, the direct cleavage of the long C–C bond of **3** needs 28.0 kcal/mol to form the final dissociation products **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ as shown in **Path 3**, while the 1,3-H-shift via **TS3/5** can lead to the low-lying isomer **5** over the (**3** \rightarrow **5**) barrier of only 9.3 kcal/mol. Thus, **Path 4** should be both kinetically and thermodynamically more favorable than **Path 3**. Noticing that the overall potential barriers involved in **Path 2** and **Path 4** (13.3 and 14.4 kcal/mol, respectively) are very close, both the ‘rotating’ and the ‘shifting’ mechanisms may contribute to the cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$.

3.3. Effects of temperature on products

To reveal the effects of temperature on the final products, we have also listed the standard (298.15 K, 1 atm) entropies (S°) and enthalpies (H°) in Table 1. According to the conventional transition state theory, from the common intermediate **2**, the relative contributions of the (**2** \rightarrow **6**) conversion in **Path 1** and the (**24**) conversion in **Path 2** can be estimated from the rate constant formula as follows:

$$k(T) = (k_B T/h) \cdot \exp(\Delta S^\ddagger/R) \cdot \exp(-\Delta H^\ddagger/RT),$$

where k_B is the Boltzmann constant, h the Planck constant, R the gas constant, T the absolute temperature, ΔS^\ddagger the standard activation entropy, and ΔH^\ddagger the standard activation enthalpy. Noticing that the respective (**2** \rightarrow **6**) ΔS^\ddagger and ΔH^\ddagger values are 34.1 cal/mol K and 17.2 kcal/mol larger than those for (**2** \rightarrow **4**) conversion, the products may be kinetically dominated by the latter in low temperature but by the former in high temperature above 500 K. Similarly, noticing that the respective ΔS^\ddagger and ΔH^\ddagger values for the (**3** \rightarrow **6**) conversion in **Path 3** is 36.1 cal/mol K and 20.1 kcal/mol larger than those for the (**3** \rightarrow **5**) conversion in **Path 4**, the products may be kinetically dominated by the later in low temperature but by the former in high temperature above 560 K. As far as the

overall barriers are concerned, both **Path 2** and **Path 4** may compete intensely due to their very similar ΔS^\ddagger and ΔH^\ddagger values. In summary, the cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$ should lead mainly to the low-lying isomers **4** and **5** in low temperature but to the dissociation products **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ in high temperature above 600 K.

4. Conclusions

We have investigated in detailed the cycloreversion of cyclobutane radical cation (**1** $c\text{-C}_4\text{H}_8^+$) at the UB3LYP/6-31++G(d,p) level of theory. The ‘rotating’ mechanism of cycloreversion via the ‘tightly bound’ intermediate of tetramethylene radical cation (**2** $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2^+$) has been revealed for the first time, in addition to the previous ‘shifting’ one via the ‘loosely bound’ complex (**3** $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{H}_4^+$). Both the ‘rotating’ and the ‘shifting’ mechanism should be involved in the cycloreversion of **1** $c\text{-C}_4\text{H}_8^+$, which may lead mainly to the low-lying isomers **4** $c\text{-CH}_2\text{CH}_2\text{CH}-\text{CH}_3^+$ and **5** $\text{CH}_3\text{CH}_2\text{CHCH}_2^+$, respectively, in low temperature but to the dissociation product **6** $\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4^+$ in high temperature above 600 K.

Acknowledgements

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