J. Phys. Chem. A **2002,** *106,* 10415−10422

Water-Assisted Isomerization from Linear Propargylium (H_2CCCH^+) to Cyclopropenylium (c-$C_3H_3^+$)

Gui-xia Liu, Ze-sheng Li,* Yi-hong Ding, Qiang Fu, Xu-ri Huang, Chia-chung Sun, and Au-chin Tang

Institute of Theoretical Chemistry, State Key Laboratory of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, People's Republic of China

Received: May 14, 2002; In Final Form: September 6, 2002

Calculations at the QCISD(T)/6-311+G(d,p)//B3LYP/6-31G(d) level indicate that the participation of water can effectively lower the isomerization barrier from linear propargylium (H_2CCCH^+) to cyclopropenylium (c-$C_3H_3^+$). With the increase of the amount of H_2O (nH_2O, $n = 1$, 2, or 3) participating in the isomerization, the isomerization barrier decreases, and with three H_2O molecules the isomerization becomes nearly barrierless. In contrast to previous studies on the catalytic effects of water on carbonyl systems and the reaction of H_2O(g) with SO_3(g), the so-called reactant and the catalyst do not associate into cyclic structures, but rather into open-chain structures. This work may be useful for further studies on the catalytic effect of other species having lone electronic pairs, such as H_2S, NH_3, and HF.

1. Introduction

The gas-phase chemistry of the $C_3H_3^+$ ion has received considerable attention in recent years as a possible precursor for soot formation in hydrocarbon flames[1−8] and for interstellar synthesis of molecules such as c-C_3H_2 and C_3H.[9−15] For $C_3H_3^+$, four stable structures have been reported,[16] of which the cyclopropenylium (c-$C_3H_3^+$) is the lowest in energy, followed by the linear propargylium (H_2CCCH^+). Many experimental studies[5,17−21] have shown that c-$C_3H_3^+$ is relatively unreactive whereas H_2CCCH^+ is reactive toward various neutrals such as C_2H_2, C_4H_2, and simple alcohols. The interconversion between H_2CCCH^+ and c-$C_3H_3^+$ is difficult.

It is now well-established that in the reactions $H_2O(g) + SO_3(g) \rightarrow H_2SO_4(g)$ and $H_2O(g) + CO_2(g) \rightarrow H_2CO_3(g)$, the presence of a second H_2O molecule can lower the reaction barrier and thus make the reactions more feasible. In 1999, Lin et al.[22] studied the catalytic effect of the second water on a variety of carbonyl systems and found that the participation of water can modify the reaction forbiddenness in addition to providing strain relief for the transition structure and further found that the water-assisted reactions are more effective for the monocarbonyl series than for the dicarbonyl series.

In this paper, we will examine the catalytic effects of nH_2O ($n = 1$, 2, or 3) for the isomerization from linear propargylium (H_2CCCH^+) to cyclopropenylium (c-$C_3H_3^+$). The main goals are to address following two questions:

(1) Can the participation of water lower the isomerization barrier effectively, and make the isomerization easier?

(2) How does the catalytic effect depend on the number of water molecule?

This paper may be helpful for the future study of catalytic effect of such species as H_2O, for example, H_2S, NH_3, and HF, all of which have lone electronic pairs.

2. Computational Methods

All calculations presented in this paper were done with the GAUSSIAN98 program.[23] All equilibrium geometries and transition state structures were fully optimized at the B3LYP/6-31G(d) level. Intrinsic reaction coordinate (IRC) calculations were carried out at the same level to confirm that the transition states connect the right reactants and products. The relative energies are evaluated using the single-point QCISD(T)/6-311+G(d,p) method at the B3LYP/6-31G(d) geometries with inclusion of the B3LYP/6-31G(d) zero-point vibration energies (ZPVE).

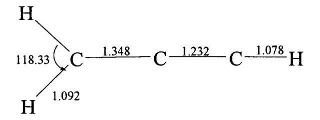
3. Results and Discussion

The equilibrium geometries are drawn in Figure 1, and the geometries of the transition states are drawn in Figure 2. The total and relative energies of the equilibrium geometries and the transition states at the QCISD(T)/6-311+G(d,p) level are listed in Table 1, and the calculated energy profiles for the isomerization from linear propargylium (H_2CCCH^+) to cyclopropenylium (c-$C_3H_3^+$), with and without the assistance by nH_2O ($n = 1$, 2, or 3) are presented in Figure 3a−c.

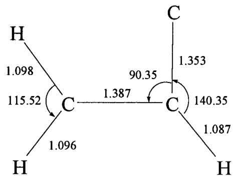
In Figure 3a−c, we use the number "0" to label the water-free isomerization channel, the number "1" to label the water-assisted isomerization channel by one H_2O molecule, and "2" and "3" (or "3′") to represent the water-assisted isomerization channels by two and three H_2O molecules, respectively. Note that 3 and 3′ represent two different water-assisted isomerization channels by three H_2O molecules. In later discussions of this article, curves 3 and 3′ will be explained in detail.

It should also be noted that the energy zero is assigned to linear propargylium (H_2CCCH^+) [or H_2CCCH^+ plus nH_2O ($n = 1$, 2, or 3) at infinite separation for the water-assisted isomerization]. For example, for the water-free isomer channel (i.e., curve 0 in Figure 3a−c), the energy zero is assigned to the linear propargylium (H_2CCCH^+), whereas for the water-assisted isomerization channel by one H_2O molecule (i.e., curve 1 in Figure 3a−c), the energy zero is assigned to H_2CCCH^+ plus one H_2O at infinite separation. For simplicity and convenience of drawing, the energy zero points of the water-free and water-assisted (by nH_2O, $n = 1$, 2, or 3) isomerization channels are drawn at the same level.

