Molecular Orbital Study of Ion-Molecule Reactions Producing Hydrocarbons in Interstellar Space#

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The reaction mechanisms involving the formation of hydrocarbons in interstellar space were examined in terms of an *ab initio* molecular orbital calculation. The reaction energies and potential energy surfaces producing CH and C_2H were evaluated based on the scheme for ion-molecule reactions proposed by the late H. Suzuki. According to the very attractive potentials of positive ions with the hydrogen molecule, most of the reactions proceed via energy-rich intermediates, such as CH_4^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, and C_3H^+. Consequently, the model proposed by Suzuki has been confirmed concerning the result that the reactions are exothermic and without an energy barrier up to C_3^+ formation.

Many interstellar molecules have been found by observations with radiotelescopes in conjunction with laboratory detection by microwave experiments. The reaction schemes concerning the formation of these interstellar species have been discussed for many years. The widely accepted mechanisms are ion-molecule reactions initiated by the ionization of various atoms, followed by collisions with hydrogen molecules.[1—3]

The hydrocarbon species found in molecular clouds are C_nH (n=1—6), C_3H_2, and C_4H_2. It seems to be peculiar that the molecules which contain carbon atoms are highly unsaturated species, in spite of the fact that the largest number of molecules in interstellar space is the hydrogen molecule. Suzuki[4] and Herbst[5] have proposed a mechanism for hydrocarbon chemistry in interstellar space, especially for diffuse molecular clouds. Figure 1 shows Suzuki's scheme for ion-molecule reactions in the formation of hydrocarbon species. The key feature of this mechanism is that a carbon atom ionized by UV radiation or cosmic-ray reacts with hydrogen molecules successively. Once the ion species can not react with a hydrogen molecule, a recombination with an electron becomes prior to other chemical reactions. The neutralized species formed by such a dissociative recombination have been observed by radiotelescopes. A further attack by an ionized carbon atom on such a relatively stable neutral molecule results in an elongation of the carbon chain.

Since each part of the reaction has been little confirmed by experiment, we performed *ab initio* molecular orbital calculations in order to clarify whether the reactions are possible or not. A theoretical calculation based on the molecular orbital theory seems to be reasonable, since the condition of a molecular cloud is extremely low density and low temperature.

Computational Procedure

Ab initio molecular orbital theory was applied in order to study the reaction energies and potential energy surfaces of the major ion-molecule reactions proposed by Suzuki, as shown in Fig. 1. The geometries and their energies were calculated by optimizing each species using the Hartree–Fock (HF) method and second-order Møller–Presset pertubation theory (MP2).[6] The basis sets used were double-zeta (DZ) and double-zeta plus polarization (DZ+P) basis functions by Huzinaga[7] and Dunning.[8] Each structure obtained by geometry optimization has been confirmed to be a stable structure based on an analytical second-derivative method. The calculations were carried out by using the Gaussian 86 program system.[9] The energies used in the text are the values obtained with the MP2/DZ+P method without any specification.

Results and Discussion

Reaction Energies for Suzuki's Scheme. One of the characteristics of the ion-molecule reaction is that the reaction can occur effectively due to an attractive potential between the ion and a neutral molecule. In order to confirm the reaction scheme proposed for the formation of hydrocarbon molecules, we have to make sure that the reaction is exothermic, since there is no extra energy in interstellar space. It is also important that there is either no, or a very small, energy barrier in the reaction pathway.

The ion-molecule reactions treated in the present study are indicated by numbers (1)—(7) in Fig. 1. Table 1 summarizes the reaction energies evaluated by taking the energy differences between the reactants and products for reaction schemes (1)—(7). The energies used are those of the optimized geometries at each level of the methods. Since an electron correlation is very important to obtain the electronic energy for unstable radicals, such as C_2^+ and C_3^+, one should notice that the energies calculated by the HF method are not reliable for any system involving these species. This reflects the big difference for the reaction energies of (3), (4), and (7) between the HF and MP2 methods.

