Exploring the Multiple Reaction Pathways for the H + cyc-C_3H_6 Reaction

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Reaction pathways for the hydrogen atom plus cyclopropane (cyc-C_3H_6) reaction are studied using an extrapolated coupled-cluster/complete basis set (CBS) method based on the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets. For this activated reaction, results reveal two reaction mechanisms, a direct H-abstraction and a H-addition/ring-opening. The hydrogen-abstraction reaction yields the H_2 and cyclopropyl (cyc-C_3H_5) radical products. The vibrationally adiabatic ground-state (VAG) barrier height is predicted to be 13.03 kcal/mol. The isomerization barrier height from the product cyclopropyl to allyl radical is 21.98 kcal/mol via a cyc-C_3H_5 ring-opening process. In addition, the H-addition and ring-opening mechanism will lead to an *n*-C_3H_7 radical, which can result in a variety of products such as $CH_3 + C_2H_4$, H + CH_3CHCH_2, and $H_2 + C_3H_5$, etc. The VAG barrier height of the H-addition reaction is 16.49 kcal/mol, which is slightly higher than that of the direct H-abstraction reaction. Although the H + cyc-$C_3H_6 \rightarrow CH_4 + CH_2CH$ reaction is exoergic by 11.90 kcal/mol, this reaction is unlikely due to a high barrier of 43.05 kcal/mol along the minimum energy path.

I. Introduction

The chemical reactivity and formation of hydrocarbon radicals is of major importance in combustion chemistry and hydrocarbon-rich planetary atmospheres.[1,2] One such species is the allyl (CH_2CHCH_2) radical because the nascent allyl radical can thermally decompose into the propargyl (CH_2CCH) radical in a combustion process.[2] Propargyl plays a key role in the soot formation process and particularly the initial formation of benzene.[2] Due to these chain reactions there have been many studies on the properties and formation of allyl radicals.[3−8] Experimentists[9−13] often use the ring-opening reaction of the cyclopropyl (cyc-C_3H_5) radical to produce allyl radicals. In the early experimental studies[9,10] cyclopropyl was generated by a radical- or atom-induced decomposition of cyclopropane, i.e., X + cyc-$C_3H_6 \rightarrow$ HX + cyc-C_3H_5 for X = CH_3, Cl, and F, etc. Such a reaction was postulated to occur after the hydrogen-atom transfer process.[8−13] In particular, the ring-opening mechanism of the cyclopropyl radical has been studied in detail by Mann and Hase[14] using an ab initio direct dynamics method. They found that both conrotary and disrotary ring-opening processes could happen, although they are symmetry forbidden according to the Woodward−Hoffmann rules.[15] In addition, the ring opening of cyclopropyl to allyl has also been confirmed experimentally in the photoinitialized unimolecular reaction of cyclopropyl iodide and cyclopropyl cyanide.[12−13]

Recently, the H + cyc-$C_3H_6 \rightarrow H_2(v,j) + C_3H_5$ reaction at 1.6 eV collision energy has been elegantly studied by Valentini and co-workers[16] using a molecular beam method. The rovibrational states and translational energies of the product H_2 were measured in detail. Surprisingly, except for expected H_2 products, their results point out that a significant fraction (about 15%) of H_2 is extremely hot. The translational energy of these hot hydrogen molecules exceeds the total released energy if the reaction occurs via a direct hydrogen-abstraction process in which the coproduct is the cyclopropyl radical. Although these unexpected results could not be explained using the accepted reaction mechanism mentioned above, the mysterious findings definitely suggest another reaction pathway available for the H + cyc-$C_3H_6 \rightarrow H_2(v,j) + C_3H_5$ reaction.

To understand this unusual behavior, here we will use high-level ab initio theory to fully explore the possible reaction pathways for the H + cyc-C_3H_6 reaction. The computational method is briefly described in section II. Results and reaction pathways are discussed in section III, which is followed by Conclusions.