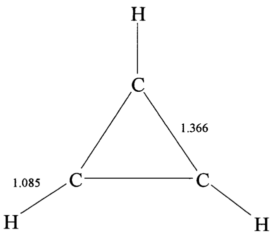
10.1021/jp0212085 CCC: \$22.00



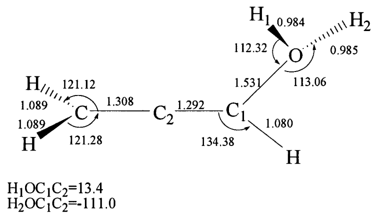
H_2CCCH^+ (C_{2v})



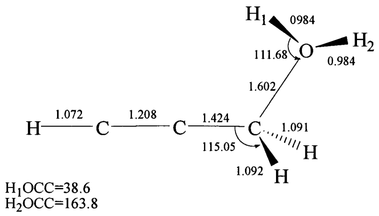
CH_2CHC^+ (C_s)



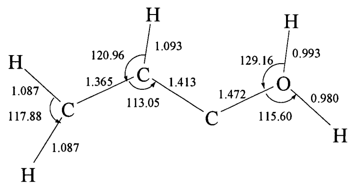
c-$C_3H_3^+$ (D_{3h})



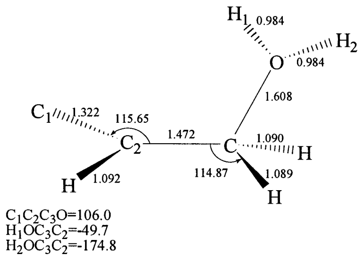
$[H_2CCCH \cdot H_2O]^+$ (C_1)



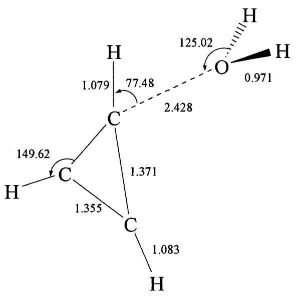
$[HCCCH_2 \cdot H_2O]^+$ (C_1)



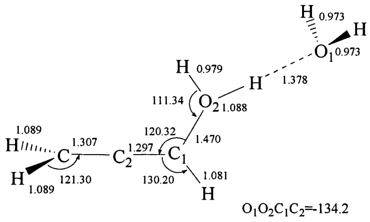
$[CH_2CHC \cdot H_2O]^+$ (C_s)



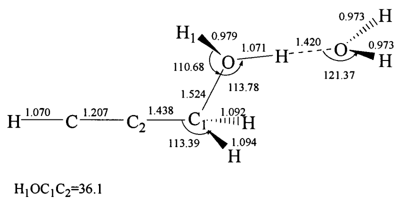
$[CCHCH_2 \cdot H_2O]^+$ (C_1)



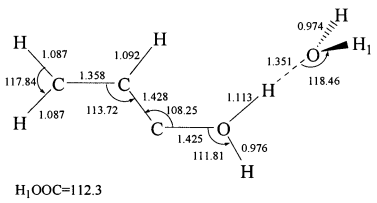
$[c\text{-}C_3H_3 \cdot H_2O]^+$ (C_s)



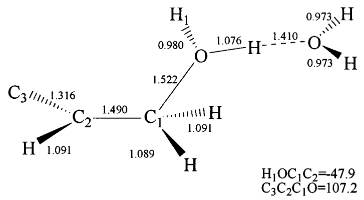
$[H_2CCCH \cdot 2H_2O]^+$ (C_1)



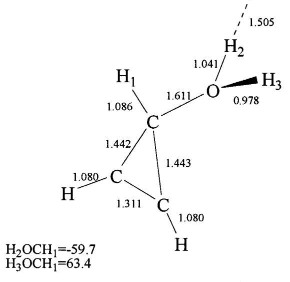
$[HCCCH_2 \cdot 2H_2O]^+$ (C_1)



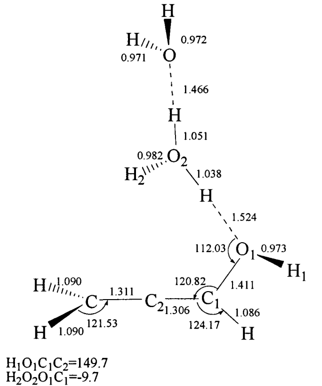
$[CH_2CHC \cdot 2H_2O]^+$ (C_s)



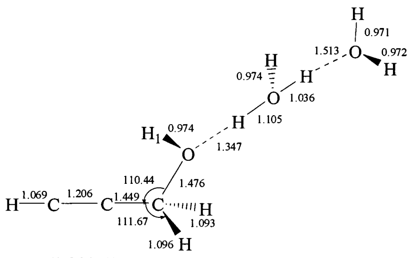
$[CCHCH_2 \cdot 2H_2O]^+$ (C_1)



$[c\text{-}C_3H_3 \cdot 2H_2O]^+$ (C_1)



$[H_2CCCH \cdot 3H_2O]^+$ (C_1)



$[HCCCH_2 \cdot 3H_2O]^+$ (C_1)