Consequently, all of the reaction energies for schemes (1)—(7) obtained with the MP2 method are positive,

#This paper is dedicated to the late Professor Hiroshi Kato.

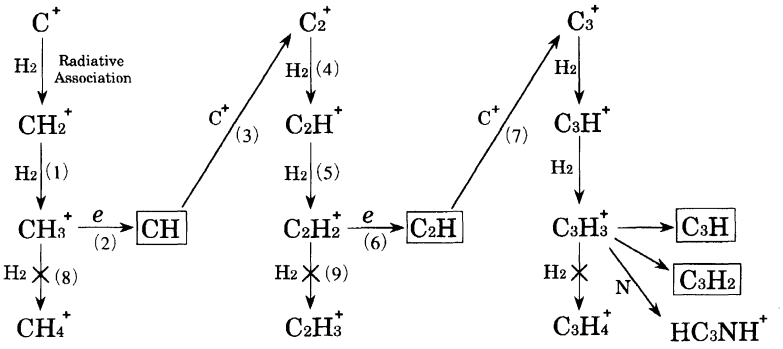

Fig. 1. Suzuki's scheme of ion-molecule reactions for the formation of hydrocarbon molecules in interstellar space. The species indicated with a square are the observed interstellar molecules.

Table 1. The Reaction Energies Calculated for Schemes (1)—(8) with Various Methods

The energies are shown in kJ mol^{-1}. [a] The positive value indicates that the reaction is exothermic, and the negative value indicates the endothermic reaction.

		HF/DZ	HF/DZ+P	MP2/DZ	MP2/DZ+P
(1)	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	87	85	92	97
(2)	$CH_3^+ + e \rightarrow CH + H_2$	436	431	437	428
	$\rightarrow CH_2 + H$	513	495	486	456
	$\rightarrow CH + 2H$	91	74	47	1
(3)	$CH + C^+ \rightarrow C_2^+ + H$	47	95	189	212
(4)	$C_2^+ + H_2 \rightarrow C_2H^+ + H$	170	156	52	45
(5)	$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$	110	118	187	182
(6)	$C_2H_2^+ + e \rightarrow C_2H + H$	528	492	477	464
	$\rightarrow C_2 + 2H$	−207	−231	120	55
(7)	$C_2H + C^+ \rightarrow C_3^+(linear) + H$	−173	−136	247	280
	$\rightarrow C_3^+(cyclic) + H$	−46	116	59	190
(8)	$CH_3^+ + H_2 \rightarrow CH_4^+ + H$	−288	−261	−292	−269

a) The unit conversion 1 hartree=27.2116 eV=627.494 kcal mol^{-1}=2625.5 kJ mol^{-1} is used.

which confirms that the Suzuki's schemes (1)—(7) are all exothermic reactions.

Table 1 also shows that reaction energies for an impossible reaction (8), indicated by a cross in Fig. 1. Because reaction (8) is endothemic, CH_3^+ is the terminal molecule containing one carbon atom, and should react with some species other than the hydrogen molecule. The radiative association reaction of CH_3^+ and H_2 to produce CH_5^+ is, of course, a possible reaction in interstellar space,[3] even though this pathway is not included in Suzuki's scheme, whose main interest was the mechanism which produces carbon chain molecules.

The reaction mechanisms for the formation of many other interstellar molecules, such as CH_3OH, CH_3NH_2, H_2CO, and CH_3CN, are proposed to be the ion-molecule reactions starting from the CH_3^+ molecule.[3] Although an elongation of the carbon chain may be initiated by the reaction of CH_3^+ with a carbon atom, it would be more probable that a neutral species formed by electron recombination reacts with an ionized carbon atom due to the long lifetime of a neutral species with a large ionization energy. This would also explain how the observed interstellar species, such as CH, C_2H, and C_3H, are produced, as in reactions (2) and (6).