II. Computational Method

In this work, geometrical optimizations and harmonic normal-mode frequencies at the stationary points on the ground-state potential-energy surface for the H + cyc-C_3H_6 system are carried out using the coupled-cluster theory including single- and double-excitation terms[17−19] with the correlation-corrected double-ζ basis set of Dunning,[20] i.e., the UCCSD/cc-pVDZ method. The energies at the optimized geometries are further corrected for basis set and CI truncation errors. The CI truncation errors are estimated at the UCCSD(T)/cc-pVTZ level.[21,22] The basis set errors are obtained using the extrapolation approach of Halkier et al.[23−25] Here, the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets are employed in the extrapolation procedure at the UCCSD(T) and UMP2 theory levels. The final complete basis set (CBS) energies can be written as

$$E_{\mathrm{CBSI}} = E_{\mathrm{UCCSD(T)/cc-pVTZ}} + \frac{8}{19}(E_{\mathrm{UCCSD(T)/cc-pVTZ}} - E_{\mathrm{UCCSD(T)/cc-pVDZ}})$$

$$E_{\mathrm{CBSII}} = E_{\mathrm{UCCSD(T)/cc-pVTZ}} + \frac{64}{37}(E_{\mathrm{UMP2/cc-pVQZ}} - E_{\mathrm{UMP2/cc-pVTZ}})$$

where E_{CBSI} is the energy extrapolated using the UCCSD(T) method and the cc-pVDZ and cc-pVTZ basis sets. E_{CBSII} is the

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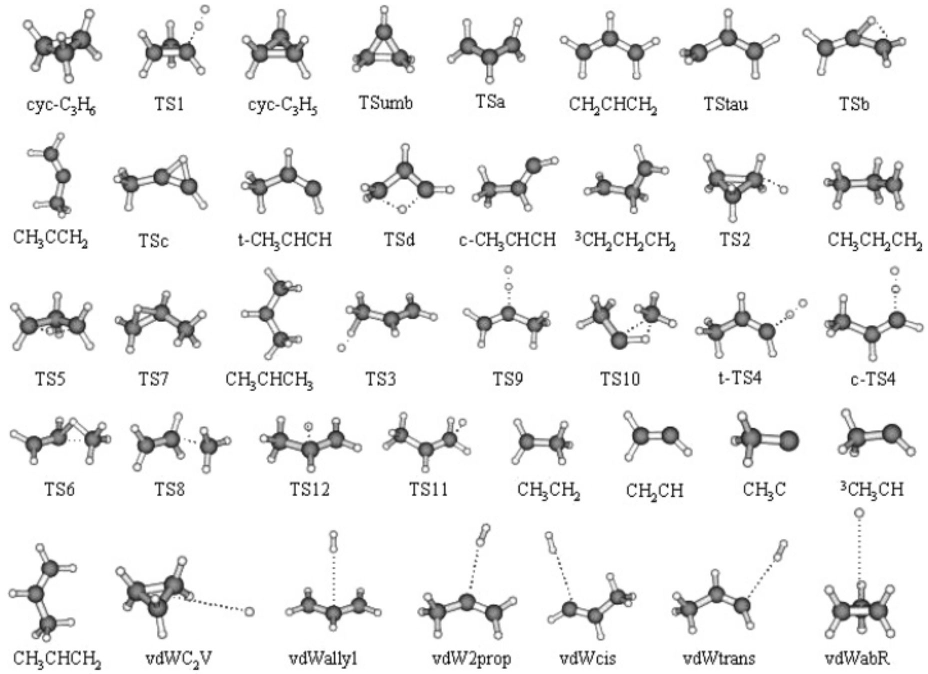

Figure 1. Structures of the stationary points on the ground-state potential energy surface for the H + cyc-C_3H_6 reaction, calculated with the UCCSD/cc-pVDZ theory.

energy extrapolated using the cc-pVTZ and cc-pVQZ basis sets at the UMP2 level. Theoretically, this extrapolation scheme should be applied only to the correlation energy of the system. The HF energy needs be extrapolated separately. In practice, the effect on energy differences between dealing with the HF energy separately and treating the total energy is small. As shown in previous studies,[25,26] the results show that this scheme can significantly improve the accuracy of the calculated energies and provide nearly chemically accurate values.[25] In this work, two extrapolation methods are used to verify the accuracy of our calculations.

In most of the present calculations the Berny algorithm[27] has been used in the geometry optimization, but some complicated transition states were searched employing a combination approach of synchronous transit-guided quasi-Newton algorithms and an *M*-point reaction path method of Ayala and Schlegel.[28] All electronic structure calculations were performed using the Gaussian 03 program.[29]

III. Results and Reaction Pathways

For the H + cyc-C_3H_6 system, optimized geometries of the stationary points except for a few of small well-known molecules are shown in Figure 1. Six van der Waals (vdW) complexes are also displayed. They are optimized with the UCCSD/cc-pVDZ method. The geometrical parameters are not given in these structures. Nevertheless, their Cartesian coordinates can be obtained upon request as well as in the Supporting Information.[30] The relative energies and zero-point energies of the reactants and products are given in Table 1 together with a comparison with the experimental reaction enthalpies (298 K) available. The theoretical enthalpies (298 K) are calculated by adding the zero-point energies and the thermal energy corrections into the CBSII electronic energies. The zero-point and thermal energies were evaluated using the UCCSD/cc-pVDZ theory. Table 1 clearly shows that the agreement between theoretical and experimental results is quite good. Compared to the UCCSD/cc-pVDZ values, the CBS methods have substantially improved the accuracy. Importantly, the maximum difference between the two CBS methods is less than 1.0 kcal/mol. This result reveals that our extrapolation schemes used are accurate for studying this system. In the following subsections we will discuss the results in detail based on the CBSII energies.