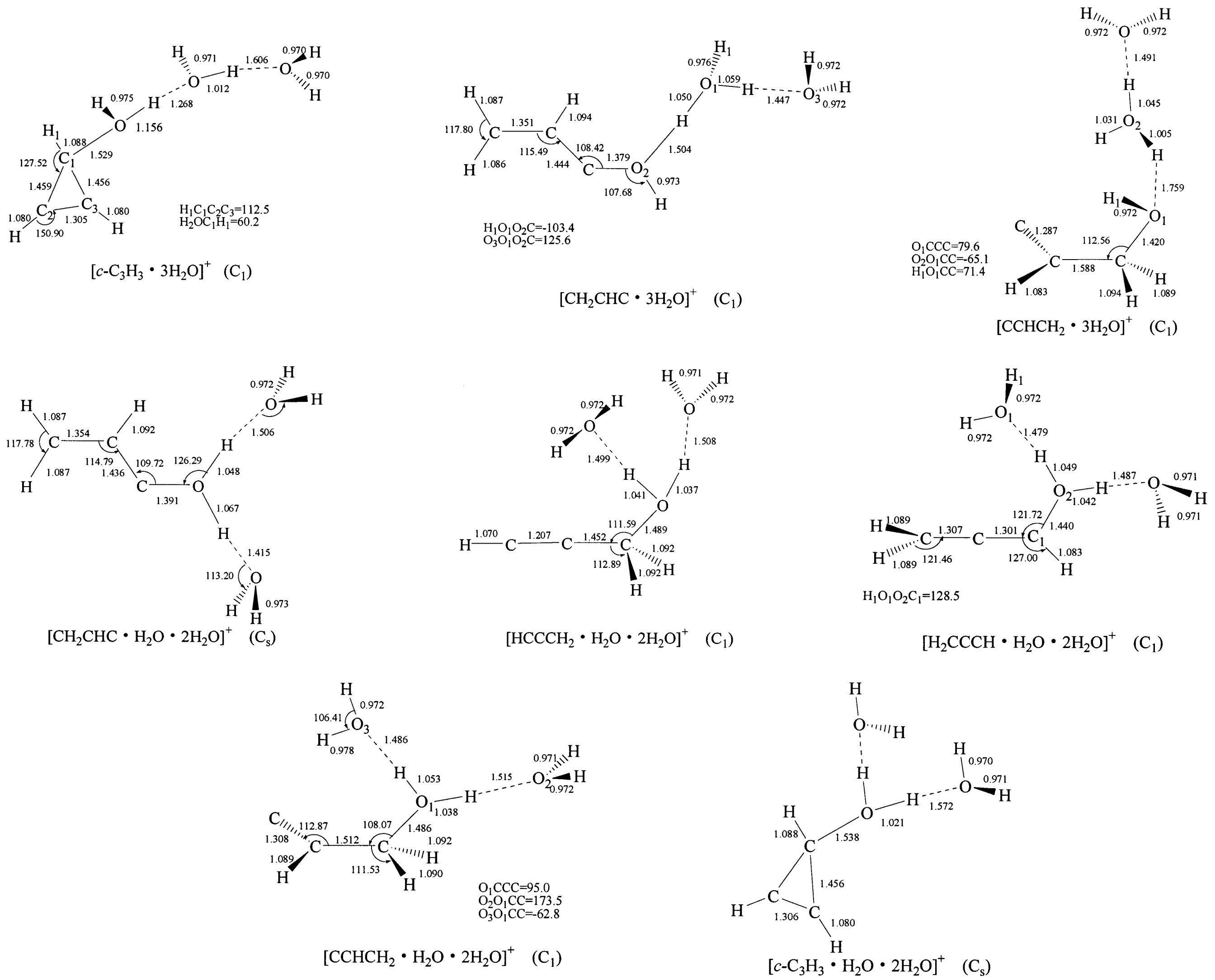
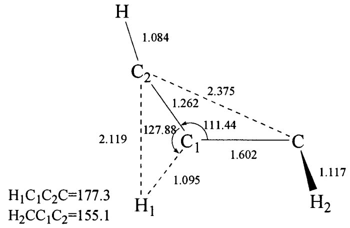


Figure 1. Optimized equilibrium geometries of $C_3H_3^+$ and $[C_3H_3{\cdot}nH_2O]^+$ (n = 1, 2, or 3) at the B3LYP/6-31G(d) level. Bond lengths are in angstroms, and angles, in degrees.

Three channels for the water-free isomerization from linear propargylium (H_2CCCH^+) to cyclopropenylium (c-$C_3H_3^+$) have been reported before at the MP4/6-311G(d,p)//MP2/6-31G(d)[24] and QCISD(T)/TZ3P//MP2/TZP[25] levels of theory. Here, we only investigate the two energetically more favorable paths. One, corresponding to curve 0 of Figure 3a, is the direct isomerization from H_2CCCH^+ to c-$C_3H_3^+$ via the transition state TS1, which is associated with a concerted process, namely, 1,2-H-shift and the C_3-ring closure. The barrier for this process is 87.6 kcal/mol, which is close to the value of 88.0 kcal/mol calculated by Maluendes et al.[25] The other channel, corresponding to curve 0 of Figure 3b,c, goes through a transition state (TS6)−intermediate (CH_2CHC^+)−transition state (TS11) process. Starting from H_2CCCH^+ (0.0), CH_2CHC^+ (40.8) may be obtained via the 1,2-H-shift transition state TS6 (48.5). Then, CH_2CHC^+ may lead to c-$C_3H_3^+$ (−25.6) via transition state TS11 (41.0), which is also associated with a concerted process, i.e., the 1,3-H-shift as well as the C_3-ring closure. The corresponding barriers for the two processes are 48.5 and 0.2 kcal/mol, which also approach to Maluendes et al.'s[25] calculated results of 49.3 and 0.2 kcal/mol. In view of the large barriers (87.6 kcal/mol for **TS1** in Figure 3a or 48.5 kcal/mol for TS6 in Figure 3b,c), the isomerization from H_2CCCH^+ to c-$C_3H_3^+$ is difficult through both channels. In the above and later discussions, the values in parentheses are relative energies in kcal/mol with reference to H_2CCCH^+ [or H_2CCCH^+ plus nH_2O (n = 1, 2, or 3) at infinite separation].

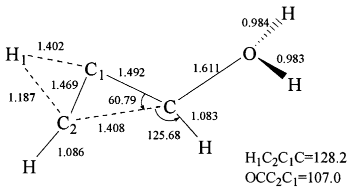
Similar processes with the assistance of nH_2O (n = 1, 2, or 3) are also calculated to investigate the catalytic effects of nH_2O (n = 1, 2, or 3). The chain forms ($H_2CCCH{\cdot}nH_2O$ or $HCCCH_2{\cdot}nH_2O$, n = 1, 2, or 3) are formed between the linear H_2CCCH^+ and nH_2O. Also, under the participation of $3H_2O$, H_2CCCH^+ and $3H_2O$ may associate into two open-chain forms [$H_2CCCH{\cdot}3H_2O$ (or $HCCCH_2{\cdot}3H_2O$) and $H_2CCCH{\cdot}H_2O{\cdot}2H_2O$ (or $HCCCH_2{\cdot}H_2O{\cdot}2H_2O$)] (see Figure 1). In Figure 3a−c, the corresponding water-assisted isomerization channels by $3H_2O$ are denoted by curves 3 and 3′, respectively.