Reaction (9) ($C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$) is shown to be impossible in Fig. 1. Recent theoretical work indicates that reaction (9) is almost thermoneutral, and has an energy barrier of 22.6 kJ mol^{-1}.[10] This theoretical calculation and the experimental data[11] for reaction (9) suggest that it is possible via tunneling.

Potential Energy Surfaces. Even if reactions (1)—(7) are shown to be exothermic, they are not necessary to occur under interstellar conditions. When the reaction has an energy barrier, its process would hardly take place due to no excess energy in interstellar space. In this respect, we calculated the potential energy surfaces for each reaction pathway in order to clarify whether an energy barrier exists or not.

The first step of the reaction of C^+ and H_2, which produces CH_2^+, has been discussed by several authors, since this step is very important for following all of the other steps of hydrocarbon species.[12] Since the hydrogen abstraction reaction to produce CH^+ is endothermic,[13] the reaction $C^+ + H_2 \rightarrow CH^+ + H$ can be excluded in the chemistry of a diffuse molecular cloud.[14] The direct formation of CH_2^+ from C^+ and H_2 should experience

radiative emission from the energetically rich collision complex $[CH_2^+]^*$. Consequently, this radiative association is necessary, even if this reaction rate is small.[15]

Potential Energy Surface of Reaction (1) $CH_2^+ + H_2 \rightarrow CH_3^+ + H$. Once the CH_2^+ molecule is formed, the second step related to the H_2 molecule is to from the CH_3^+ species. We first tried to obtain the hydrogen abstraction reaction pathway (1). We found the energy barrier to be a few kcal mol^{-1} for the linear hydrogen abstraction pathway under the C_{2v} symmetry restriction. The result of a vibrational analysis indicates, however, that this transition state has two imaginary frequencies. When we removed the symmetry constraint of the transition state geometry, we could not find the real transition state, but obtained the minimum structure of CH_4^+. This means that the hydrogen abstraction pathway directly forming the CH_3^+ molecule does not exist as a reaction path.

When the geometrical configuration of the H_2 and CH_2^+ molecules set to be C_s symmetry, the interaction between the two species becomes very attractive. During the course of reaction (1), it is found that there is deep energy minimum which corresponds to the CH_4^+ species. Figure 2 illustrates the potential energy surface of reaction (1) with the structures of each species optimized with the MP2 method using DZ+P basis set.

Although the minimum energy path indicates that reaction (1) proceeds via CH_4^+ as an intermediate, the collision complex between CH_2^+ and H_2 would be loosely bound because of the large excess energy. This surplus energy can be released to the kinetic energy of the leaving hydrogen atom.

Dissociative Recombination Reaction (2) $CH_3^+ + e \rightarrow CH + H_2$. As discussed before, the primary destination of the reaction of C^+ and H_2 is the CH_3^+ molecule. The observed interstellar molecule CH is thought to be formed by the recombination of CH_3^+ with an electron. The adiabatic ionization energy of CH_3^+ was calculated to be 9.5 eV using the MP2/DZ+P method. This value is underestimated by 0.3 eV, compared with the experimental value.[16]

In Table 1, the excess energies of dissociative recombination reactions (2) are displayed for three decomposition pathways. The electron recombination of CH_3^+ leads to two possible products, CH and CH_2. When the CH molecule is produced together with H_2, an extra energy of more than 400 kJ mol^{-1} is expected to be distributed in the translational and internal motions of both the CH and H_2 molecules. This strongly suggests that some emission or radiative transition would be necessary to give the vibrationally ground state of the CH molecule. The excess energy (430—450 kJ mol^{-1}) is, however, large enough to cause a further dissociation of CH_2 or the hydrogen molecule. Noticing that 430 kJ mol^{-1} is almost the same as the bond energy of H_2 molecule (4.5 eV), the formation of a CH molecule with two hydrogen atoms would also be possible in addition to the formation of $CH + H_2$ or $CH_2 + H$. The dissociation pathway of the CH_3 molecule has been discussed by Yu, Sevin, Kassab and Evleth in detail.[17]

