

(*E*)-3,3,3-Trifluoro-1-phenylpropene. In the above reaction, zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl bromide (3.0 g, 20 mmol), *trans*- β -bromostyrene (1.83 g, 10 mmol), and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) in tetrahydrofuran (25 mL) were used. Distillation gave (*E*)-3,3,3-trifluoro-1-phenylpropene in 42% yield, bp 70–72 °C (25 mmHg).

3,3,3-Trifluoro-1-phenylpropene from Phenylacetylene. A flask, equipped with a dry ice-acetone reflux condenser, containing commercially available zinc powder (1.30 g, 0.02 g-atom) and copper(I) iodide (0.72 g), trifluoromethyl bromide (3.0 g, 20 mmol), and phenylacetylene (1.02 g, 10 mmol) in tetrahydrofuran (30 mL), is irradiated for 2 h in the water bath of an ultrasound laboratory cleaner. Then, the solution was poured into a 2% HCl solution and an oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 3,3,3-trifluoro-1-phenylpropene in a yield of 55% (1.11 g), bp 71–73 °C (25 mmHg).

5,5,5-Trifluoro-2-methyl-2-pentene. In the above reaction, zinc powder

(1.30 g, 0.02 g-atom), dichlorobis[π -cyclopentadienyl]titanium (0.25 g, 1 mmol), trifluoromethyl iodide (2.25 g, 12 mmol) and isoprene (3.06 g, 45 mmol) in tetrahydrofuran (30 mL) were used. Distillation gave 5,5,5-trifluoro-2-methyl-2-pentene in 56% yield, bp 102–105 °C. ^{19}F NMR (CDCl_3) δ 0.5 (CF_3 , t, $J_{\text{CF}_3-\text{CH}_2} = 5.2$ Hz). ^1H NMR (CDCl_3) δ 2.06, 2.09 ($\text{CH}_3 \times 2$), 4.48 ($\text{CH}=\text{C}$), 2.70 (CH_2 , d q, $J_{\text{CH}_2-\text{CH}} = 3$ Hz)

(-)-2-(Trifluoromethyl)pentan-3-one. A flask equipped with a dry ice-acetone reflux condenser, containing zinc powder (2.60 g, 0.04 g-atom), trifluoromethyl iodide (4.3 g, 22 mmol), optically active enamine (6, $\text{R}_1 = \text{C}_2\text{H}_5$, $\text{R}_2 = \text{CH}_3$ 5.5 g, 30 mmol), and dichlorobis[π -cyclopentadienyl]titanium (0.5 g, 2 mmol) in *N,N*-dimethylformamide (30 mL), was irradiated in the water bath (50–60 °C) of an ultrasound laboratory cleaner (45 kHz, 100 W) for 3 h. Then, the solution was poured into a 40% H_2SO_4 solution and an oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave (-)-2-trifluoromethylpentan-3-one, bp 65–68 °C (140 mmHg).

A Theoretical Evaluation of the Mechanism of Acetylene Formation in the Reactions of Atomic Carbon with Hydrocarbons

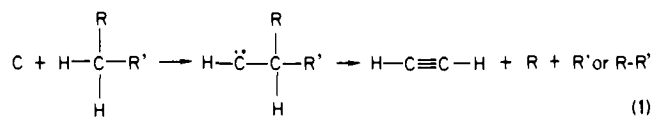
Michael L. McKee* and Philip B. Shevlin

Contribution from the Department of Chemistry, Auburn University, Auburn, Alabama 36849.
Received February 4, 1985

Abstract: A study has been made of the C_2H_4 potential energy surface, for the reaction of atomic C with CH_4 , in which energies are calculated at the MP3/6-31G** level and zero-point energies are included at the 3-21G basis set level. The reaction of $\text{C}(^3\text{P})$ with CH_4 on the lowest triplet surface and the reaction of $\text{C}(^1\text{D})$ on the two lowest singlet surfaces have been followed. The observed acetylene formation from nucleogenic carbon atoms and methane is calculated to occur via the formation of the $^1\text{A}'$ excited singlet state of ethylidene from $\text{C}(^1\text{D})$ which sequentially eliminates two hydrogen atoms. Several other pathways to acetylene were found to be unimportant due to high barriers or to rapid vibrational deexcitation to ethylene.

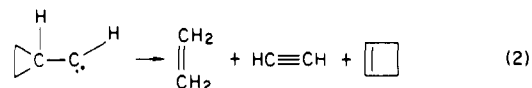
Of the many interesting reactions that have been reported for atomic carbon,¹ perhaps the most intriguing is the formation of acetylene in the reaction of carbon atoms with compounds containing C–H bonds. In the case of ^{11}C atoms produced by nuclear reaction,^{1d,e} this process must involve the reaction of a single atom of carbon. There are not sufficient atoms of ^{11}C generated to allow dimerization to C_2 and subsequent hydrogen abstraction to give C_2H_2 , a process that is important when C_2 is generated directly in a carbon arc.^{1a}

The mechanism most often proposed² for the production of C_2H_2 in the reaction of C_1 with saturated hydrocarbons involves initial insertion of C_1 into a CH bond generating a carbene which subsequently cleaves to C_2H_2 and other fragments as shown in eq 1. This mechanistic interpretation is weakened by the fact that



carbenes, when generated by conventional methods, generally do

not cleave the two bonds β to the carbene carbon to give C_2H_2 but undergo 1,2 migration to give an olefin.³ A notable exception is the cyclopropyl carbene, which cleaves and rearranges as shown in eq 2.^{4,5} In this case, relief of ring strain undoubtedly provides a thermodynamic driving force. Thus, such β -cleavages of



carbenes are possible and may occur in the highly exothermic reactions of atomic carbon. It is of interest that a study of the reaction of ^{11}C atoms with saturated hydrocarbons showed that cyclopropane gave the highest yield of $\text{H}^{11}\text{C}=\text{CH}$.⁶

Another factor which must be considered in the process shown in eq 1 is the electronic state of the reacting carbon and of the resultant carbene. Carbon atoms may react in any of three states: $\text{C}(^3\text{P})$ ($\Delta H_f = 171$ kcal/mol), $\text{C}(^1\text{D})$ ($\Delta H_f = 201$ kcal/mol), and $\text{C}(^1\text{S})$ ($\Delta H_f = 232$ kcal/mol). However, it has been proposed that $\text{C}(^3\text{P})$ and $\text{C}(^1\text{D})$ rather than $\text{C}(^1\text{S})$ serve as acetylene precursors in these systems^{2,7} and that $\text{C}(^1\text{S})$ is rather unreactive in general.⁸ Consequently, we have considered three electronic surfaces on which carbon can insert into the C–H bond. The triplet surface,

(1) For reviews of the chemistry of atomic carbon, see: (a) Skell, P. S.; Havel, J. J.; McGlinchey, M. J. *Acc. Chem. Res.* 1973, 6, 97–105. (b) MacKay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. I, pp 1–36. (d) Wolf, A. P. *Adv. Phys. Org. Chem.* 1964, 2, 202. (e) Wolfgang, R. *Prog. React. Kinet.* 1965, 3, 97.

(2) Taylor, K. K.; Ache, H. J.; Wolf, A. P. *J. Am. Chem. Soc.* 1976, 98, 7176 and reference cited therein.

(3) Kimmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971.

(4) Shevlin, P. B.; Wolf, A. P. *J. Am. Chem. Soc.* 1966, 88, 4735.

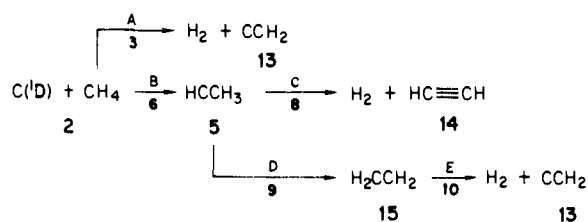
(5) Friedman, L.; Shelter, H. *J. Am. Chem. Soc.* 1960, 82, 1002.

(6) Welch, M. J.; Wolf, A. P. *J. Am. Chem. Soc.* 1969, 91, 6584.

(7) Finn, R. D.; Ache, H. J. *Radiochim. Acta* 1972, 17, 131.

(8) Donovan, R. J.; Husain, D. *Chem. Rev.* 1970, 70, 489.