The direct isomerization process with and without nH_2O (n = 1, 2, or 3) is presented in Figure 3a, from which it can be seen that the relative energies of the transition states (TS1−TS5) decrease with the increasing number of H_2O (nH_2O, n = 1, 2, or 3) that participate in the isomerization. In this article, the energy barrier E_a is defined with reference to H_2CCCH^+ [or H_2CCCH^+ plus nH_2O (n = 1, 2, or 3) at infinite separation for the water-assisted isomerization]. The lowering in energy barrier, defined as $\Delta E_a = E_a(\text{with } H_2O) - E_a(\text{without } H_2O)$, is given in Table 2. The energy barrier of direct isomerization from H_2CCCH^+ to c-$C_3H_3^+$ with assistance by nH_2O (n = 1,



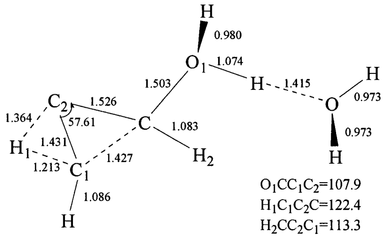
$H_1C_1C_2C=177.3$
$H_2CC_1C_2=155.1$

TS1 (C_1)



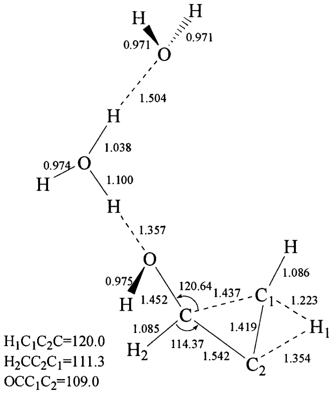
$H_1C_2C_1C=128.2$
$OCC_2C_1=107.0$

TS2 (C_1)



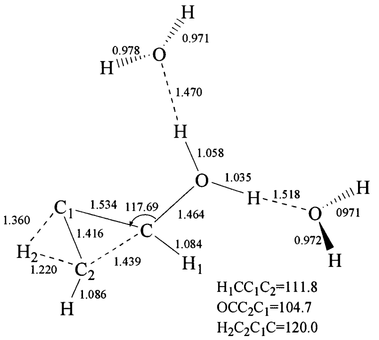
$O_1CC_1C_2=107.9$
$H_1C_1C_2C=122.4$
$H_2CC_2C_1=113.3$

TS3 (C_1)



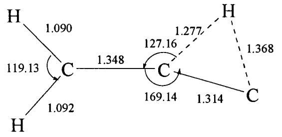
$H_1C_1C_2C=120.0$
$H_2CC_2C_1=111.3$
$OCC_1C_2=109.0$

TS4 (C_1)

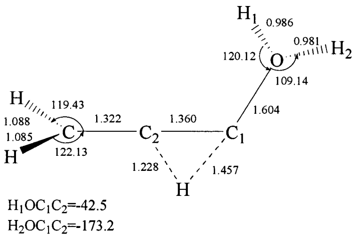


$H_1CC_1C_2=111.8$
$OCC_2C_1=104.7$
$H_2C_2C_1C=120.0$

TS5 (C_1)

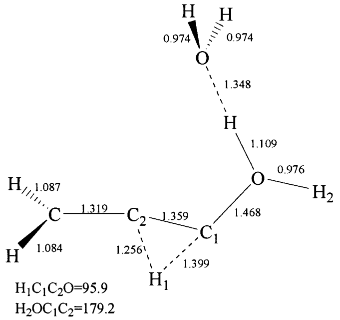


TS6 (C_s)



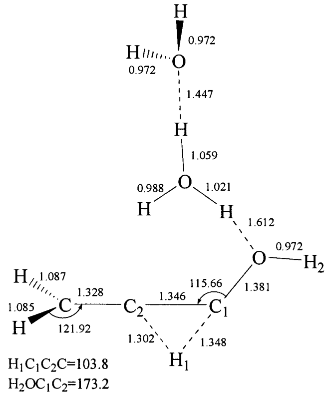
$H_1OC_1C_2$=-42.5
$H_2OC_1C_2$=-173.2

TS7 (C_1)



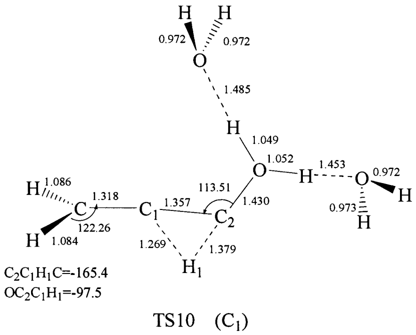
$H_1C_1C_2O=95.9$
$H_2OC_1C_2=179.2$

TS8 (C_1)



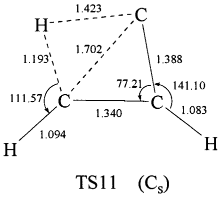
$H_1C_1C_2C=103.8$
$H_2OC_1C_2=173.2$

TS9 (C_1)

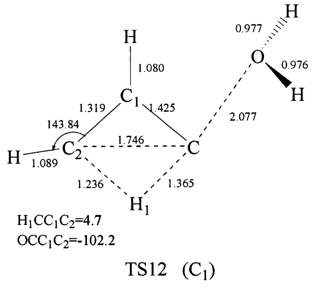


$C_2C_1H_1C$=-165.4
$OC_2C_1H_1$=-97.5

TS10 (C_1)



TS11 (C_s)



$H_1CC_1C_2=4.7$
OCC_1C_2=-102.2

TS12 (C_1)