Reaction (3) $CH + C^+ \rightarrow C_2^+ + H$. Figure 3 illustrates the potential energy surface of reaction scheme (3). The potential surface of reaction (3) is similar to reaction pathway (1). One should, however, note that reaction (3) involves two electronic states. When the ground state of the CH molecule ($^2\Pi$) linearly approaches to $C^+(^2P)$, the ground state of $CC^+(^4\Sigma^-)$[18] is expected to be formed via an intermediate species, $CCH^+(^3\Sigma)$. Since this intermediate $C_2H^+(^3\Sigma)$ is the excited state of C_2H^+,[19] a nonlinear path is necessary to produce the ground-state C_2H^+ ($^3\Pi$), although the energies of these two electronic states are very close. The potential energy between CH and C^+ is extremely attractive due to C–C bond formation. The result of the present calculation confirms that there is no energy barrier via either a linear or nonlinear pathway of reaction (3).

Since the energy difference between the ground state $^4\Sigma^-$ and lowest excited state $^2\Pi$ of C_2^+ is very small, electronically excited C_2^+ is also possible as a product after C–H bond cleavage.

Potential Energy Surface of Reaction (4) $C_2^+ + H_2 \rightarrow C_2H^+ + H$. We first tried the linear hydrogen abstraction pathway for the ground-state $CC^+(^4\Sigma^-)$. This reaction path has an energy barrier, and the electronic state correlates to the excited state of $C_2H^+(^3\Sigma)$. When the nonlinear pathway is chosen, the vinyliden-like intermediate $CCH_2^+(^4A_2)$ is found to be an energy minimum on the potential surface of the quartet state. The C-H bond dissociation of $CCH_2^+(^4A_2)$ species turns out to be the ground state of C_2H^+ ($^3\Pi$).

As shown in Fig. 4, the potential energy surface of the doublet state has a deep energy minimum of $C_2H_2^+(^2\Pi_u)$, in addition to the quartet surface. This stable doublet state is correlated from the excited state of the reactant, $C_2^+(^2\Pi)$ without an energy barrier. While the intermediate $C_2H_2^+(^4A_2)$ has only a vinylidene structure, the vinylidene-type $C_2H_2^+(^2A_1)$ is unstable and easily isomerizes to the acetylene cation radical.[20] The ground-sate C_2H^+ and H as the product of reaction (4) can be formed through both the ground state and the excited state of $C_2H_2^+$, even if the spin-forbidden transition from the quartet state to the doublet state is possible during the course of reaction (4).

Potential Energy Surface of Reaction (5) $C_2H^+ + H_2 \rightarrow C_2H_2^+ + H$. Figure 5 illustrates the potential energy surface of the reaction between the ground-state $C_2H^+(^3\Pi)$ and H_2 molecules to produce the acetylene cation radical and hydrogen atom. When two molecules, C_2H^+ and H_2, merge in a nonlinear pathway, there is a deep energy minimum of the triplet state of $C_2H_3^+$. The intermediate $C_2H_3^+$ ($^3A''$) is the excited state of the protonated acetylene. The ground state of protonated acetylene is correlated from the