Scheme I



which correlates $\text{C}({}^3\text{P}) + \text{CH}_4$ and the ${}^3\text{A}''$ state of HCCH_3 , was studied as well as two surface arising from singlet coupling of electrons. The surface designated ${}^1\text{A}'$ connects one microstate of $\text{C}({}^1\text{D})$ and CH_4 to the ground state of HCCH_3 (${}^1\text{A}'$), while the other singlet surface designated ${}^1\text{A}''$ connects another microstate of $\text{C}({}^1\text{D})$ and CH_4 with a low-lying singlet excited state of HCCH_3 of ${}^1\text{A}''$ symmetry which can be derived from the ground state by excitation of one electron from the occupied orbital on the carbon to the empty p orbital perpendicular to the molecular plane. The triplet surface will be referred to as the ${}^3\text{A}''$ surface while the singlet surfaces will be designated the ${}^1\text{A}'$ or closed-shell surface and the ${}^1\text{A}''$ or open-shell surface, respectively. However, particular points on these surfaces may correspond to electronic states with higher or lower symmetry than these designation indicate. The closed-shell singlet surface refers to the ground-state singlet obtained from a restricted Hartree-Fock solution, while the open-shell singlet surface refers to an unrestricted Hartree-Fock solution obtained from exciting one electron from the HOMO to the LUMO. If the HOMO and LUMO are of different symmetries, such a solution will approximate the lowest excited state. Since the unrestricted Hartree-Fock method does not produce wave functions which give good quantum numbers for the spin-squared operator, the desired solution is often contaminated with solutions of higher multiplicities.

It is proposed that CH insertion could produce a carbene in any one of three multiplicities and the probability of the cleavage could be dictated by the electronic state of the carbene. This proposal is in accord with theoretical⁹⁻¹⁴ and experimental¹⁵ studies that demonstrates a higher barrier for 1,2 migration in triplet carbenes than in the ground-state singlets. Thus cleavage may become competitive with migration in some open-shell carbenes.

In order to attempt to elucidate the mechanism of C_2H_2 formation in the reactions of C_1 , we have carried out detailed ab initio studies on the reaction of carbon atoms with the representative hydrocarbon methane. The goal of these studies has been to answer the following questions: (1) Is there an energetically accessible alternate to the pathway shown in eq 1 for C_2H_2 production? (2) If not, what are the energetics of C_2H_2 formation? (3) Which electronic states of carbon are most likely to be the precursors of C_2H_2 ?

Method of Calculations

The GAUSSIAN 82 program was used throughout.¹⁶ Geometries are optimized by using the 3-21G basis set at the single configurational level

(9) (a) Altmann, J. A.; Csizmadia, I. G.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 4196. (b) Kohler H. J.; Lischka, H. *J. Am. Chem. Soc.* **1982**, *104*, 5884.

(10) Harding, L. B. *J. Am. Chem. Soc.* **1981**, *103*, 7469.

(11) (a) Ahmed, S. N.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 3942. (b) McPherson, D. W.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1983**, *105*, 6493.

(12) (a) Blint, R. J.; Newton, M. D. *Chem. Phys. Lett.* **1975**, *32*, 178. (b) Harding, L. B. *J. Phys. Chem.* **1983**, *87*, 441.

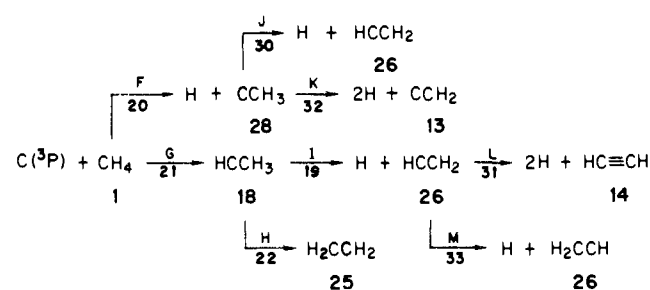
(13) Harding, L. B. *J. Phys. Chem.* **1981**, *85*, 10.

(14) Pople, J. A.; Raghavachari, K.; Frisch, M. J.; Binkley, J. S.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 6389.

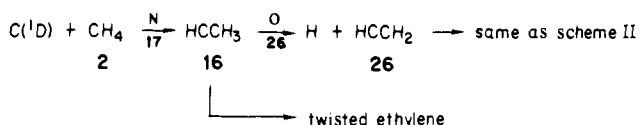
(15) Sohn, M. B.; Jones, M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 8280.

(16) References to basis sets used are collected here. The program package GAUSSIAN 82 was used throughout: Carnegie-Mellon University, Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R. Pople, J. A. 3-21G basis: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. 6-31G** basis: Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 212. MP2, MP3 correlation treatment: Møller, C.; Plesset M. S. *Phys. Rev.* **1934**, *46*, 618. Pople, J. A.; Binkley, J. S.; Seeger, R., *Int. J. Quantum Chem., Sym.* **1976**, *10*, 1. CPHF: Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem., Symp.* **1979**, *13*, 225.

Scheme II



Scheme III



with the restricted Hartree-Fock formalism for closed-shell systems and the unrestricted Hartree-Fock formalism for open-shell systems. Single-point calculations are made by using the 6-31G** basis (d functions on carbon and p functions on hydrogen) with correlation estimated at the MP2 and MP3 perturbation levels. Vibrational frequencies are calculated at the 3-21G level by using the CPHF method and are used to characterize stationary points and to calculate zero-point energies.

Table I contains the relative energies of all reported species where a species notation has been assigned and used consistently throughout. Absolute energies are given in Table II along with zero-point energies and the number of calculated negative vibrational frequencies.

Several geometries at the 3-21G level were taken from the Carnegie-Mellon Quantum Chemistry Archive.¹⁷ The same species notation used in Tables I and II is used in Scheme I-III and in Figures 1 and 2. Schemes I-III diagram the reactions on the ${}^1\text{A}'$, ${}^3\text{A}''$, and ${}^1\text{A}''$ surfaces, respectively, Figure 1 shows geometries of relevant species, and Figure 2 combines the MERP (minimum energy reaction path) for all three surfaces. Table III contains the barriers in kcal/mol for the reactions in Schemes I-III. All relative energies unless otherwise indicated refer to calculations at the MP3/6-31G** level with zero-point corrections included at the 3-21G level. This investigation illustrates the use of high-level ab initio calculations to elucidate reaction mechanisms in a system with a number of rather complex energy surfaces.

Results and Discussion

Initial Reaction of Carbon with Methane. Unlike the reaction between carbon and water^{11a} or ammonia,^{11b} but like the reaction between carbon and H_2 ,¹² no stable complex between C and CH_4 could be located for any electronic state of carbon. This is not surprising as such a complex would involve the donation of an electron pair in a relatively high energy HOMO to an unoccupied or singly occupied p orbital on carbon. While H_2O or NH_3 has such an electron pair available to form a complex (eq 3), CH_4 obviously does not.



Two stationary points, however, were located, one on the ${}^1\text{A}'$ surface (12) and one on the ${}^3\text{A}''$ surface (24), corresponding to an end-on approach of $\text{C}({}^1\text{D})$ and $\text{C}({}^3\text{P})$, respectively. The stationary points, 12 and 24 (both yield three imaginary frequencies), are 92.0 and 82.3 kcal/mol higher than methane and $\text{C}({}^1\text{D})$ or $\text{C}({}^3\text{P})$, respectively.

Since no state of carbon is predicted to form a stable complex with CH_4 , we examined the reaction pathways available between methane and carbon in the $\text{C}({}^3\text{P})$ and $\text{C}({}^1\text{D})$ electronic states. The $\text{C}({}^1\text{S})$ state is thought to be relatively unreactive.^{2,8}

Initial Reactions of $\text{C}({}^1\text{D})$ on the ${}^1\text{A}'$ surface (Scheme I). To correctly describe the $\text{C}({}^1\text{D})$ state of carbon one needs to take a linear combination of configurations.²⁰ Since this cannot be done

(17) "Carnegie-Mellon Quantum Archive", 2nd ed.; Whiteside, R. A., Frisch, M. J., Binkley, J. S., DeFrees, D. J., Schlegel, H. B., Raghavachari, K., Pople, J. A., Eds.; Carnegie-Mellon University, Pittsburgh, PA, 1981.