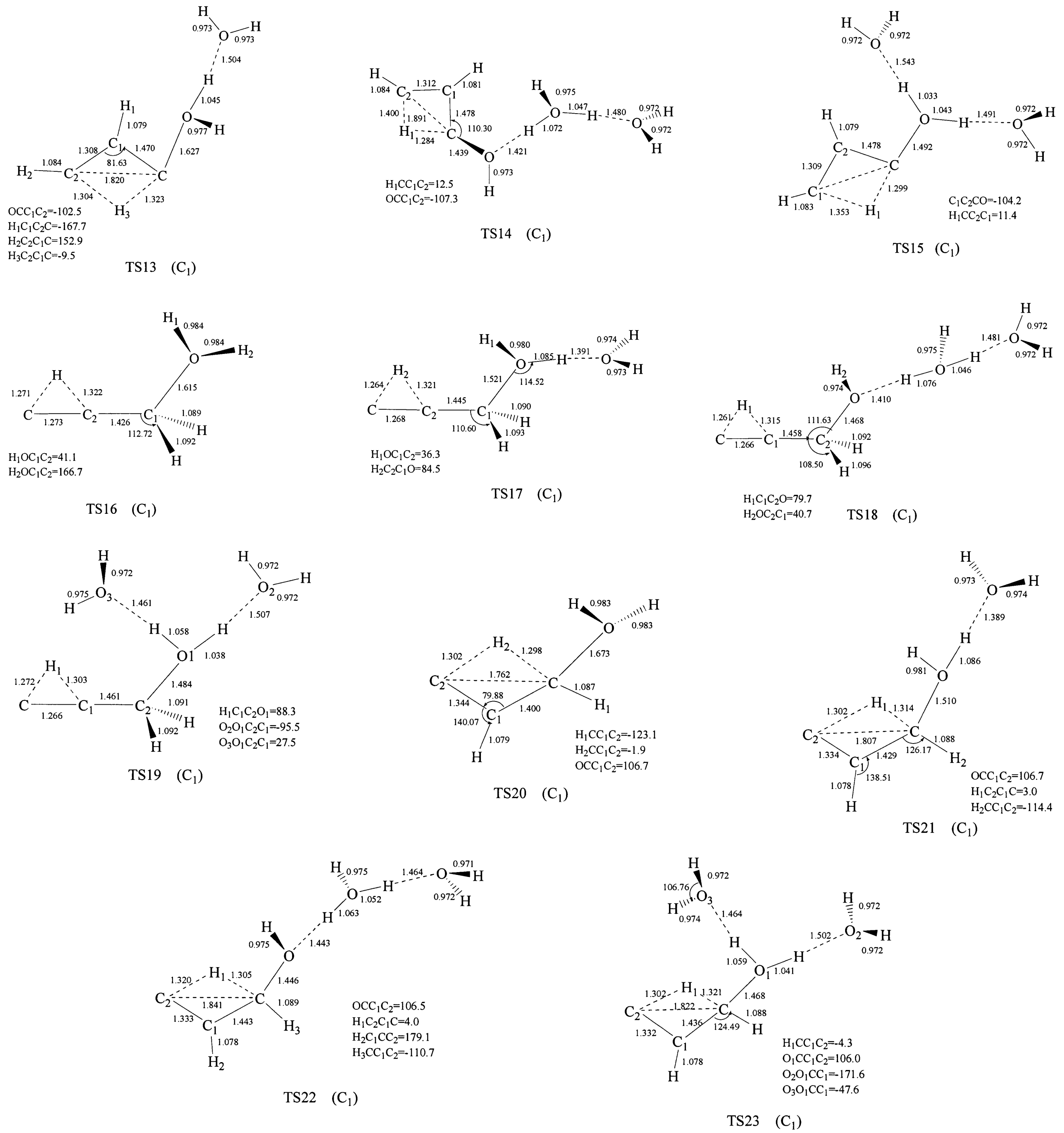
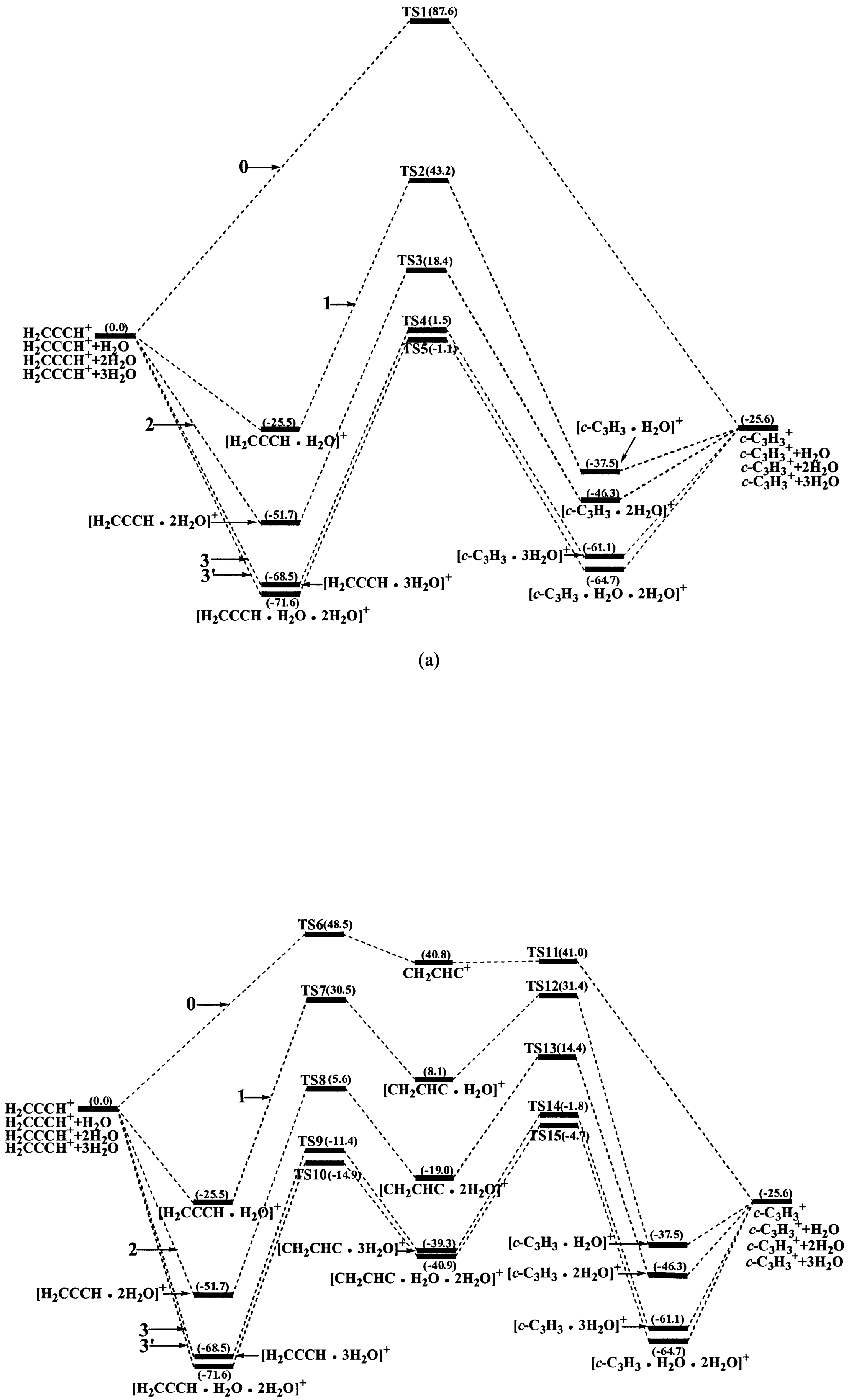


Figure 2. Optimized geometries of the transition states for the isomerization from H_2CCCH^+ to c-$C_3H_3^+$ at the B3LYP/6-31G(d) level. Bond lengths are in angstroms, and angles, in degrees.