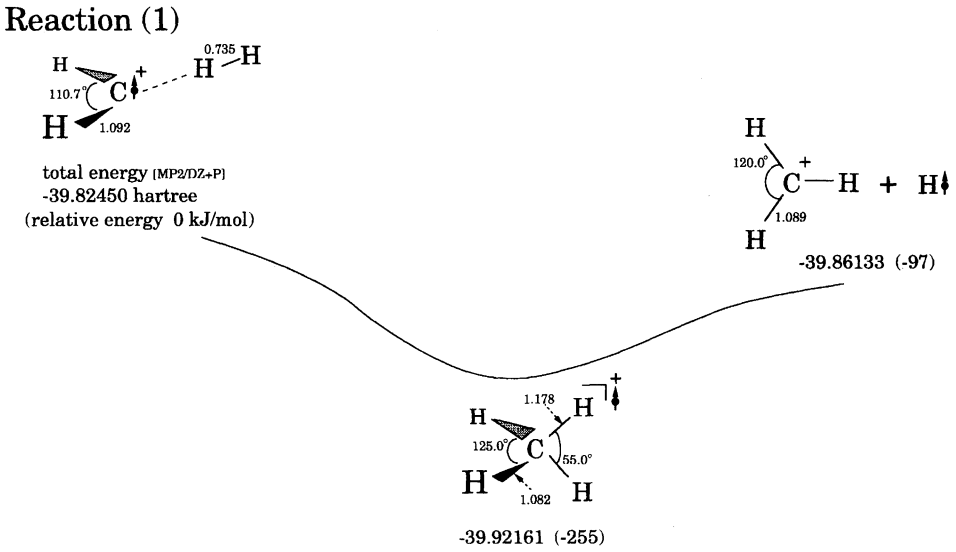

Fig. 2. Schematic potential energy surface for the reaction of CH_2^+ and H_2 to produce CH_3^+. The geometries and energies were obtained with MP2 method using DZ+P basis set. The Units of bond length, bond angle and energy are in Å, deg., and hartree. The relative energies in kJ mol^{-1} are shown in parentheses.

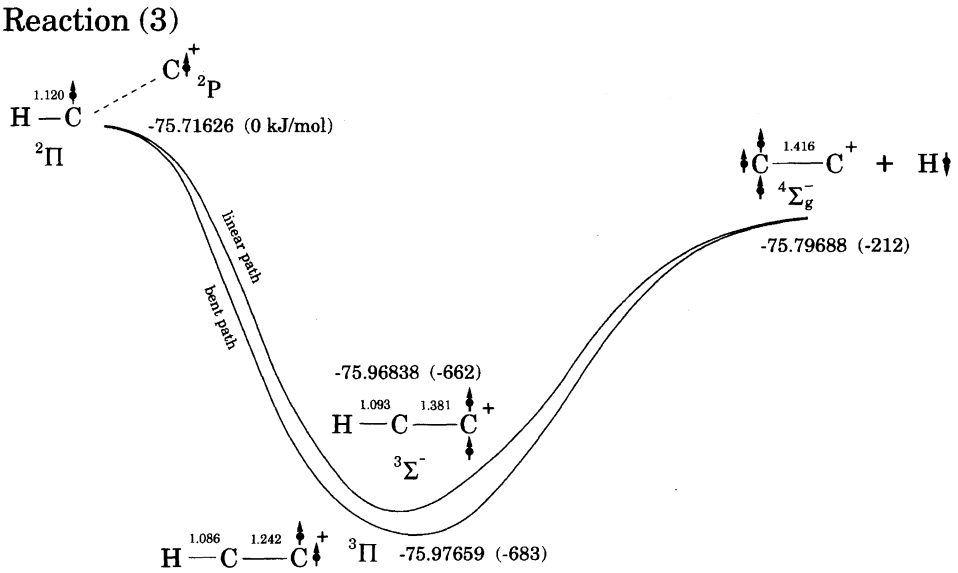

Fig. 3. Potential energy surface of the reaction of C^+ and CH calculated by the MP2/DZ+P method.

high-lying excited singlet state of C_2H^+. The potential energy surface of protonated acetylene has been discussed by many authors.[21] Whichever spin-forbidden transition from the triplet state to the singlet state of $C_2H_3^+$ is possible, a dissociation of the C–H bond leads to the ground state of $C_2H_2^+(^2\Pi)$ in both electronic states. This potential surface is very similar to the reactions discussed above.