(18) Husain, D.; Krisch L. J. *Trans. Faraday Soc.* **1971**, *27*, 2886.

(19) Husain, D.; Newton, D. P. *J. Chem. Soc., Faraday Trans. 2*, **1982**, *78*, 51.

Table I. Relative Energies (kcal/mol) at the MP3/6-31G** Level for Species Optimized at the 3-21G Level on the C₂H₄ Potential Energy Surface

species notation	molecular symmetry	electronic symmetry	description	rel energy (including ZPC)	exptl rel energy ^a
1	<i>K</i> , <i>T_d</i>	³ P, ¹ A ₁	C(³ P) + methane	0.0 (0.0)	12.8
2	<i>K</i> , <i>T_d</i>	¹ D, ¹ A ₁	C(¹ D) + methane (assumed)	30.0	42.8
3	<i>C_s</i>	¹ A'	TS (C(¹ D) + CH ₄ → CCH ₂ + H ₂)	67.9 (62.5)	
4	<i>C₁</i>	¹ A	carbene (lower symmetry)	-53.1 (-51.8)	
5	<i>C_s</i>	¹ A'	carbene	-52.8 (-51.9)	
6	<i>C_s</i>	¹ A'	C(¹ D) insertion TS (1 NEV) ^b	40.6 (38.7)	
7	<i>C_s</i>	¹ A'	C(¹ D) insertion (2 NEV)	43.7 (41.4)	
8	<i>C_s</i>	¹ A'	TS (HCCH ₃ → HCCH + H ₂)	-7.8 (-10.2)	
9	<i>C₁</i>	¹ A'	1,2 migration in carbene	-50.7 (-50.4)	
10	<i>C_s</i>	¹ A'	TS (H ₂ CCH ₂ → CCH ₂ + H ₂)	-27.6 (-29.8)	
11	<i>C_{2v}</i>	¹ A'	double bridged stationary point	84.2 (83.2)	
12	<i>C_{2v}</i>	¹ A'	end-on carbon approach	128.6 (122.0)	
13	<i>C_{2v}</i> , <i>D_{∞h}</i>	¹ A ₁ , ¹ Σ _g ⁺	CCH ₂ + H ₂	-36.0 (-42.9)	
14	<i>D_{∞h}</i> , <i>D_{∞h}</i>	¹ Σ _g ⁺ , ¹ Σ _g ⁺	HCCH + H ₂	-78.2 (-82.8)	-86.0
15	<i>D_{2h}</i>	¹ A _g	H ₂ CCH ₂	-132.2 (-127.7)	-127.7
16	<i>C_s</i>	¹ A''	carbene (open shell)	-45.7 (-44.3)	
17	<i>C_s</i>	¹ A''	C(¹ D) insertion TS (open shell)	45.8 (41.0)	
18	<i>C_s</i>	³ A''	carbene (triplet)	-64.9 (-63.2)	
19	<i>C₁</i>	³ A	TS (HCCH ₃ → HCCH ₂ + H)	-9.3 (-14.2)	
20	<i>C_s</i>	³ A''	TS (C(³ P) + CH ₄ → CCH ₃ + H)	76.2 (71.9)	
21	<i>C_s</i>	³ A''	C(³ P) insertion TS	38.7 (33.9)	
22	<i>C₁</i>	³ A	1,2 migration in carbene (triplet)	-9.6 (-12.4)	
23	<i>C_{2v}</i>	³ A ₂	double bridged stationary point	42.2 (35.1)	
24	<i>C_{4v}</i>	³ A ₂	end-on carbon approach (triplet)	89.7 (82.3)	
25	<i>D_{2d}</i>	³ A ₁	H ₂ CCH ₂ (staggered)	-67.8 (-67.9)	
26	<i>K</i> , <i>C_s</i>	² S, ² A'	H + HCCH ₂ (σ radical)	-11.6 (-17.4)	-19.1
27	<i>C_{∞v}</i> , <i>D_{3h}</i>	² Π, ² A ₂	CH + CH ₃	34.4 (27.8)	36.1
28	<i>K</i> , <i>C_s</i>	² S, ² A'	H + CCH ₃ (² A')	32.4 (25.5)	
29	<i>K</i> , <i>C_s</i>	² S, ² A''	H + CCH ₃ (² A'')	35.1 (28.9)	
30	<i>K</i> , <i>C_s</i>	² S, ² A''	H + TS (CCH ₃ → HCCH ₂)	44.3 (34.6)	
31	<i>K</i> , <i>C_s</i>	² S, ² A'	H + TS (HCCH ₂ → HCCH + H)	38.8 (26.6)	
32	<i>K</i> , <i>C_s</i>	² S, ² A'	H + TS (CCH ₃ → CCH ₂ + H)	79.4 (67.1)	
33	<i>K</i> , <i>C_{2v}</i>	² S, ² B ₂	H + TS (HCCH ₂ → H ₂ CCH)	41.4 (31.3)	
34	<i>K</i> , <i>C_s</i>	² S, ² A'	H + TS (CCH ₃ → HCCH ₂)	88.5 (78.6)	
35	<i>K</i> , <i>C_s</i>	² S, ² A'	H + HCCH ₂ (π radical)	48.3 (40.2)	
36	<i>K</i> , <i>C_{2v}</i>	² S, ² B ₂	H + HCCH ₂ (linear HCC)	-5.1 (-12.7)	
37	<i>C_{∞v}</i> , <i>D_{3h}</i>	⁴ Σ, ² A ₂	CH + CH ₃	43.1 (37.2)	
38	<i>C_{3v}</i>	³ A ₁	C(³ P) abstraction TS	37.6 (33.3)	
39	<i>C_s</i>	³ A'	C(³ P) abstraction TS	43.8 (38.0)	

^a Enthalpies from: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; John Wiley & Sons: New York, 1976. For purposes of comparing, the experimental relative energies are compared to ethylene which was given a value of -127.7 kcal/mol. ^b Number of negative eigenvalues from vibrational frequency calculation.

with the single configurational method used here, we chose to use C(³P) as the reference state and add to it the experimental C(³P) - C(¹D) separation of 30 kcal/mol to determine the energy of the C(¹D) state. With use of the assumed state separation, C(¹D) is predicted to react with methane to generate the closed-shell ethylidene, **5** (Table I and Scheme I), in a reaction calculated to be exothermic by 81.9 kcal/mol. Although the heat of formation of **5** has not been measured, one may estimate the experimental ΔH_f for the insertion of C(¹D) to be 81.4 ± 10 kcal/mol.²¹ The calculated barrier to C-H insertion is 8.7 kcal/mol (barrier B, Table III). The transition state, **6**, involves a very long nascent C-C bond (2.12 Å) with the transferring hydrogen nearly equidistant between the two carbons (1.31, 1.29 Å). A second stationary point, **7**, was located for the carbon insertion reaction which was 2.7 kcal/mol higher than that for **6**. A vibrational analysis resulted in two imaginary frequencies indicating that **7** is not a true transition state. The two structures **6** and **7** were obtained by allowing C(¹D) to approach in a region exterior (**6**) or interior (**7**) to the angle swept out by methyl carbon and the two hydrogens in the molecular plane. It should be pointed out that the barriers represented by **6** and **7** may be lower than that

calculated due to the fact that they, like C(¹D), should be calculated by a multiconfigurational method.

Interestingly, the 3-21 global minimum for ethylidene is a *C₁* structure, **4**, which remains 0.3 kcal/mol more stable at the MP3/6-31G** level. When zero-point corrections are made, however, the *C_s* structure, **5**, becomes 0.1 kcal/mol more stable than **4** and therefore **5** will be used henceforth to compare relative energies for ethylidene.²³

The possibility that vinylidene could be involved in the formation of C₂H₂ via the reaction **2** → **13** in Scheme I was also examined. The transition state, **3**, is characterized by a concerted loss of H₂ in which one of the departing hydrogens is bridging both carbons. Although correlation has a large effect on the barrier, reducing it by almost 40 kcal/mol (barrier A, Table III), the final barrier including zero-point corrections (32.5 kcal/mol) is still too large to be competitive with C-H insertion (8.7 kcal/mol).

In contrast to insertion followed by migration to give ethylene, a concerted reaction is possible which will give ethylene directly from C(¹D) and methane. A stationary point corresponding to this direct reaction has been found (**11**); however, the 3-21G vibrational frequencies revealed two negative modes. The stationary point of *C_{2v}* symmetry is 53.2 kcal/mol above C(¹D) plus methane.