2, or 3) molecules is +43.2, +18.4, and +1.5 (for curve 3 of Figure 3a) or −1.1 (for curve 3′ of Figure 3a) kcal/mol, respectively. With the assistance of three H_2O molecules the energy barrier is nearly 0 kcal/mol (+1.5 or −1.1 kcal/mol); namely, the isomerization from H_2CCCH^+ to c-$C_3H_3^+$ with the assistance by $3H_2O$ is almost a barrierless process.

The other mechanism, i.e., transition state−intermediate−transition state channel with and without the assistance of nH_2O (n = 1, 2, or 3) is also calculated. There are two kinds of probable initial associations between H_2CCCH^+ and nH_2O (n = 1, 2, or 3); namely, the oxygen atom of H_2O either associates with the terminal carbon atom that connects one hydrogen atom, forming $H_2CCCH{\cdot}nH_2O$ (see Figure 3b), or associates with the terminal carbon atom that connects two hydrogen atoms, forming $HCCCH_2{\cdot}nH_2O$ (see Figure 3c). To compare with the direct isomerization discussed above, we put emphasis on the first transition states (TS6−TS10, TS16−TS19) of the transition state−intermediate−transition state channels. For the first kind of transition state−intermediate−transition state channel (see Figure 3b), the energy barriers of the isomerizations with the aid of nH_2O (n = 1, 2, or 3) are +30.5, +5.6, and −11.4 (for curve 3 of Figure 3b) or −14.9 (for curve 3′ of Figure 3b) kcal/mol, respectively. And for the second kind of transition state−intermediate−transition state channel (see Figure 3c), the energy


TS1(87.6)
TS2(43.2)
TS3(18.4)
TS4(1.5)
TS5(-1.1)
0
1
2
3
3'
H_2CCCH^+ (0.0)
H_2CCCH^++H_2O
H_2CCCH^++2H_2O
H_2CCCH^++3H_2O
(-25.5)
$[H_2CCCH \cdot H_2O]^+$
(-51.7)
$[H_2CCCH \cdot 2H_2O]^+$
(-68.5)
$[H_2CCCH \cdot 3H_2O]^+$
(-71.6)
$[H_2CCCH \cdot H_2O \cdot 2H_2O]^+$
$[c\text{-}C_3H_3 \cdot H_2O]^+$
(-37.5)
(-46.3)
$[c\text{-}C_3H_3 \cdot 2H_2O]^+$
$[c\text{-}C_3H_3 \cdot 3H_2O]^+$
(-61.1)
(-64.7)
$[c\text{-}C_3H_3 \cdot H_2O \cdot 2H_2O]^+$
(-25.6)
$c\text{-}C_3H_3^+$
$c\text{-}C_3H_3^+$+H_2O
$c\text{-}C_3H_3^+$+2H_2O
$c\text{-}C_3H_3^+$+3H_2O
TS6(48.5)
(40.8)
CH_2CHC^+
TS11(41.0)
TS7(30.5)
TS12(31.4)
TS13(14.4)
TS8(5.6)
(8.1)
$[CH_2CHC \cdot H_2O]^+$
TS14(-1.8)
TS15(-4.7)
TS9(-11.4)
TS10(-14.9)
(-19.0)
$[CH_2CHC \cdot 2H_2O]^+$
$[CH_2CHC \cdot 3H_2O]^+$
(-39.3)
(-40.9)
$[CH_2CHC \cdot H_2O \cdot 2H_2O]^+$

(a)

(b)

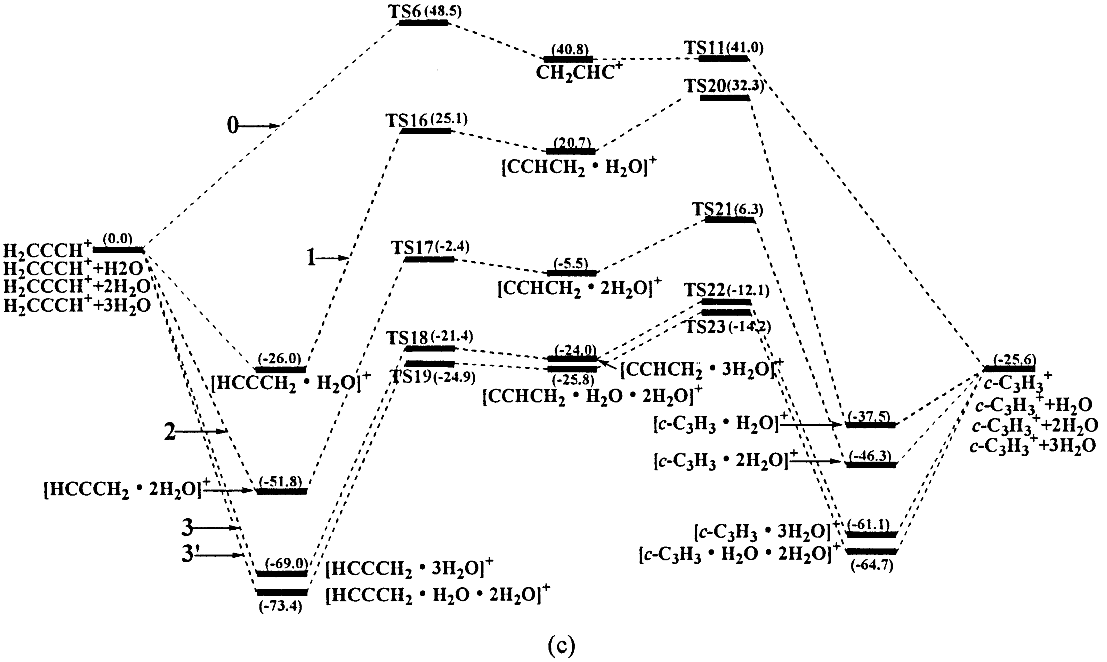


Figure 3. Energy profiles for the isomerization from H_2CCCH^+ to c-$C_3H_3^+$ at the QCISD(T)/6-311+G(d,p)//B3LYP/6-31G(d) level with zero-point vibration energy correction: (a) for the direct isomerication channel; (b) for the first kind of transition state−intermediate−transition state channel; (c) for the second kind of transition state−intermediate−transition state channel.