Hydrogen-Abstraction Mechanism. The H + cyc-$C_3H_6 \rightarrow H_2$ + cyc-C_3H_5 reaction is a typical activation reaction. The transition state (**TS1**) has a nearly collinear H−H−C bond with a bond angle of 176.0°, where the H−H and H−C bond lengths are 0.8832 and 1.4385 Å, respectively. They are longer by 0.122 and 0.343 Å than those in the single molecules H_2 and cyc-C_3H_6, respectively. Therefore, this transition state lies near the exit channel. The barrier height is predicted to be 14.84 kcal/mol. If the zero-point energy (ZPE) corrections are included, the vibrationally adiabatic ground-state (VAG) barrier height is 13.03 kcal/mol. The reaction is endothermic with an endothermicity of 4.03 kcal/mol (ZPE corrections included). At room temperature the reaction enthalpy obtained is 4.81 kcal/mol, which is higher than the experimental value[31−35] of 2.06 kcal/mol. Actually, this reaction is very similar to the benchmark H + $CH_4 \rightarrow H_2 + CH_3$ reaction in the aspects of energetics and transition-state structure.[36] For the H + CH_4 reaction, the best estimated VAG and enthalpy are 14.2 and 0.6 kcal/mol, respectively.

As shown in Figure 2 the cyc-C_3H_5 product can easily become its mirror-image conformer through an umbrella motion via the **TSumb** transition state. The inversion VAG barrier height is only 1.39 kcal/mol. On the other hand, if the collision energy of the reaction is high enough, the produced cyclopropyl radical would have a ring-opening reaction to form one of its isomers, the allyl (CH_2CHCH_2) radical. The isomerization VAG barrier height (the **TSa** transition state) of 21.98 kcal/mol agrees with the experimental value[37,38] of 22 ± 2 kcal/mol as well as recent ab initio results of 22.48 kcal/mol (CCSD(T)/6-311G(2d))[8] and 22.2 kcal/mol (CASSCF(3,3)/6-31G(d)).[14] This isomerization reaction will release an energy of 29.87 kcal/mol, which is smaller than the CCSD(T)/6-311G(2d) value[8] of 31.31 kcal/mol but larger than the experimental one[31−35] (298 K) of 26.0

TABLE 1: Calculated Energetics and Zero-Point Energies (ZPE) for the H + cyc-C_3H_6 Reaction