(20) The energy of an open-shell singlet carbon is calculated to be 17.1 kcal higher than C(³P) at the UMP3/6-31G** level, while a closed-shell singlet carbon is 46.3 kcal higher than C(³P). The actual energy of C(¹D) is between these values.

(21) The ΔH_f of **5** of 101.8 kcal/mol was estimated by subtracting the difference in energy between methane and ethane from the ΔH_f of CH₂(¹A₁) which in turn was estimated from the ΔH_f of CH₂(³B₁)²² and the theoretical singlet-triplet splitting.

(22) The ΔH_f of CH₂(³B₁) is taken as 93.6 kcal/mol. Lengel, R. K.; Zare, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 7495.

(23) Calculations at a higher level (MP4SDTQ/6-31G**//6-31G*) including zero-point correction (6-31G*) predict that the *C₁* structure is 0.2 kcal/mol lower than the *C_s* structure (see ref 14).

Table II. Absolute Energies (–hartrees) at Different Levels of Theory and Zero-Point Energy (kcal/mol) at the 3-21G Level^a

species notation	3-21G	6-31G**	MP2/6-31G** ^b	MP3/6-31G** ^b	ZPE ^c
1 ^e	77.45795	77.88256	78.09758	78.12919	30.12 (0)
2 ^e					
3	77.25389	77.71499	77.99161	78.02093	24.66 (1)
4	77.48509	77.92885	78.18424	78.21385	31.45 (0)
5 ^e	77.48475	77.92842	78.18356	78.21332	31.06 (1)
6	77.33916	77.77096	78.03322	78.06445	28.20 (1)
7	77.33473	77.76579	78.02803	78.05948	27.78 (2)
8 ^e	77.38841	77.83898	78.11959	78.14162	27.70 (1)
9 ^e	77.45189	77.90977	78.18634	78.20997	30.38 (1)
10	77.40892	77.86175	78.14953	78.17314	27.92 (1)
11	77.21170	77.68355	77.97520	77.99495	29.06 (2)
12	77.17221	77.62669	77.89466	77.92420	23.45 (3)
13 ^e	77.45746	77.89865	78.15846	78.18662	23.22 (0)
14 ^e	77.51892	77.95310	78.23724	78.25388	25.52 (0)
15 ^e	77.60099	78.03881	78.31664	78.33982	34.57 (0)
16	77.49108	77.93239	78.17336	78.20208	31.53 (1)
17	77.36917	77.80291	78.02412	78.05614	25.26 (1)
18 ^e	77.53370	77.97035	78.20584	78.23263	31.88 (0)
19	77.45826	77.89261	78.11989	78.14400	25.28 (1)
20	77.33675	77.76147	77.97809	78.00769	25.74 (1)
21	77.38400	77.81764	78.03586	78.06751	25.35 (1)
22 ^e	77.42444	77.87146	78.11852	78.14443	27.29 (1)
23	77.33099	77.77990	78.03594	78.06199	23.05 (2)
24	77.25837	77.70889	77.95973	77.98622	22.69 (3)
25 ^e	77.53160	77.97160	78.20871	78.23717	29.96 (0)
26 ^e	77.45899	77.89411	78.12396	78.14766	24.29 (0)
27 ^e	77.39452	77.83133	78.03992	78.07442	23.59 (0)
28 ^e	77.38770	77.82496	78.04945	78.07552	23.22 (1)
29 ^e	77.38856	77.82661	78.04604	78.07327	23.95 (0)
30	77.33640	77.79063	78.03531	78.05853	20.40 (1)
31	77.37759	77.80732	78.05074	78.06729	17.92 (1)
32	77.31806	77.75420	77.97742	78.00264	17.82 (1)
33 ^e	77.33371	77.78220	78.04566	78.06318	20.03 (1)
34	77.27473	77.72433	77.96080	77.98810	20.24 (1)
35	77.35558	77.79881	78.02448	78.05218	21.98 (0)
36 ^e	77.44757	77.88175	78.11351	78.13730	22.50 (1)
37 ^e	77.41321	77.84286	78.03190	78.06043	24.27 (0)
38	77.40264	77.82838	78.03956	78.06925	25.86 (1)
39	77.37743	77.80651	78.02602	78.05939	25.28 (1)
C(³ P) ^a	37.48107	37.68086	37.73297	37.74636	0.00 (0)
H ₂	1.12296	1.13133	1.15766	1.16316	6.66 (0)
H	0.49620	0.49823	0.49823	0.49823	0.00 (0)
CH (² π)	38.05191	38.26688	38.34723	38.36426	4.12 (0)
CH (⁴ Σ)	38.07060	38.27841	38.33921	38.35027	4.80 (0)
CH ₃	39.34261	39.56445	39.69269	39.71016	19.47 (0)

^aIn order to determine energies of individual species the energies of C(³P), H₂, H, CH, and CH₃ are given here. ^bFrozen core approximation. ^cZero-point energy. In parentheses is given the number of calculated imaginary modes. ^dNo calculations were made on C(¹D). The energy of C(¹D) was assumed to be 30 kcal/mol greater than that of C(³P). ^eGeometry available at the 3-21G level from the Carnegie-Mellon Chemistry Archive, see ref 17.

Initial Reaction of C(³P) on the ³A'' Surface (Scheme II) and C(¹D) on the ¹A'' Surface (Scheme III). The insertion reaction of C(³P) with CH₄ to form triplet ethylidene, **18**, is found to occur with a barrier of 33.9 kcal/mol (barrier G, Scheme II). The transition state, **21**, contains an exceptionally long forming C–C bond (2.57 Å). In fact, the transition vector is made up predominantly of the migrating hydrogen motion while the carbons indicate little relative motion in the transition state. In this sense the insertion mechanism might equally well be viewed as abstraction followed by addition. To address the distinction between the two mechanisms one would need to determine the crucial geometries at a higher level of theory, including polarization and possibly correlation as well.

An additional triplet transition state of C_{3v} symmetry (**38**) connecting C(³P) + CH₄ and CH(⁴Σ) + CH₃ (**1** → **37**) was located. This transition state (**38**) is similar in geometry to the ³A'' insertion/abstraction transition state, **21**, with transferring CH distances of 1.21 and 1.51 Å. The much larger spin-squared value of **38** relative to **21** (2.71 and 2.34, respectively, compared to an expected value of 2.00) indicates that the former is a transition state to products with greater unpairing of spins (i.e., CH(⁴Σ) + CH₃). In contrast to **21**, the triplet transition state **38** corresponds unambiguously to abstraction of a hydrogen and at the highest level of computation the transition state is calculated to be lower in energy than open-shell products. The best estimate for the barrier to the products, **37**, is then simply the difference in energy between **1** and **37** or 37.2 kcal/mol.

A transition state of C_s symmetry on the ³A' surface, **39**, connecting **1** and **27** was located which was 38.0 kcal/mol above **1**. The geometry is very similar to that of **38** with transferring CH distances of 1.29 and 1.57 Å and only a slight distortion from C_{3v}. The structure **39** is related to the electron configuration of **38** by promoting one electron in the singly occupied e orbital to an a₁ orbital thereby leading to a Jahn–Teller distortion. As the abstraction proceeds the unpaired electron in an a' orbital can couple with the hydrogen atom leading to formation of CH(²Σ) rather than the less stable CH(⁴Σ). In summary C(³P) can abstract a hydrogen to form open-shell products, **27** or **37**, or it can insert to form carbene **18**. However, these processes all have barriers in the range of 34–38 kcal/mol and will only be important for highly energetic carbon atoms.

Hydrogen abstraction by C(¹D) to generate CH + CH₃, **27**, was found to proceed with an exothermicity of 2.2 kcal/mol (experimental 6.7 kcal/mol). Although we have not calculated a direct transition state to **27**, the carbon insertion transition states on the ¹A'' and ³A'' surfaces, **17** and **21**, closely resemble a complex of CH and CH₃ and further indicate that abstraction may compete with insertion on the ¹A'' and ³A'' surfaces.