When we used the HF method to obtain the linear hydrogen abstraction pathway, we found a stationary point having two imaginary frequencies. The MP2 calculation, however, indicates that there is a pathway for hydrogen abstraction without an energy barrier. This reaction path smoothly correlates to the ground-state $C_2H_2^+$.

Consequently, the formation of $C_2H_2^+$ has been confirmed to be possible without an energy barrier via either a direct hydrogen abstraction pathway or an energy-rich intermediate.

Dissociative Recombination Reaction (6) $C_2H_2^+ + e \rightarrow C_2H + H$. In the sequence of the reaction C_2^+ with hydrogen molecules, the acetylene cation radical is one of the terminal molecules which can not react with a hydrogen molecule further, although there is also a possibility for the formation of $C_2H_3^+$, as discussed by Yamashita and Herbst.[10] The following sequence to produce the observed species (C_nH (n=2—6)) should experience the neutralization process with an electron. The electron recombination of $C_2H_2^+$ causes C–H bond dissociation. The excess energy by producing a C_2H

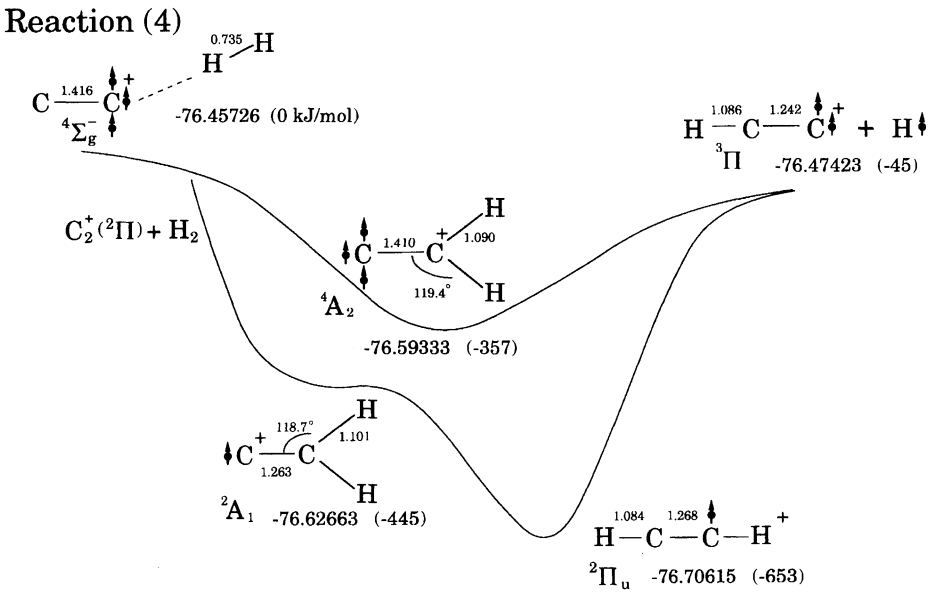

Fig. 4. Calculated potential energy surface of the reaction between C_2^+ and H_2 by using the MP2/DZ+P method.