species	E_{UCCSD}	E_{CBSI}	E_{CBSII}	ZPE	$E_{CBSII} + \Delta ZPE$	$\Delta H°$ (theor.)	$\Delta H°$ (expt.)[4,31−35]
H + cyc-C_3H_6	0.0	0.0	0.0	51.38	0.00	0.00	0.0
H + $^3CH_2CH_2CH_2$	58.95	64.77	65.15	46.28	60.05	61.28	
H + CH_3CHCH_2	−8.02	−7.28	−7.82	50.19	−9.00	−8.53	−7.86
H_2 + cyc-C_3H_5	7.57	6.61	6.78	48.63	4.03	4.81	2.06
H_2 + CH_2CHCH_2	−21.12	−22.44	−22.21	47.75	−25.84	−24.79	−23.94
H_2 + CH_3CCH_2	−1.56	−1.76	−1.66	47.75	−5.29	−3.97	−4.54
H_2 + c-CH_3CHCH	1.71	1.74	1.90	47.82	−1.66	−0.44	
H_2 + t-CH_3CHCH	2.01	2.10	2.26	47.95	−1.16	0.06	
H_2 + TSumb	10.47	9.10	9.21	47.59	5.42	6.10	
H_2 + TStau	−5.80	−6.63	−6.67	46.91	−11.14	−10.13	
H_2 + TSa	34.22	30.19	30.86	46.52	26.01	26.90	
H_2 + TSb	49.46	44.90	44.57	44.52	37.71	38.88	
H_2 + TSc	53.77	49.54	49.32	43.58	41.52	43.17	
H_2 + TSd	47.87	44.90	45.08	44.48	38.18	39.07	
$^3CH_2$+ CH_3CH_2	50.34	57.67	57.03	48.42	54.07	55.48	55.91
CH_3 + C_2H_4	−18.70	−18.79	−18.38	50.68	−19.08	−18.04	−17.48
CH_3 + $^3CH_3CH$	47.94	54.84	53.87	48.59	51.08	52.45	
CH_4 + CH_2CH	−13.04	−12.62	−11.88	51.36	−11.90	−11.01	−12.48 ± 2.1
CH_4 + CH_3C	32.56	36.49	37.09	50.69	36.40	37.32	
$CH_3CH_2CH_2$	−45.51	−44.77	−44.64	55.86	−40.15	−40.50	−41.94
CH_3CHCH_3	−48.48	−47.78	−47.78	55.72	−43.44	−43.70	−42.84
TS1	16.75	14.86	14.84	49.57	13.03	12.31	
TS2	19.45	15.33	15.46	52.41	16.49	15.49	
TS3	3.40	1.75	1.54	48.64	−1.20	−1.66	
t-TS4	10.96	9.53	9.49	48.60	6.72	6.52	
c-TS4	10.97	9.43	9.37	48.61	6.60	6.41	
TS5	−0.29	−2.23	−2.13	52.97	−0.54	−1.34	
TS6	48.24	43.05	42.88	51.63	43.14	42.69	
TS7	−1.45	−4.59	−4.70	53.25	−2.82	−3.44	
TS8	−10.06	−12.47	−11.59	53.12	−9.84	−10.04	
TS9	8.32	6.81	6.70	50.00	5.32	5.02	
TS10	47.99	45.83	45.72	52.37	46.72	46.40	
TS11	−4.62	−6.01	−6.08	51.03	−6.42	−6.77	
TS12	−3.10	−4.62	−4.65	51.29	−4.74	−5.24	
vdWC_2V	−0.04	−0.15	−0.16	51.48	−0.06	0.29	
vdWabR	−0.04	−0.16	−0.18	51.50	−0.06	0.27	
vdWallyl	−21.54	−22.93	−22.67	48.50	−25.55	−24.27	
vdW2prop	−2.02	−2.24	−2.12	48.59	−4.92	−3.43	
vdWcis	1.31	1.36	1.53	48.55	−1.30	0.17	
vdWtrans	1.59	1.65	1.81	48.71	−0.86	0.59	

[a] The UCCSD/cc-pVDZ, and two CBS results are relative to the values of −118.029516 (UCCSD),−118.222188 (CBSI), and −188.236414 au (CBSII) of the reactants, respectively. Experimental reaction enthalpies ($\Delta H°$, 298K) are also included for comparison. All energies are in kcal/mol.

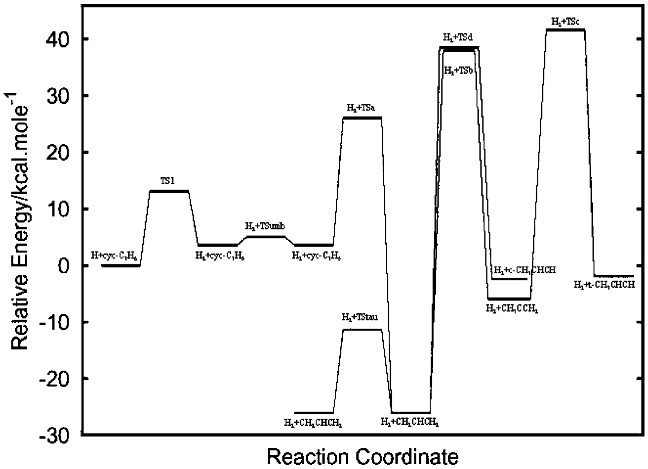

Figure 2. Relative CBSII energy (including the zero-point energy corrections) diagram for the hydrogen abstraction reaction mechanism of the H + cyc-C_3H_6 reaction.

kcal/mol. However, for the overall reaction H + cyc-C_3H_6 → H_2 + CH_2CHCH_2 the theoretical enthalpy of −24.79 kcal/mol is in good agreement with the measured result of −23.94 kcal/mol. This may imply that the major source of the errors rises from the heat of formation of the cyclopropyl radical. As addressed by Arnold and Carpenter,[8] it is not clear whether the discrepancy results from the calculations, the experiment, or both.