A stationary point (**23**) corresponding to a concerted addition of C(³P) to CH₄ giving triplet ethylene was located 35.1 kcal/mol above C(³P) plus methane or only 1.2 kcal/mol higher than the insertion barrier which is the lowest energy process for reaction

Table III. Tabulated Barrier Heights (kcal/mol) for Reactions in Schemes I–III at Different Basis Set Levels

	barrier ^a	3-21G	6-31G**	MP2/6-31G**	MP3/6-31G**	MP3/6-31G** + ZPC
A	2 → 13	98.0	75.1	36.5	37.9	32.5
B	2 → 5	44.5	40.0	10.4	10.6	8.7
C	5 → 14	60.7	56.4	45.3	45.0	41.6
D	5 → 15	20.8	12.0	–1.7	2.1	1.4
E	15 → 13	90.1	87.9	99.2	104.6	97.9
F	1 → 28	76.0	76.0	75.0	76.2	71.9
G	1 → 18	46.4	40.7	38.7	38.7	33.9
H	18 → 25	68.6	62.0	54.8	55.3	50.8
I	18 → 26	47.3	48.8	53.9	55.6	49.0
J	28 → 26	32.2	21.5	8.9	11.9	9.1
K	28 → 13	43.7	44.4	45.2	47.0	41.6
L	26 → 14	51.1	54.4	45.9	50.4	44.0
M	26 → 26	78.6	70.2	49.1	53.0	48.7
N	2 → 16	25.7	20.0	16.1	15.8	11.0
O	16 → 26 ^b	28.2	12.1	19.1	22.0	15.0

^aLetters and boldfaced numbers correspond to those in Schemes I–III. ^bAt the 3-21G level there was no transition state to the elimination of hydrogen. The barrier at all levels was therefore computed as the difference between reactants and products minus a 11.9 kcal/mol correction due to spin contamination of **16**.

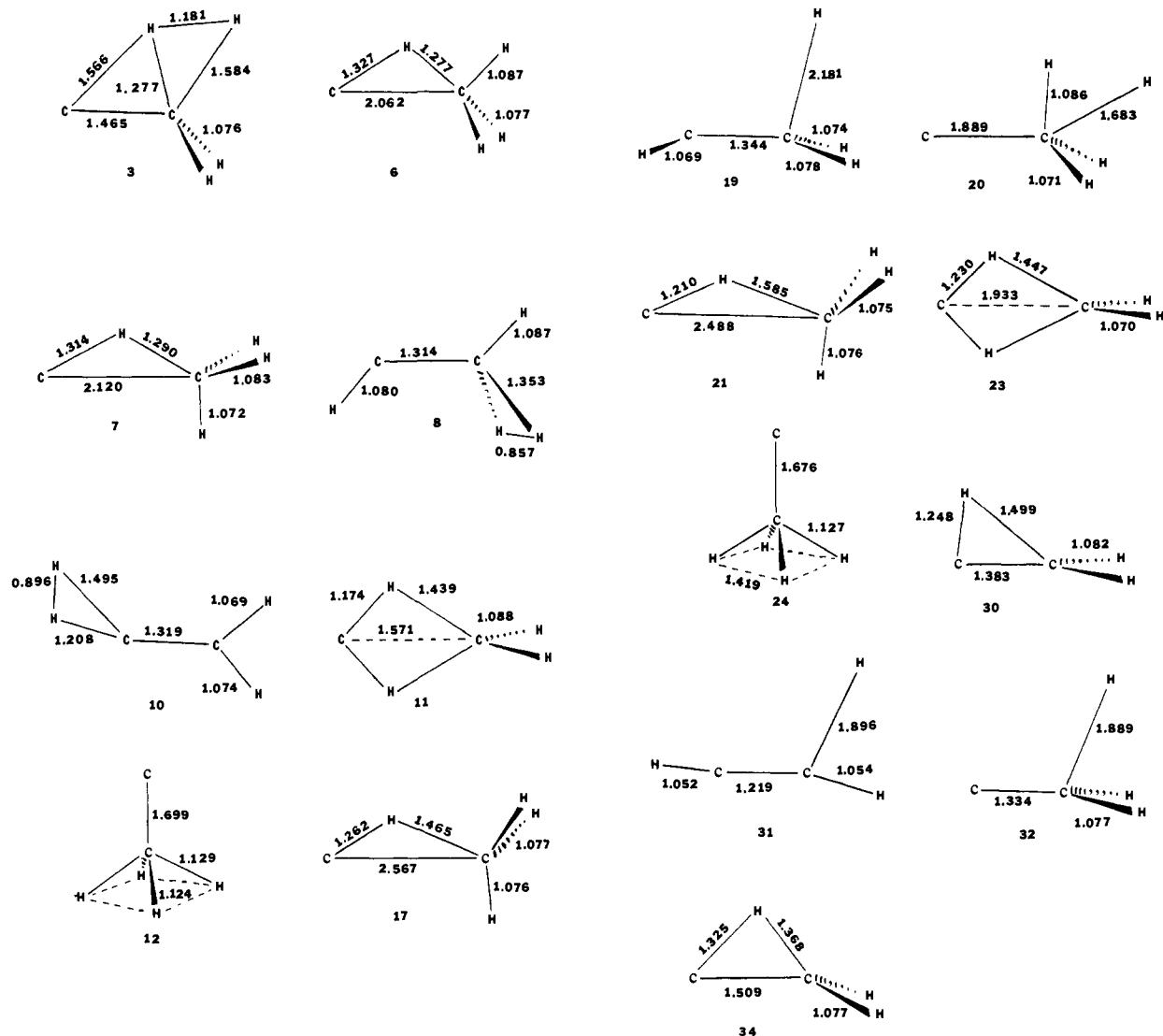


Figure 1. Geometry of relevant species on the various C₂H₄ energy surfaces.

on the triplet surface. Since triplet ethylene (**25**) is twisted, the stationary point (**23**) can more readily form the triplet product than is the case for the closed-shell singlet (**11** → **15**), and consequently the triplet barrier is much lower (35.1 compared to 53.2 kcal/mol). The vibrational frequencies at the 3-21G level revealed two negative modes, indicating that at the 3-21G level **23** is not a transition state for product formation. However, at a higher level of computation (including polarization and correlation), it is possible that **23** would become a transition state (one negative mode of force constant matrix) since it is known that correlation will favor a doubly bridged species relative to a single bridged species.

A concerted reaction was considered on the ³A'' surface between C(³P) and methane to give CCH₃ and H. In the transition state, **20**, the forming CC bond is 1.89 Å (1.50 Å in CCH₃) while the breaking CH bond is 1.68 Å. A high barrier of 71.9 kcal/mol is calculated which makes reaction by this pathway on the ³A'' surface unlikely. A similar mechanism is possible on the ¹A'' surface, but the barrier would still be greater than 40 kcal/mol (71.9 kcal/mol – singlet/triplet difference of atomic carbon) and hence unlikely to be competitive with insertion. However, the CCH₃ radical, **28** and **29**, could be involved in secondary reactions between carbon and the methyl radical (vide infra).

The barrier to C(¹D) insertion on the ¹A'' surface to generate excited singlet ethylidene, **16**, is 11.0 kcal/mol which is slightly higher than the barrier to insertion on the ¹A' surface. However, the insertion barriers are most prone to uncertainty due to the use of a single configurational method in the case of the ¹A' and

¹A'' surfaces and the lack of a pure spin state in the latter surface. The qualitative pictures which result, however, are likely to be accurate. Thus C(³P) and methane will have to cross a substantial barrier (33.9 kcal/mol) to undergo C–H insertion while reaction from the C(¹D) is much easier and likely to occur on both the closed-shell surface ($\Delta H^\ddagger = 8.7$ kcal/mol) and the open-shell surface ($\Delta H^\ddagger = 11.0$ kcal/mol).

Subsequent Reactions of Ethylidene. Since there do not appear to be any direct routes to C₂H₂ from carbon in any electronic states which have lower barriers than that of formation of ethylidene, we conclude that ethylidene is the precursor to acetylene. Accordingly, we have investigated the reaction of **5**, **16**, and **18** on the ¹A', ¹A'', and ³A'' electronic surfaces, respectively, in order to determine if one of these surfaces could lead to C₂H₂ formation. Turning first to the relative energy of the carbene, we decided to compensate specifically for the systematic underestimation of the ³A''–¹A'' separation of **18** compared to **16** which is due to spin contamination in **16**.