TABLE 1: Total (au) and Relative[a] (kcal/mol) Energies of the Equilibrium Geometries and the Transition States at the QCISD(T)/6-311+G(d,p) Level with Zero-Point Energy Corrections (au)

species	ZPVE B3LYP/ 6-31G(d)	TE QCISD(T)/ 6-311+G(d,p)	RE	species	ZPVE B3LYP/ 6-31G(d)	TE QCISD(T)/ 6-311+G(d,p)	RE
			Water-Free				
H_2CCCH^+	0.043031	−115.399038	0.0	TS1	0.037623	−115.253988	87.6
c-$C_3H_3^+$	0.045333	−115.442160	−25.6	TS6	0.038453	−115.317171	48.5
CH_2CHC^+	0.042265	−115.333318	40.8	TS11	0.040190	−115.330803	41.0
			H_2O				
$H_2CCCH^+ + H_2O$	0.064198	−191.685526	0.0	$[CCHCH_2{\cdot}H_2O]^+$	0.071173	−191.659510	20.7
c-$C_3H_3^+ + H_2O$	0.066500	−191.728648	−25.6	TS2	0.067463	−191.619979	43.2
$[H_2CCCH{\cdot}H_2O]^+$	0.072281	−191.734198	−25.5	TS7	0.066202	−191.638891	30.5
$[c$-$C_3H_3{\cdot}H_2O]^+$	0.069195	−191.750248	−37.5	TS12	0.064872	−191.636146	31.4
$[CH_2CHC{\cdot}H_2O]^+$	0.071018	−191.679387	8.1	TS16	0.067231	−191.648532	25.1
$[HCCCH_2{\cdot}H_2O]^+$	0.072686	−191.735375	−26.0	TS20	0.067100	−191.636887	32.3
			$2H_2O$				
$H_2CCCH^+ + 2H_2O$	0.085365	−267.972014	0.0	$[CCHCH_2{\cdot}2H_2O]^+$	0.095301	−267.990784	−5.5
c-$C_3H_3^+ + 2H_2O$	0.087667	−268.015136	−25.6	TS3	0.092070	−267.949321	18.4
$[H_2CCCH{\cdot}2H_2O]^+$	0.096067	−268.065047	−51.7	TS8	0.090138	−267.967804	5.6
$[c$-$C_3H_3{\cdot}2H_2O]^+$	0.096706	−268.057204	−46.3	TS13	0.090277	−267.953979	14.4
$[CH_2CHC{\cdot}2H_2O]^+$	0.095283	−268.012206	−19.0	TS17	0.091352	−267.981866	−2.4
$[HCCCH_2{\cdot}2H_2O]^+$	0.096978	−268.066214	−51.8	TS21	0.091816	−267.968378	6.3
			$3H_2O$				
$H_2CCCH^+ + 3H_2O$	0.106532	−344.258501	0.0	$[CCHCH_2{\cdot}H_2O{\cdot}2H_2O]^+$	0.120538	−344.313664	−25.8
c-$C_3H_3^+ + 3H_2O$	0.108834	−344.301624	−25.6	TS4	0.115978	−344.265541	1.5
$[H_2CCCH{\cdot}3H_2O]^+$	0.121668	−344.382800	−68.5	TS5	0.117184	−344.270869	−1.1
$[H_2CCCH{\cdot}H_2O{\cdot}2H_2O]^+$	0.120597	−344.386592	−71.6	TS9	0.117019	−344.287222	−11.4
$[c$-$C_3H_3{\cdot}3H_2O]^+$	0.119566	−344.368868	−61.1	TS10	0.115118	−344.290855	−14.9
$[c$-$C_3H_3{\cdot}H_2O{\cdot}2H_2O]^+$	0.121215	−344.376275	−64.7	TS14	0.114417	−344.269301	−1.8
$[CH_2CHC{\cdot}3H_2O]^+$	0.121103	−344.335765	−39.3	TS15	0.114834	−344.274256	−4.7
$[CH_2CHC{\cdot}H_2O{\cdot}2H_2O]^+$	0.120062	−344.337268	−40.9	TS18	0.115944	−344.302019	−21.4
$[HCCCH_2{\cdot}3H_2O]^+$	0.120867	−344.382730	−69.0	TS19	0.116627	−344.308234	−24.9
$[HCCCH_2{\cdot}H_2O{\cdot}2H_2O]^+$	0.121917	−344.390779	−73.4	TS22	0.116774	−344.288023	−12.1
$[CCHCH_2{\cdot}3H_2O]^+$	0.120928	−344.311145	−24.0	TS23	0.116883	−344.291461	−14.2

[a] With inclusion of the B3LYP/6-31G(d) zero-point vibrational energy (ZPVE) corrections.

barriers are +25.1, −2.4, and −21.4 (for curve 3 of Figure 3c) or −24.9 (for curve 3′ of Figure 3c) kcal/mol, respectively. It is obvious that the isomerizations with the aid of $3H_2O$ molecules via the transition state−intermediate−transition state mechanism are also barrierless processes. As seen from Figure 3c, the isomerization with the assistance by $2H_2O$ molecules is already a barrierless process, as the energy barrier is −2.4 kcal/mol.