The allyl radical can interconvert from one conformer to another by rotating one terminal CH_2 group around its joining C−C bond. The torsion VAG barrier height (the **TStau** transition state) is obtained as 14.70 kcal/mol. Furthermore, three other isomers, 2-propenyl (CH_3CCH_2) and *trans*- and *cis*-propenyl (c/t-CH_3CHCH) radicals, can be produced via either a 1,2-H-shift or a 1,3-H-shift reaction of allyl. These isomers are less stable by 20.55 (2-propenyl), 24.68 (*trans*-propenyl), and 24.18 kcal/mol (*cis*-propenyl) than allyl. The calculations are consistent with the G3//B3LYP results[7]of 19.5, 23.7, and 23.2 kcal/mol, respectively. Although the H + cyc-C_3H_6 → H_2 + C_3H_5 (except for the cyclopropyl isomer) reactions are exoergetic, they are unlikely to yield 2-propenyl and propenyl radicals due to the high barriers (**TSb**, **TSc,** and **TSd**) as shown in Figure 2. The VAG barrier heights with respect to allyl are obtained as 63.55 (**TSb**), 67.36 (**TSc**), and 64.02 kcal/mol (**TSd**). Again, these values are comparable to the G3//B3LPY results[7] of 64.1, 68.0, and 64.3 kcal/mol, respectively.

In short, Figure 2 essentially shows the H-abstraction mechanism of the H + cyc-C_3H_6 reaction. At low collision energies, less than 38 kcal/mol (or 1.65 eV), only cyclopropyl and allyl radicals are energetically accessible. Furthermore, if the collision

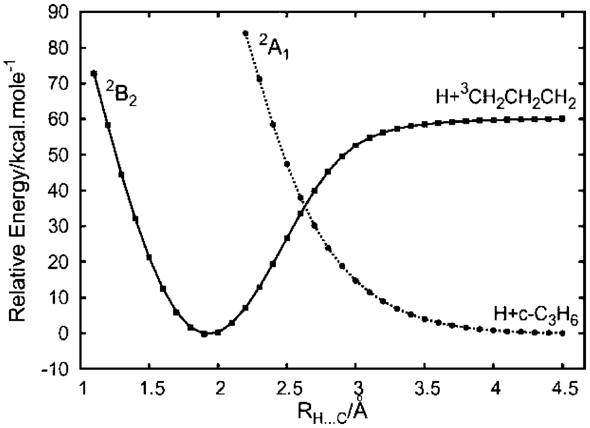

Figure 3. Minimum energy curves for the $^2A_1$ (dot points) and $^2B_2$ (square points) electronic states in C_{2v} symmetry, calculated with the UCCSD/cc-pVDZ theory. R_{CH} refers to the distance of the impact hydrogen atom to the far middle carbon atom of cyc-C_3H_6 or $^3CH_2CH_2CH_2$. All other coordinates are optimized.

energy is smaller than about 26 kcal/mol, the nascent cyc-C_3H_5 product would not have enough energy to form the more stable allyl radical via a ring-opening unimolecular reaction.

Hydrogen-Addition and Ring-Opening Mechanism. While the H-abstraction process is clear for the H + cyc-C_3H_6 reaction, it is not sufficient to understand the recent molecular beam results of Valentini and co-workers[16] at a collision energy of 1.6 eV as mentioned in the Introduction. This is because the H-abstraction reaction is endothermic, so that the maximum translational energy disposed in H_2 should be less than the collision energy. On the contrary, Valentini et al. observed that the translational energy of H_2 could be larger than this threshold value. Their results motivated us to search for another reaction pathway, the H-addition and ring-opening process.

Before discussing this new mechanism, let us consider a conical intersection problem of two doublet electronic states first. This conical intersection occurs for the attack of H on C_3H_6 in C_{2v} symmetry, where the incident hydrogen and three carbon atoms are coplanar, say in the *xz* plane. In such a case, the two lowest doublet states are $^2A_1$ and $^2B_2$. Their electronic configurations are

$$(\text{core})a_1^{\,2}b_2^{\,2}a_1^{\,2}b_1^{\,2}a_1^{\,2}a_2^{\,2}b_2^{\,2}b_1^{\,2}b_2^{\,2}a_1 \text{ for } {}^2\text{A}_1$$

$$(\text{core})a_1^{\,2}b_2^{\,2}a_1^{\,2}b_1^{\,2}a_1^{\,2}a_2^{\,2}b_2^{\,2}b_1^{\,2}a_1^{\,2}b_2 \text{ for } {}^2\text{B}_2$$