Since the orbital occupation is the same in **18** and **16**, the only qualitative difference is a spin exchange term calculated over orbitals on carbon and therefore the separation should be mainly determined by carbon and not by its substituents. As can be seen in Table IV, the calculated separation of the two states is nearly constant. If we consider the ³A''–¹A'' separation in methylene (³B₁–¹B₁) as the sum of the best calculated singlet–triplet splitting²⁴ (10.6 kcal/mol) plus the observed²⁵ S₀–S₁ energy difference (21.1

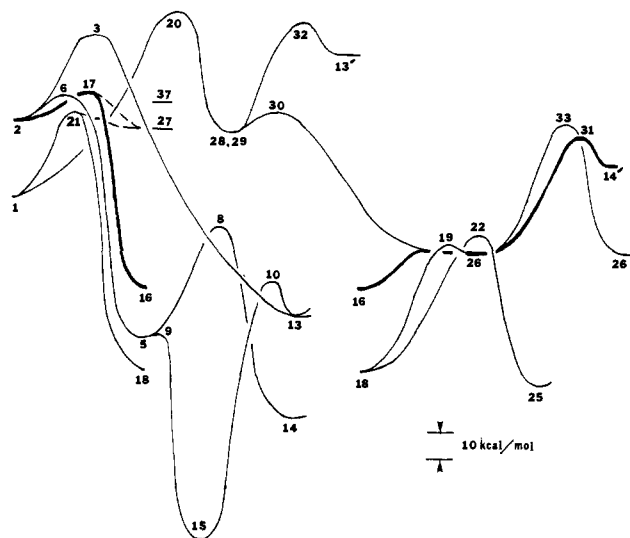


Figure 2. MERP for the reaction of C(3P) and C(1D) on the lowest triplet surface and the two lowest singlet surfaces. Species notation is identical with that in Tables I–III. The heavy line represents reaction on the $^1A'$ surface, which is believed to give rise to the observed acetylene formation. The dashed line represents the competition between insertion and abstraction on the $^1A''$ and $^3A''$ surfaces. The minima $13'$ and $14'$ are related to 13 and 14 by the bond dissociation energy of hydrogen which is 97.9 kcal/mol at the MP3/6-31G** plus zero-point correction level. Not shown is the reaction $1 \rightarrow 39$ (TS) $\rightarrow 27$ on the $^3A'$ surface which has a barrier of 38.0 kcal/mol and the reaction $1 \rightarrow 38$ (TS) $\rightarrow 37$ on the $^3A''$ surface which has a barrier of 37.2 kcal/mol.

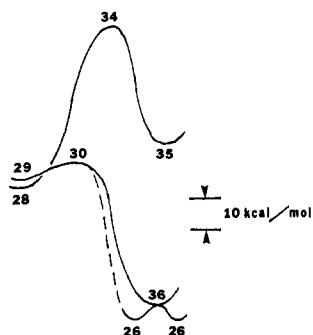


Figure 3. MERP for the 1,2 migration in CCH_3 for the 28 ($^2A'$) and 29 ($^2A''$) electronic states. The dashed line between 30 and 26 indicates that after the transition state (30) has been reached symmetry will be lost until a new symmetry plane is realized in 26 .

Table IV. Energy Separation (kcal/mol) between Triplet and Excited Singlet States for Several Carbenes

	$:\dot{C}:$	$\begin{array}{c} \ddot{C} \\ \diagup \quad \diagdown \end{array}$	$\begin{array}{c} \ddot{C} \\ \diagup \quad \diagdown \\ \quad \quad \quad OH \end{array}$	$\begin{array}{c} \ddot{C} \\ \diagup \quad \diagdown \\ \quad \quad \quad CH_3 \end{array}$
exptl	30.0 ^a	31.7 ^b		
MP3/6-31G**	17.1	19.8	18.6	19.2
MP2/6-31G**	17.5	21.0	19.5	20.4
6-31G**	16.0	23.7	24.1	23.8

^a Moore, C. E. *Natl. Bur. Stand. (U.S.) Circ.* **1949**, *1*, No. 467.

^b Best calculated singlet–triplet splitting (10.6 kcal/mol) added to observed $S_0 - S_1$ energy difference (21.1 kcal/mol).

kcal/mol), we obtain 31.7 kcal/mol as the $^3B_1 - ^1B_1$ separation. Therefore to compensate for the lack of a pure spin state in the open-shell carbene, 16 , the 11.9-kcal/mol difference between the calculated and observed separation of the 3B_1 and 1B_1 states of methylene will be added to the open-shell carbene when constructing potential energy diagrams and MERP. Although other stationary points on the open shell singlet potential energy surface may also be overestimated relative to the triplet surface, the

(25) Herzberg, G.; Johns, J. W. C. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 107.

corrections would not be as great as for the carbenes where the open-shell singlet–triplet mixing is a maximum.

As expected, the most facile reaction on the $^1A'$ surface was the 1,2-hydrogen migration to generate ethylene ($5 \rightarrow 15$, Scheme I). This prediction is consistent with a great deal of experimental data indicating that 1,2-hydrogen migrations occur readily in singlet carbenes in general⁴ and specifically in 5 .¹⁹ Other theoretical investigations have reached the same conclusion.^{14,15} The reaction is calculated to proceed with a barrier of only 1.4 kcal/mol (barrier D, Table III) and is exothermic by 75.8 kcal/mol.²⁷ The exothermicity of this reaction could provide a pathway to C_2H_2 via decomposition of vibrationally excited C_2H_2 as shown in Scheme I ($5 \rightarrow 15 \rightarrow 13$) in which the exothermicity of the C(1D) to ethylene conversion supplies the energy to pass over the barrier to vinylidene. Although we have not included the conversion of vinylidene, 13 , to acetylene, 14 , in Scheme I, very accurate calculations predict a barrier of only 1 or 2 kcal/mol.^{13,14,28}

We have determined the geometry of the transition state, 10 , for the reaction $15 \rightarrow 13$ (Scheme I) which is characterized by asymmetric loss of H_2 . In a MINDO/3 calculation²⁹ of this reaction a barrier of 85 kcal/mol (no reverse barrier) was found. The activation barrier for the reaction $15 \rightarrow 13$ (barrier E, Table III) is found to be 97.9 kcal/mol which is less than the exothermicity of the reaction of C(1D) with methane to generate ethylene, ($2 \rightarrow 15$, Scheme I) 157.7 kcal/mol. Hence the process $15 \rightarrow 13$ could provide a route to C_2H_2 from C(1D). In fact Frey has observed this reaction when 5 is generated by photolysis of the corresponding diazo compound.²⁶

However, this process has been observed to be pressure dependent when 5 is generated by photolysis of diazoethane.¹⁹ At a pressure of 40 mm, the C_2H_2 formation is substantially suppressed with $C_2H_4:C_2H_2 = 40$ and increasing with pressure. In contrast, the ratio of $C_2H_4:C_2H_2$ in the reaction of ^{13}C with CH_4 is independent of CH_4 pressure and is ≈ 0.9 at a pressure of 40 mm.⁶ Thus the process $15 \rightarrow 13$ may play a role in the formation of C_2H_2 by carbon atom reactions when pressures are low or the carbon atoms are highly energetic, but in most of the experimental studies this process has been minimal.

An extensive search of the $HCCH_3$ $^1A'$ surface did reveal a concerted pathway to $HCCH$ ($5 \rightarrow 14$, Scheme I). However, this reaction had a barrier (C, Table III) of 41.6 kcal/mol and would not be expected to compete with the extremely facile formation of ethylene from $HCCH_3$ with $\Delta H^\ddagger = 1.4$ kcal/mol (barrier D, Table III). The transition state, 8 , is characterized by a symmetric loss of hydrogen in which the breaking CH bonds are 1.353 Å while the forming HH bond is 0.857 Å. Although a search was made, no transition state for asymmetric loss of hydrogen could be found.