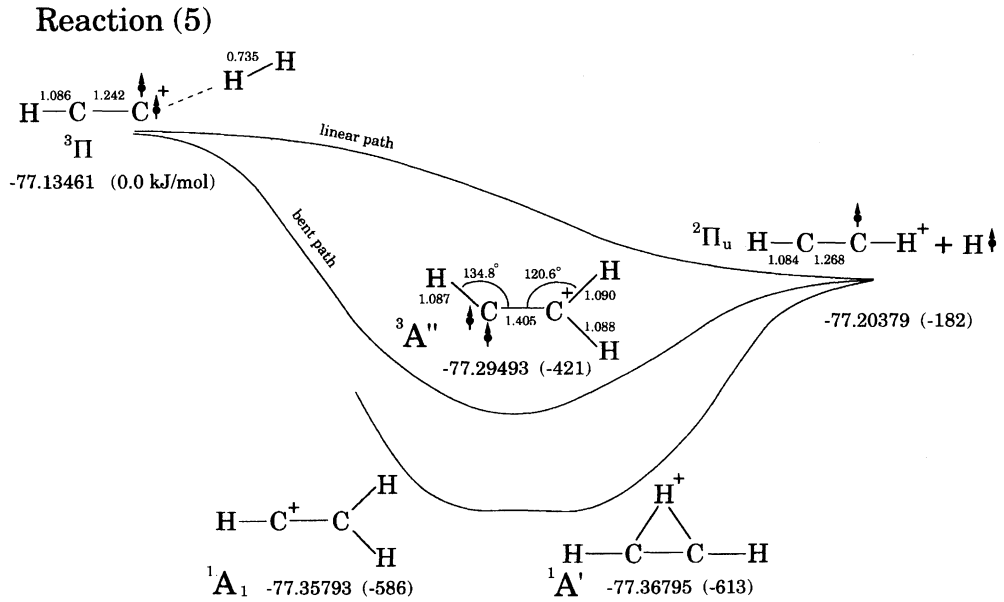

Fig. 5. Potential energy surface for the reaction of C_2H^+ and H_2 to produce the acetylene cation radical calculated with MP2/DZ+P method.

molecule was calculated to 464 kJ mol^{-1}. This energy may be used for a further dissociation to C_2 and a hydrogen atom. This process is also exothermic, as shown in Table 1. In this respect, the dissociative recombination of $C_2H_2^+$ involves two possible dissociation products, C_2H and C_2 molecules, which have been observed in carbon stars.[22]

Reactions (7) $C_2H+C^+ \rightarrow C_3^+ + H$. The potential energy surface of reaction (7) is illustrated in Fig. 6. The linear pathway for reaction (7) is the minimum energy path which smoothly connects the ground state of the reactant and the product via the C_3H^+ species. Since the intermediate C_3H^+ is a very stable closed-shell molecule, the excess energy gained by forming a C–C bond can be diverted to C–H bond-breaking.

It should be noted that the C_3^+ molecule produced by reaction (7) has two isomers, i.e., linear and cyclic.[23] A detailed *ab initio* study by Martin, Francois and Gijbels concluded that this molecule is extremely floppy and that the energy difference and barrier between the cyclic and linear structures is small.[24] It is very important that the structures of the C_3^+ product can be either linear or cyclic,[19] since linear and cyclic structures are observed for the interstellar C_3H molecule.[25] In this respect, we must consider both the linear and cyclic pathways of the reaction of C_3^+ and hydrogen molecules. The potential energy surfaces of additional ion-molecule reactions will be discussed in a separate paper.