At the dissociation limit, the $^2A_1$ state correlates to the H + cyc-C_3H_6 reactants while $^2B_2$ links to the H + $^3CH_2CH_2CH_2$ products. Here, $^3CH_2CH_2CH_2$ is a triplet state whose structure is shown in Figure 1. Since these two electronic states have different symmetry, their potential-energy surfaces can cross as displayed in Figure 3. The energy at the crossing point is about 36 kcal/mol relative to the H + cyc-C_3H_6 asymptote. The $^2A_1$ surface is repulsive, but the $^2B_2$ one is attractive. The minimum on the $^2B_2$ state really is a transition state (**TS5**) in full dimensionality, which corresponds to the 1,3-H-shift of propyl ($CH_3CH_2CH_2$) radical.

When the impacting hydrogen atom moves out of the plane of the three carbon atoms, but in C_S symmetry, the $^2A_1$ state will become $^2A'$ whereas $^2B_2$ will be $^2A''$. Therefore, the two electronic surfaces are also allowed to cross under such a motion of H. However, on the other hand, if the incident H moves in the *xz* plane and in C_S symmetry, both $^2A_1$ and $^2B_2$ states will reduce to a $^2A'$ state. As the two electronic states have the same symmetry in this C_S geometry, their accidental degeneracy will split into two nondegenerate ones in terms of the avoided crossing rule. This is also true for the system in C_1 symmetry. As a result, the lowest doublets actually form two cone states.

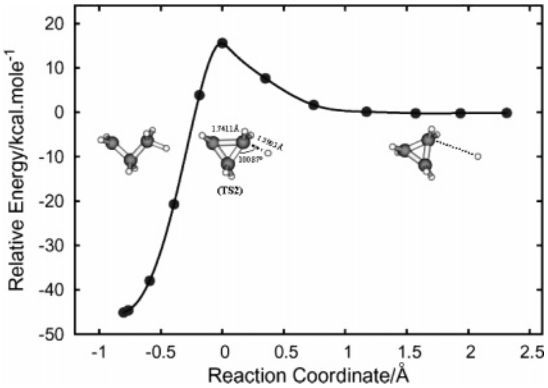

Figure 4. Minimum energy path at the CBSII level for the H + cyc-C_3H_6 → $CH_3CH_2CH_2$ reaction. The geometries of the transition state (TS2) and two points near either reactants or product are inserted.

Furthermore, the above analysis also implies that there exists a transition state in C_S symmetry with the attacking H and three C atoms being in the *xz* plane. The pathway of H approaching out of the plane of the C_3 ring gives a repulsive surface. In this work, we observed this trend and optimized a transition state (**TS2**) as expected. A minimum energy path is given in Figure 4, which clearly illustrates a H-addition and ring-opening reaction, i.e., H + cyc-C_3H_6 → $CH_3CH_2CH_2$. The classical barrier height of **TS2** is predicted to be 15.46 kcal/mol or a VAG barrier height of 16.49 kcal/mol. This barrier height is larger by only 3.46 kcal/mol than that of the H-abstraction transition state (**TS1**) but much smaller than the crossing point energy of 36 kcal/mol as shown in Figure 3. The **TS2** transition state is located in the entrance channel. The distance from the impacting H to the nearest C atom of **TS2** is 1.5903 Å with a HCC angle of 100.87°. The C_3 triangle has significantly distorted. Three C−C distances are 1.4832, 1.5132, and 1.7411 Å. The longest value corresponds to the breaking bond, which is the one opposite the vertex (see the inserted structures in Figure 4). In other words, it is difficult for the incident hydrogen to cleave the perpendicular C−C bond despite this C−C bond being directly attacked by the hydrogen atom.

Figure 5 shows a comparison of the molecular orbitals of the **TS2** transition state with those of the cyc-C_3H_6 reactant. For cyc-C_3H_6, two HOMOs are doubly degenerate. It was noticed that the LUMO and HOMO-1 of **TS2** resemble the LUMO and first HOMO′ of cyclopropane, respectively. On the other hand, the HOMO of **TS2** results from the interaction of the *s*-orbital of hydrogen with the second HOMO of cyc-C_3H_6. As one can see, there is a large electronic density along the forming and breaking bonds. This is consistent with the transition-state structure of **TS2**.