Since theoretical and experimental studies have demonstrated that 1,2 migrations are suppressed in triplet carbenes,^{9–15} it was anticipated that a pathway to C_2H_2 from 18 might be competitive with hydrogen migration ($18 \rightarrow 25$). The barrier to hydrogen migration in 18 ($18 \rightarrow 25$, Scheme II) has recently been calculated by Harding¹⁰ to be 53.3 kcal/mol.³⁰ This value is in good agreement with the 50.8-kcal/mol barrier calculated in the present study (barrier H, Table III). However, we find that a slightly lower energy process (49.0 kcal/mol, barrier I, Table III) is cleavage to a hydrogen atom and a vinyl radical ($18 \rightarrow 26$ Scheme II). Subsequent homolysis of a second CH bond in 26 to generate C_2H_2 , 14 , has a calculated barrier of 44.0 kcal/mol (barrier L, Table III).

(26) Frey, H. M. *J. Chem. Soc.* **1962**, 2293.

(27) Using the estimated ΔH_f^\ddagger for 5 of 101.8 kcal/mol²³ the experimental exothermicity of $5 \rightarrow 15$ can be estimated as 89.1 kcal/mol. At the MP4SDTQ/6-31G**//6-31G* level plus zero-point correction the exothermicity is calculated¹⁴ to be 77.1 kcal/mol. At the same level the 1,2 migration barrier is 0.0 kcal/mol (with respect to ethylidene in the C_1 structure).

(28) Osamura, Y.; Schaefer, H. F.; Gray, S. K.; Miller, W. H. *J. Am. Chem. Soc.* **1981**, *103*, 1904.

(29) Chiu, S. W.; Li, W. K. *J. Mol. Struct.* **1980**, *66*, 221.

(30) At the MP4SDQ/6-31G**//6-31G* plus zero-point correction level the barrier is 50.1 kcal/mol.¹⁴ It was pointed out that this is below the energy of CH plus CH_3 .

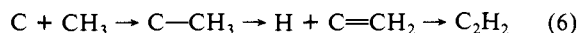
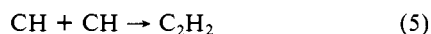
Pertinent in particular to the vinyl radical and in general to the competition between 1,2-hydrogen migration and cleavage in open-shell systems is the study by Harding.¹⁰ Using the POL-CI method but without zero-point correction, he predicted that hydrogen cleavage in the vinyl radical is favored over migration by 13.2 kcal/mol and that zero-point corrections decrease this difference by about 2.5 kcal/mol. The present study predicts that hydrogen cleavage is favored by 4.7 kcal/mol over migration (compare barriers L and M, Table III). A more recent study,³¹ including zero-point correction, of the cleavage reaction in the vinyl radical predicts a barrier of 37.4 kcal/mol and an enthalpic difference between reactant and products of 29.1 kcal/mol which compares to 44.0 and 32.5 kcal/mol, respectively, in the present study.

Thus the lowest enthalpy intramolecular pathway available to **18** is sequential cleavage of hydrogen atoms to generate C₂H₂. Entropic considerations would also favor this pathway over C₂H₄ formation.

The energetics of C₂H₂ formation have also been calculated on the ¹A'' surface. At the 3-21G level there is no reverse barrier to the reaction **16** → **26** (Scheme 3), therefore we computed the forward barrier using the difference in energy between reactant and products reduced by 11.9 kcal/mol, the approximate overestimation of **16** due to triplet contamination. Thus, the barrier to loss of H from **16** is 15.0 kcal/mol (barrier O, Table III, Scheme III).

Rearrangement of **16** to excited ethylene is in competition with cleavage of the CH bond. Since, in analogy with triplet migration, the hydrogen migration in the open-shell singlet will involve the loss of symmetry, the open-shell singlet transition state for hydrogen migration could not be located. It must be remembered that points on the ¹A'' surface represent excited singlet states and can only be calculated if the desired state is the lowest state of a given symmetry. Thus **16** is the lowest state of ¹A'' symmetry that can be computed by using the correct choice of initially occupied orbitals. The hydrogen migration transition state in the open-shell singlet would correspond to the second lowest singlet state and thus cannot be calculated by the procedure used here. While the barrier to H migration is not directly calculable, it seems reasonable that it would be higher than the barrier to cleavage by at least several kcal/mol. Thus we may expect competition between rearrangement and cleavage in **16** where the cleavage is favored.

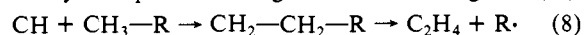
Bimolecular Routes to Acetylene. Several bimolecular reactions leading to acetylene may be envisioned. In addition to dimerization of C to C₂ followed by hydrogen abstraction (vide supra), the dimerization of CH and the reaction between carbon and a methyl radical could lead to acetylene as shown in eq 4-7. An alternate reaction of carbon on the ¹A'' and ³A'' surfaces is hydrogen abstraction to generate CH and CH₃ (eq 4). C-CH₃ could serve as an acetylene precursor via the reactions in eq 6 and 7. The reactions in eq 5-7 will not be important in the case of nucleogenic carbon atoms as the number of reactive species generated is too small for bimolecular reaction to occur.^{1d,e}



In contrast to C plus CH₄, C plus CH₃ forms a very stable complex. The C_{3v} structures will not, of course, be a stable geometry for the radical due to Jahn-Teller splitting of the degenerate electronic state.³¹ Two states are obtained, one of ²A' symmetry, **28**, and one of ²A'' symmetry **29**, separated by 3.4 kcal/mol. Interestingly, correlation reverses the stability of the two doublets. The ²A' state, **28**, which is 1.0 kcal/mol higher in energy than ²A'', **29**, at the 6-31G** level is preferentially sta-

bilized by correlation. Comparing CCH₃ (²A') and C(³P) + CH₃, one finds that the CC bond strength is 73.2 kcal/mol.³² The fate of CCH₃ can be seen from Scheme II. In contrast to triplet carbene and the vinyl radical, the barrier to 1,2-hydrogen migration **29** → **26** is lower than hydrogen cleavage **28** → **13** (9.1 kcal/mol, barrier J, Table III; compared to 41.6 kcal/mol, barrier K, Table III) ruling out the process in eq 6. This is due to the fact that CCH₃ has two low-lying states **28** and **29** which interconvert through a C_{3v} species.³⁴ The elimination occurs from the ²A' surface which correlates a hydrogen atom and the ground state of vinylidene (**28** → **13**). The 1,2-hydrogen migration (**29** → **26**) occurs from the ²A'' state which will correlate with the vinyl σ radical (²A', **26**). The ²A'' state of CCH₃, **29**, can be visualized to correlate with the ²A' σ radical, **26**, in the following way (Figure 3). After reaching the ²A'' transition state, **30**, the migrating hydrogen adopts a linear orientation in **36** which is only 6.5 kcal/mol above **26**. A motion perpendicular to the original reaction coordinate will then reduce the symmetry of **36** to ²A' and produce the σ radical **26** (Figure 3). In reality, symmetry cannot be maintained along the path **30** → **36** since there is no minimum between the two transition states **30** and **36**. The 1,2 migration from the ²A' state (**28** → **35**, transition state **34**) which correlates with the π vinyl radical is indeed higher than the cleavage barrier (53.1 kcal/mol compared to 41.6 kcal/mol, barrier K, Table III). The splitting of the σ-π states in the vinyl radical of 57.6 kcal/mol is in good agreement with the experimental value of 57.2 kcal and a previous theoretical value of 55.0 kcal.³⁵ The above considerations indicate that the route to C₂H₂ in eq 7 is viable while the pathway in eq 6 is not.

In the reaction of carbon with hydrocarbons, CH is postulated to serve as a precursor to ethylene via the insertion-decomposition mechanism in eq 8.³⁶ Since the formation of CH in the reaction between C and CH₄ is endothermic for C(³P) in the reaction between C and CH₄, ethylene formation by the mechanism in eq 8 should only be important for singlet carbon and energetic C(³P).



Conclusions and Comparison with Experimental Observations. The calculations lead to the conclusion that C(¹D) should react with CH₄ by a conventional route generating **5** which should rapidly rearrange to C₂H₄, **15**. Acetylene production by unimolecular decomposition of excited C₂H₄ generated in this route **2** → **5** → **14**, Scheme I, will be important only at low pressures and/or high exothermicities.