From Table 2, it can be seen that the ΔE_a values are most significant for the direct isomerization (see Figure 3a), and then

TABLE 2: Energy Barrier Lowering ($\Delta E_a = E_a$(with H_2O) − E_a(without H_2O) in kcal/mol) for the Isomerization from H_2CCCH^+ to *c*-$C_3H_3^+$

		without H_2O	H_2O	$2H_2O$	$3H_2O^a$
Figure 3a	E_a	87.6	43.2	18.4	1.5 (−1.1)
	ΔE_a		−44.4	−69.2	−86.1 (−88.7)
Figure 3b	E_a	48.5	30.5	5.6	−11.4 (−14.9)
	ΔE_a		−18.0	−42.9	−59.9 (−63.4)
Figure 3c	E_a	48.5	25.1	−2.4	−21.4 (−24.9)
	ΔE_a		−23.4	−50.9	−69.9 (−73.4)

[a] The values before parentheses are for curve 3 of Figure 3a-c, and the values in parentheses are for curve 3′ of Figure 3a-c.

the second kind of transition state−intermediate−transition state mechanism for the isomerization (see Figure 3c); the last is the first kind of transition state−intermediate−transition state mechanism for the isomerization (see Figure 3b). All the values listed in Table 2 indicate that the assistance of nH_2O ($n = 1$, 2, or 3) for the isomerization from H_2CCCH^+ to *c*-$C_3H_3^+$ is effective. The participation of water can lower the isomerization barrier effectively and make the isomerization easier. The ΔE_a values may also indicate that the higher the amount of H_2O participating in the isomerization is, the more the lowering of the isomerization barrier is. However, whether the participation of more than three water molecules can lower the isomerization barrier much more needs to be investigated in the future experimental or theoretical studies.

The oxygen atom of the first H_2O molecule may play a major role, which offers the lone electronic pair to form a covalent bond between H_2CCCH^+ and H_2O and partly neutralizes the positive charge of H_2CCCH^+. This might make the H-shift energetically more favorable and lower the isomerization barrier.

4. Conclusion

The isomerization from linear propargylium (H_2CCCH^+) to cyclopropenylium (*c*-$C_3H_3^+$) with and without the assistance of nH_2O ($n = 1$, 2, or 3) is investigated at the QCISD(T)/6-311+G(d,p)//B3LYP/6-31G(d) level of theory. Our calculations indicate that the participation of nH_2O ($n = 1$, 2, or 3) plays an important role, lowering the isomerization barrier and making the isomerization easier. Furthermore, the isomerization barrier decreases with the increasing amount of H_2O (nH_2O, $n = 1$, 2, or 3). In the case of the participation by three H_2O molecules, the isomerization from H_2CCCH^+ to *c*-$C_3H_3^+$ becomes nearly a barrierless process. Those might be attributed to the oxygen atom of the first H_2O molecule, which bring charge transfers. In this article, the $C_3H_3^+$ cations combine the H_2O molecules into open-chain structures instead of cyclic structures, which are the usual structures of the transition structures with the aid of catalyst. The present study on water-assisted isomerization may be useful for the further understanding of the catalytic effect with a chain relay process and be helpful for future studies on the catalytic effect of other species having lone electronic pairs, such as H_2S, NH_3, and HF.

Acknowledgment. This work is supported by the National Science Foundation of China (G29892168, 20073014, 20103003), the Doctor Foundation by the Ministry of Education, the Foundation for University Key Teacher by the Ministry of Education, and Key Subject of Science and Technology by the Ministry of Education of China.

References and Notes

(1) Goodings, J. M.; Bohme, D. K.; Ng, C. W. *Combust. Flame* **1979**, *36*, 27.
(2) Calcotte, H. F. *Combust. Flame* **1981**, *42*, 215.
(3) Smyth, K. C.; Lias, S. G.; Ausloos, P. *Combust. Sci. Technol.* **1982**, *28*, 147.
(4) Harris, S. J.; Weiner, A. M. *Annu. Rev. Phys. Chem.* **1985**, *36*, 31.
(5) Baykut, G.; Brill, F. W.; Eyler, J. R. *Combust. Sci. Technol.* **1986**, *45*, 233.
(6) Leszczynski, J.; Wiseman, F.; Zerner, M. C. *Int. J. Quantum Chem.* **1988**, *22*, 117.
(7) Cameron, A.; Leszczynski, J.; Zerner, M. C.; Weiner, B. *J. Phys. Chem.* **1989**, *93*, 139.
(8) Calcote, H. F.; Gill, R. J. In *Soot Formation in Combustion*; Bockhorn, H., Ed.; Springer, Berlin, 1994; p 471.
(9) Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* **1983**, *269*, 329.
(10) Herbst, E.; Adams, N. G.; Smith, D. *Astrophys. J.* **1984**, *285*, 618.
(11) Adams, N. G.; Smith, D. *Astrophys. J.* **1987**, *317*, L25.
(12) Lepp, S.; Dalgarno, A. *Astrophys. J.* **1988**, *324*, 553.
(13) Turner, B. E. *Astrophys. J.* **1989**, *347*, L39.
(14) Lee, T. J.; Willetts, A.; Gaw, J. F.; Handy, N. C. *J. Chem. Phys.* **1989**, *90*, 4330.
(15) Wyss, M.; Riaplov, E.; Maier, J. P. *J. Chem. Phys.* **2001**, *114*, 10355.
(16) Li, W.-K.; Riggs, N. V. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *257*, 189.
(17) Ausloos, P. J.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 6505.
(18) Ozturk, F.; Baykut, G.; Eyler, J. R. *J. Phys. Chem.* **1987**, *91*, 4360.
(19) Smith, D.; Adams, N. G. *Int. J. Mass Spectrom. Ion Phys.* **1987**, *76*, 307.
(20) Moini, M. *J. Am. Soc. Mass Spectrom.* **1992**, *3*, 631.
(21) McEwan, M. J.; McConnell, C. L.; Freeman, C. G.; Anicich, V. G. *J. Phys. Chem.* **1994**, *98*, 5068.
(22) Lin, C.-L.; Chu, S.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 4222.
(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision x.x; Gaussian, Inc.: Pittsburgh, PA, 1998.
(24) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 6976.
(25) Maluendes, S. A.; McLean, A. D.; Yamashita, K.; Herbst, E. *J. Chem. Phys.* **1993**, *99*, 2812.