Figure 6 depicts the energy diagram for the hydrogen-addition and ring-opening processes together with the H + $^3CH_2CH_2CH_2$ limit for reference. The propyl radical lies at 40.15 kcal/mol (ZPE corrected) below the H + cyc-C_3H_6 reactants. A more stable isopropyl (CH_3CHCH_3) radical can be formed via a 1,2-H-shift reaction of propyl radical. The isomerization VAG barrier height (**TS7**) is 37.33 kcal/mol. In addition, two conformers of propyl radical can exchange through either a 1,3-H-shift or a 1,2-CH_3-shift reaction. The corresponding VAG barrier heights are 39.61 (**TS5**) and 61.28 kcal/mol (not shown). Once the propyl or isopropyl radical intermediate has been produced, it will decompose into a variety of products such as

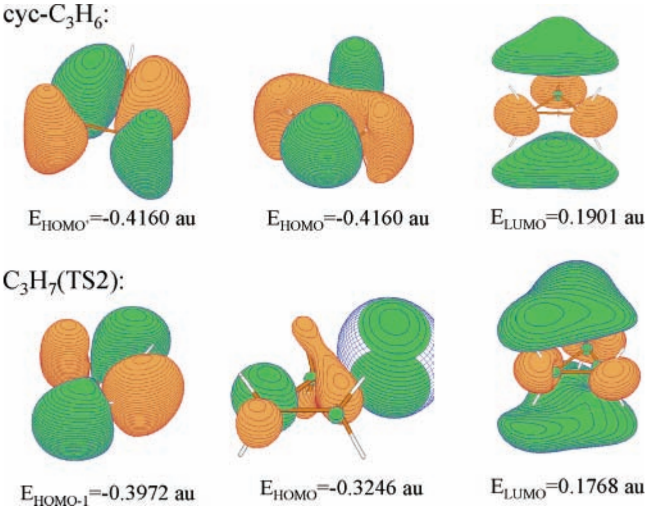

Figure 5. Comparison of the LUMO and HOMOs of the transition state (**TS2**, lower row) with those of cyclopropane (upper row), calculated at the UCCSD/cc-pVDZ level. Also labeled are the orbital energies.

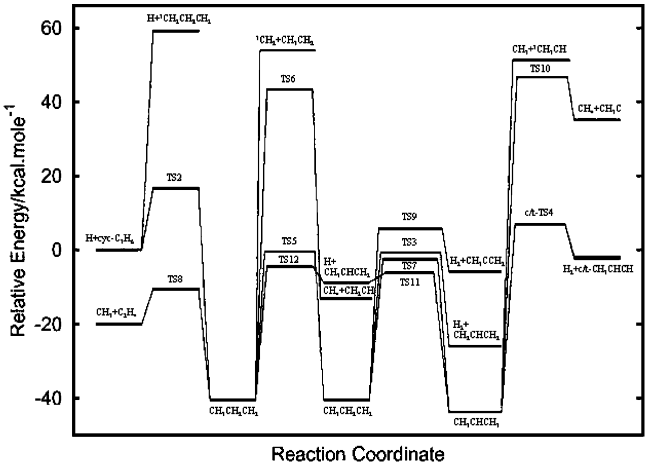

Figure 6. Relative CBSII energy (including the zero-point energy corrections) diagram for the hydrogen-addition and ring-opening mechanism of the H + cyc-C_3H_6 reaction.

$CH_3 + C_2H_4$, H +CH_3CHCH_2, and $H_2 + C_3H_5$, etc. From an energetic point of view, the $^3CH_2 + CH_3CH_2$, $CH_3 + {}^3CH_3CH$, $CH_4 + CH_3C$, and $CH_4 + CH_2CH$ product channels are unlikely. Although the H + cyc-C_3H_6 → $CH_4 + CH_2CH$ reaction is exoergic by 11.90 kcal/mol, this reaction also hardly occurs owing to a high barrier (**TS6**) of 43.14 kcal/mol.

The overall H + cyc-C_3H_6 → $CH_3 + C_2H_4$ reaction is exothermic by 19.08 kcal/mol. The obtained enthalpy (298 K) of −18.04 kcal/mol is in good agreement with the experimental value[31−35] of −17.48 kcal/mol. In the exit channel the VAG barrier height (with respect to propyl radical) is 30.31 kcal/mol (**TS8**). In addition, the H + cyc-C_3H_6 → H + CH_3CHCH_2 reaction is also preferable with an exothermicity of 9.00 kcal/mol. The theoretical enthalpy (298 K) is obtained as −8.53 kcal/mol, which is close to the experimental result[31−35] of −7.86 kcal/mol. The propene can be derived from either propyl or isopropyl radical by eliminating a hydrogen atom via the transition state **TS12** or **TS11**. Both transition states have an energy lower than the H + cyc-C_3H_6 reaction limit as similar to **TS8**.