In an investigation of the reaction between ¹³C and hydrocarbons, Taylor, Ache, and Wolf² concluded that acetylene-¹³C results from reaction by high-energy C(³P) and low-energy C(¹D). Our calculations support their conclusions in that C(¹D) is predicted to react with a small barrier (11.0 kcal/mol) to generate **16** in a reaction exothermic enough to cleave two C-H bonds giving acetylene in a stepwise manner. However, C(³P) will have to cross a substantial barrier (33.9 kcal/mol) in order to produce **18** and will do so only when the carbon atoms possess sufficient kinetic energy. Once **18** is generated, the exothermicity of the reaction should bring about its cleavage to acetylene.

An interesting feature of this theoretical treatment is the calculated substantial barrier heights leading from **18** and **16** to C₂H₂ by sequential C-H bond cleavage. The energy required to cross these barriers must come from the exothermicity of carbene formation. Generation of both **18** and **16** is calculated to be exothermic. The formation of **16** releases 44.3 kcal/mol while production of **18** is exothermic by 63.2 kcal/mol. Since this energy is far more than is required to surmount the barriers to C-H

(32) The CC bond length in monovalent carbon compound, HOC(=O)C, is calculated to be 1.50 Å³³ in agreement with the CC bond length of 1.50 Å in CCH₃ calculated here.

(33) Saebø, S.; Radom, L.; Schaefer, H. F. *J. Chem. Phys.* **1983**, *78*, 845.

(34) The symmetry of CCH₃ is similar to that of OCH₃ discussed by Kim, K. S.; So, S. P.; Schaefer, H. F. *J. Am. Chem. Soc.*, **1982**, *104*, 1457.

(35) Hunziker, H. E.; Knepe, H.; McLean, A. D.; Siegbahn, P.; Wendt, H. R. *Can. J. Chem.* **1983**, *61*, 993.

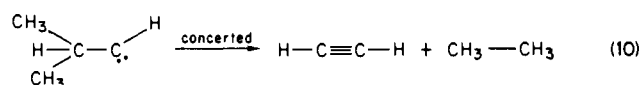
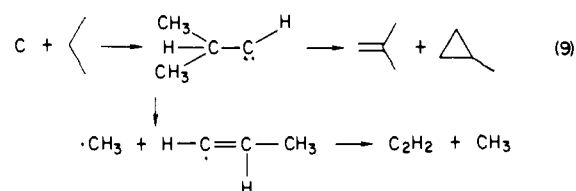
(36) Taylor, K. K.; Ache, H. J.; Wolf, A. P. *J. Am. Chem. Soc.* **1975**, *9*, 5970.

(31) Harding, L. B.; Wagner, A. F.; Bowman, J. M.; Schatz, G. C. *J. Phys. Chem.* **1982**, *86*, 4312.

cleavage, a carbene with enough internal energy to undergo this cleavage will be generated. Since it has been observed that an increase in pressure of added hydrocarbon reactant does not lower C_2H_2 yields,⁶ we must assume that cleavage of vibrationally excited **16** and **18** occurs rapidly before collisional deactivation can occur.

A major drawback to experimental studies involving nucleogenic ^{11}C atoms is the fact that only products bearing the ^{11}C label are detected. Thus, while labeled acetylene is observed, the remaining fragments from the cleavage are undetected.¹ However when C atoms are generated by the chemical decomposition of 5-diazo-tetrazole,³⁷ yields are high enough to permit detection of all products. Experiments of this type support the contention that cleavage of the bond β to the carbene carbon occurs in a stepwise manner. Thus reaction of carbon with propane gives mainly products which may be rationalized by assuming initial insertion into the 2° C-H bond to generate isopropyl carbene, which may either cleave or rearrange (eq 9). The major products from the cleavage reaction are C_2H_2 and CH_4 . The CH_4 results from hydrogen abstraction by methyl radicals. A concerted cleavage of the two C-C bonds β to the carbene carbon (eq 10) would lead

to ethane rather than methane.



Acknowledgment. We thank the Auburn University Computation Center for a generous allotment of computer time. M.L.M. thanks Auburn University for the award of a Grant-in-Aid (82-54). P.B.S. gratefully acknowledges support of this research by the National Science Foundation under Grant CHE-8401198. An insightful comment by a referee regarding the possibility of reaction on the $^3A'$ potential energy surface is acknowledged.

Registry No. C, 7440-44-0; CH_4 , 74-82-8; $CH\equiv CH$, 74-86-2; ethylidene, 4218-50-2.

(37) Shevlin, P. B.; Kammula, S. J. *Am. Chem. Soc.* 1977, 99, 2627.

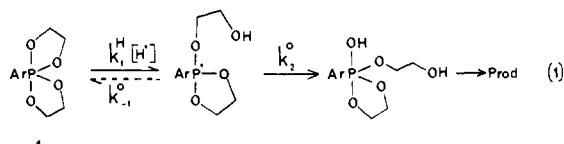
Oxyphosphorane Hydrolysis. Reversible Ring Opening of Spirophosphoranes Containing Six-Atom Rings

Glenn H. McGall and Robert A. McClelland*

Contribution from the Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. Received December 17, 1984

Abstract: A kinetic and mechanistic study is reported for the hydrolysis of two spirooxyphosphoranes containing six-atom rings (6-phenyl-1,5,7,11-tetraoxa-6-phosphospiro[5.5]undecane (**2a**) and the 3,3,9,9-tetramethyl-substituted compound (**2b**)). An intermediate is observed at pH < 9, which had been synthesized and characterized as a ring-opened phosphonium ion (**3**). Kinetic and spectral analysis show that the hydrolysis mechanism involves reversible formation of this phosphonium ion, with $K_1 = [2a][H^+]/[3a] = 3 \times 10^{-9}$, followed by rate-limiting addition to the cation of water and, at high pH, hydroxide ion. Reversibility of the ring opening is unambiguously established by the observation that addition of the cation to a solution of high pH results in ring closure to the phosphorane.

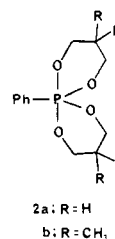
Alkoxyphosphoranes are phosphoryl group analogues of acetals and ortho esters¹ and also serve as models of hydroxyphosphoranes, the postulated intermediates in the hydrolysis of phosphate esters.² Although alkoxyphosphoranes are well established,³ investigations of their hydrolyses have been limited.⁴ We recently have initiated a program of study of the mechanisms of hydrolyses and have reported kinetic⁵ and isomerization⁶ data for spirophosphoranes **1**. The hydrolysis is characterized by an H^+ -catalyzed reaction



extending from acidic pH to about pH 9.5 where there is an abrupt

changeover to an OH^- catalyzed reaction. The latter was concluded to involve an associative process with formation of a hexacoordinated phosphoroxanide ion. For the former a dissociative mechanism with a phosphonium ion intermediate was proposed (eq 1).

In this paper we report a kinetic study of the hydrolysis of the spirophosphoranes **2** with six-membered rings in place of five.



Despite the structural similarities of **1** and **2**, considerable differences are observed, the most notable being that the phosphonium ion intermediates from **2** are observable at pH < 9. This observation permits kinetic and spectral analyses, which show that the cations and phosphoranes are in equilibrium prior to the overall hydrolysis.

Experimental Section

¹H NMR spectra were obtained at 60 MHz, unless otherwise stated. ³¹P NMR spectra were obtained at 32.3 MHz with chemical shifts relative to 85% H_3PO_4 , downfield shifts being reported as positive. Con-

(1) Fife, T. H. *Acc. Chem. Res.* 1972, 5, 264-272. Cordes, E. H.; Bull, H. G. *Chem. Rev.* 1974, 74, 581-604.

(2) Westheimer, F. H. *Acc. Chem. Res.* 1968, 1, 70-78.

(3) Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, D.C., 1980; Vol. 1 and 2, ACS Monographs 175 and 176.

(4) (a) Archie, W. C.; Westheimer, F. H. *J. Am. Chem. Soc.* 1973, 95, 5955-5959. (b) Queen, A.; Lemire, A. E.; Janzen, A. F. *Int. J. Chem. Kinet.* 1981, 13, 411-416. (c) Belskii, V. E.; Khismatullina, L. A.; Bykova, T. G.; Burykina, A. V.; Ivanov, B. E. *J. Gen. Chem. USSR* 1979, 49, 298-302.

(5) McClelland, R. A.; Patel, G.; Cirlina, C. *J. Am. Chem. Soc.* 1981, 103, 6432-6436.

(6) McGall, G.; McClelland, R. A. *Chem. Soc., Chem. Commun.* 1982, 1222-1223.