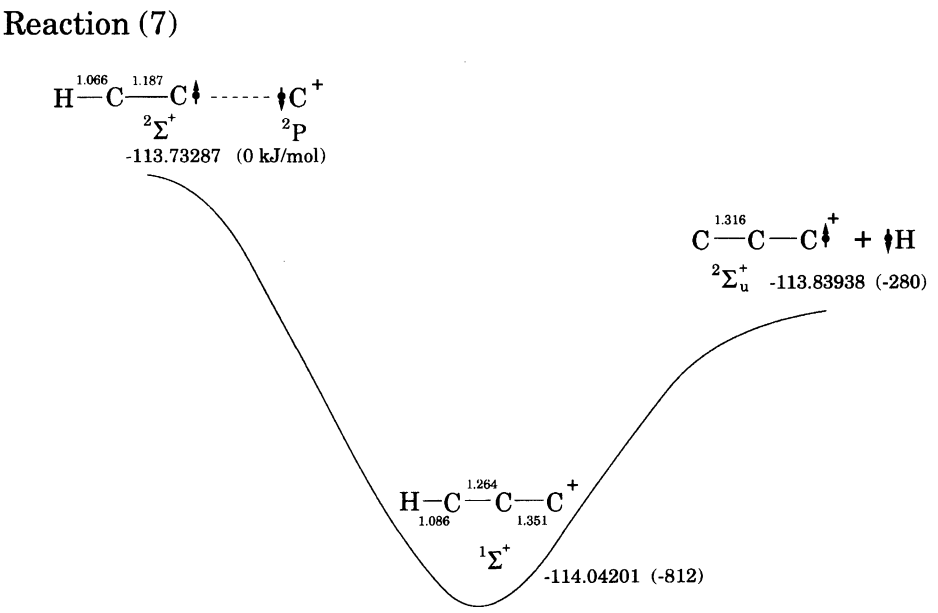

Fig. 6. Schematic potential energy surface for the reaction of C^+ and C_2H calculated by the MP2/DZ+P method.

Table 2. The Reaction Energies (kJ mol^{-1}) Calculated for Other Possible Processes
The positive value indicates that the reaction is exothermic, and the negative value indicates the endothermic reaction.

		HF/DZ	HF/DZ+P	MP2/DZ	MP2/DZ+P
(i)	$CH_2^+ + C \rightarrow C_2H^+ + H$	39	78	120	142
(ii)	$CH_3^+ + C \rightarrow C_2H_2^+ + H$	62	111	114	227
(iii)	$CH_3^+ + C \rightarrow C_2H^+ + H_2$	−49	7	28	46
(iv)	$CH + C^+ \rightarrow CH^+ + C$	65	68	22	27
(v)	$CH^+ + H_2 \rightarrow CH_2^+ + H$	113	105	66	52
(vi)	$CH + C_2^+ \rightarrow C_3^+(linear) + H$	79	56	446	450
	$\rightarrow C_3^+(cyclic) + H$	206	308	258	359
(vii)	$CH + C \rightarrow C_2 + H$	−236	−193	288	282

Other Possible Reactions. We have considered the reaction energies and potential energy surfaces for the ion–molecule reactions based on the scheme proposed by Suzuki. The processes discussed in the present paper are the main stream for the formation of interstellar hydrocarbon molecules. There should also be many additional processes or obstruction processes in the complex interstellar reactions. Table 2 depicts reactions which were calculated to be exothermic in the present study.

Processes (i)—(iii) are reactions with a neutral carbon atom. Process (iv) is a charge-transfer reaction due to the difference in the adiabatic ionization energies. The possibility of process (vi) is expected to be small. The probability of a collision of C_2^+ with H_2 is much larger than that with the CH molecule, due to the abundance ratio between H_2 and CH. Neutral–neutral reactions are generally less favorable than ion–molecule reactions. Although we have not examined each potential energy surface, these processes may contribute to the formation and destruction of hydrocarbon species in interstellar space.

Concluding Remarks. The *ab initio* potential energy surfaces for ion–molecule reactions (1)—(7) indicate that all of the processes involve a very attractive potential, leading to the formation of energy-rich intermediates during the course of the reactions. All of these reactions have been confirmed to have no energy barrier. It is not necessary to occur the reactions on a single potential energy surface. We have shown that reactions (3) and (5) especially proceed via the electronically excited state. It has been demonstrated that the potential energy surfaces for reactions (1)—(7) smoothly correlate to the products, even if spin-forbidden transitions are involved. Since the collision complex as an intermediate has an extremely high energy, the reaction would take place not only in the ground state, but also in several excited states. The presence of a stable intermediate in these reactions suggests the experimental difficulty in determining the rate constants, since without a very high vacuum the reaction can never proceed. It is also possible that such reactions produce electronically excited species, and that some radiative transition is necessary to give the final products. Consequently, we can conclude that the reaction schemes proposed by the late H. Suzuki are possible, and are

very probable for the formation of interstellar hydrocarbon molecules, CH and C_2H, as well as some other species.

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