For the H + cyc-C_3H_6 → $H_2 + C_3H_5$ reaction, where C_3H_5 refers to the allyl, 2-propenyl, and *trans*/*cis*-propenyl radicals, we calculate the exit VAG barrier height as −1.20 kcal/mol for allyl (**TS3**), 5.32 kcal/mol for 2-propenyl (**TS9**), and 6.60 or 6.72 kcal/mol for *trans*/*cis*-propenyl (**c/t-TS4**), respectively, with respect to the reactants. These barrier heights are lower than that of the **TS2** transition state. In other words, unlike the H-abstraction mechanism, 2-propenyl and propenyl radicals are possible products in these H-addition and ring-opening reaction pathways. In particular, since the H_2 product is formed after the ring opening of cyclopropane, the hydrogen molecule can pick up some ring-opening energy during the reaction. Due to the repulsive exit path (via **TS3**) and the momentum conservation requirement, the released potential energy of 24.64 kcal/mol can go almost entirely to the translational energy of H_2. As a result, the H_2 molecule has more translational energy than usually expected. This may explain the mysterious hot H_2 phenomenon observed by Valentini and co-workers.[16]

Therefore, the H-addition and ring-opening reaction pathway make several product channels open. These products are energetically competitive. Of course, the branching ratios of products should also rely on dynamical effects.

van der Waals Complexes. Six van der Waals (vdW) complexes are calculated. Their structures are displayed in Figure 1. These complexes arise from the multipole interactions of atom and molecules. Calculated energies are given in Table 1. For the H···cyc-C_3H_6 pair, there are two distinct vdW minima. One has a hydrogen atom setting above the C_3 ring in C_{3v} symmetry with a distance of 4.26 Å from H to the center-of-the-mass of cyc-C_3H_6. The well depth is 0.18 kcal/mol with respect to the H + cyc-C_3H_6 asymptote. If the zero-point energy corrections are included, one obtains a binding energy of 0.06 kcal/mol (or 21.0 cm^{-1}). The other minimum has C_{2v} symmetry with a distance of 4.27 Å. The well depth and binding energies are calculated as 0.16 and 0.06 kcal/mol (or 21.0 cm^{-1}), respectively.

For the H_2···C_3H_5 pair there are four vdW complexes corresponding to the four isomers of C_3H_5. The well depths are obtained as 0.46 kcal/mol for H_2···allyl, 0.46 kcal/mol for H_2···2-propenyl, 0.45 kcal/mol for H_2··*trans*-propenyl, and 0.37 kcal/mol for H_2···*cis*-propenyl. However, if the zero-point energies are corrected, all these vdW complexes are unstable with respect to their dissociation limits.

IV. Conclusions

The ground-state potential-energy surface for the H + cyc-C_3H_6 reaction has been carried out using an extrapolated coupled-cluster/complete basis set method. Energetics, geometries, and harmonic frequencies of the stationary points are calculated. The theoretical reaction enthalpies are in good agreement with the experimental values available. In this work we unveiled two coexisting reaction mechanisms: direct H-abstraction and H-addition/ring opening. The typical H-abstraction reaction leads to the H_2 and cyclopropyl radical products with a VAG barrier height of 13.03 kcal/mol. The cyclopropyl radical can overcome a barrier of 21.98 kcal/mol to become a more stable isomer, the allyl radical.

On the other hand, the H-addition and ring-opening mechanisms will first form a propyl radical intermediate. This reaction needs to climb a barrier of 16.49 kcal/mol, which is slightly higher than that of the direct H-abstraction reaction. Importantly, this intermediate has opened several competitive product channels such as $CH_3 + C_2H_4$, H + CH_3CHCH_2, and $H_2 + C_3H_5$, etc. Although the H + cyc-C_3H_6 → $CH_4 + CH_2CH$ reaction is exothermic, this reaction has less chance to occur due to a high barrier along the minimum energy path. The theoretical background of the critical **TS2** transition state has been illustrated. In particular, this new H-addition and ring-opening mechanism is consistent with recent molecular beam results of Valentini and co-workers,[16] which were difficult to understand before.

Finally, the reader can obtain the geometries of the stationary points for the H + cyc-C_3H_6 reaction in the Supporting Information.[30] They are listed in Cartesian coordinates in Å. The molecular names are consistent with those in Figure 1 as well as in Table 1.

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Supporting Information Available: Geometries of the stationary points for the H + cyc-C_3H_6 reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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