

2-1994

Pathways for H₂ Elimination from Ethylene: A Theoretical Study

Jan H. Jensen
Iowa State University

Keiji Morokuma
Institute for Molecular Science

Mark S. Gordon
Iowa State University, mgordon@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/chem_pubs

 Part of the [Chemistry Commons](#)

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/chem_pubs/242. For information on how to cite this item, please visit <http://lib.dr.iastate.edu/howtocite.html>.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.

Pathways for H₂ Elimination from Ethylene: A Theoretical Study

Abstract

Ab initio quantum chemical methods are applied to the study of ethylene decomposition to acetylene and molecular hydrogen in the ground electronic state. Results are reported on three different pathways for ethylene decomposition—two stepwise processes involving a hydrogen transfer followed by 1,1 elimination of H₂, or vice versa, and a 1,2 elimination. The latter proceeds through an energy maximum with two imaginary frequencies, rather than one as for conventional transition states. Ethylidene and vinylidene are predicted to be stationary points on the C₂H₄ and C₂H₂ potential energy surfaces, respectively. Recent photochemical studies have observed rotationally hot H₂. It is shown that due to the excess energy available in the photochemical experiments, all three mechanisms can give rise to rotationally hot H₂ when proper account is taken of the transverse vibrational modes along the reaction paths.

Keywords

Photochemistry, *Ab initio* calculations, Decomposition reactions, Ground states, Hydrogen reactions

Disciplines

Chemistry

Comments

The following article appeared in *Journal of Chemical Physics* 100 (1994): 1981, and may be found at <http://dx.doi.org/10.1063/1.466550>.

Rights

Copyright 1994 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

Pathways for H₂ elimination from ethylene: A theoretical study

Jan H. Jensen, Keiji Morokuma, and Mark S. Gordon

Citation: *The Journal of Chemical Physics* **100**, 1981 (1994); doi: 10.1063/1.466550

View online: <http://dx.doi.org/10.1063/1.466550>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/100/3?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Ultrafast internal conversion in ethylene. II. Mechanisms and pathways for quenching and hydrogen elimination](#)

J. Chem. Phys. **136**, 124317 (2012); 10.1063/1.3697760

[Investigation of the O + allyl addition/elimination reaction pathways from the O C H 2 C H C H 2 radical intermediate](#)

J. Chem. Phys. **129**, 084301 (2008); 10.1063/1.2966004

[A molecular orbital study on H and H 2 elimination pathways from methane, ethane, and propane](#)

J. Chem. Phys. **113**, 6139 (2000); 10.1063/1.1308555

[Ultraviolet elimination of H₂ from chloroethylenes](#)

J. Chem. Phys. **103**, 5488 (1995); 10.1063/1.470533

[Dynamics of H₂ elimination from cyclohexadiene](#)

J. Chem. Phys. **95**, 297 (1991); 10.1063/1.461487



AIP | APL Photonics

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief



Pathways for H₂ elimination from ethylene: A theoretical study

Jan H. Jensen

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

Keiji Morokuma^{a)}

Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Mark S. Gordon

Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111

(Received 6 August 1993; accepted 12 October 1993)

Ab initio quantum chemical methods are applied to the study of ethylene decomposition to acetylene and molecular hydrogen in the ground electronic state. Results are reported on three different pathways for ethylene decomposition—two stepwise processes involving a hydrogen transfer followed by 1,1 elimination of H₂, or vice versa, and a 1,2 elimination. The latter proceeds through an energy maximum with two imaginary frequencies, rather than one as for conventional transition states. Ethylidene and vinylidene are predicted to be stationary points on the C₂H₄ and C₂H₂ potential energy surfaces, respectively. Recent photochemical studies have observed rotationally hot H₂. It is shown that due to the excess energy available in the photochemical experiments, all three mechanisms can give rise to rotationally hot H₂ when proper account is taken of the transverse vibrational modes along the reaction paths.

I. INTRODUCTION

The H₂ elimination from ethylene is the prototypical reaction for alkyne formation. It has therefore been the subject of many experimental studies, the most recent being photodissociation studies by Lee and co-workers¹ who suggest both vinylidene and ethylidene as possible intermediates based on deuterium labeling. The exiting H₂ is rotationally hot, suggesting an asymmetric transition state.

Surprisingly few theoretical studies have addressed the nature of the potential energy surface (PES) of ethylene. Evleth and Sevin² present a qualitative study of the two pathways involving vinylidene and ethylidene as intermediates, for which Raghavachari *et al.*³ predict overall barriers of 93.4 and 109.3 kcal/mol. The latter study also predicts a 125.5 kcal/mol barrier for the 1,2 elimination through a "second order transition state (TS)," i.e., a stationary point on the PES with two imaginary frequencies. No attempts to locate a true TS for 1,2 elimination were reported. In their most recent experimental paper,^{1(c)} Lee *et al.* refer to unpublished energy differences obtained by Yoshimine, but few details about the surface were reported.

Therefore, the main focus of the present work is to obtain a reasonable picture of those parts of the C₂H₄ PES which lead to acetylene, thereby gaining some insight into the associated dynamics, especially with regard to the rotational motion of the H₂ product.

II. COMPUTATIONAL METHODS

Molecular geometries were calculated at the restricted Hartree-Fock (RHF) and second order Møller-Plesset perturbation (MP2) level⁴ of theory using the 6-31G(d)[6-

31G*] and 6-31G(d,p) (Ref. 5) [6-31G**] basis sets, respectively. The nature of all stationary points were verified by calculating the eigenvalues of the matrix of energy-second derivatives (Hessian). Stationary points with *n* negative eigenvalues can follow *n* downhill directions that lead to lower-energy structures, so that minima and TSs have 0 and 1 negative eigenvalues, respectively. Upon conversion to frequencies, the (unscaled) eigenvalues are used to calculate zero point vibrational energies (ZPEs) using the harmonic oscillator-rigid rotor approximation. The RHF and MP2 Hessians are calculated analytically and numerically, respectively. Higher level [MP4/6-311 + G(d,p)] energy corrections^{6,7} are evaluated at the MP2 geometries. All RHF calculations were performed with the GAMESS⁸ program, whereas the MP2 and MP4 calculations were done using GAUSSIAN88.⁹

The reaction paths leading to H₂ eliminations were explored at the RHF/6-31G* level of theory, by tracing the intrinsic reaction coordinate (IRC) using the Runge-Kutta fourth order integration method as implemented in GAMESS.¹⁰

III. RESULTS AND DISCUSSION

A. General comments

Key geometric parameters [calculated using MP2/6-31G** (bold) and RHF/6-31G*] of all stationary points are displayed in Fig. 1. The MP2 geometries are within 0.012 Å and 0.4° of experimental values (*italics*) for ethylene and acetylene, whereas RHF underestimates bond lengths by as much as 0.017 Å (for the C=C bond length in ethylene). We expect similar accuracies relative to experiment for the remaining geometries.

Table I lists the absolute and relative energies of the stationary points in Fig. 1, and the best values for the elimination pathways are used in schematic representations in Figs. 2(a), 2(b) and 3. Experimental enthalpies at 0 K

^{a)}Present address: Cherry L. Emerson Center for Scientific Computing and Department of Chemistry, 1515 Pierce Drive, Emory University, Atlanta, GA 30322.

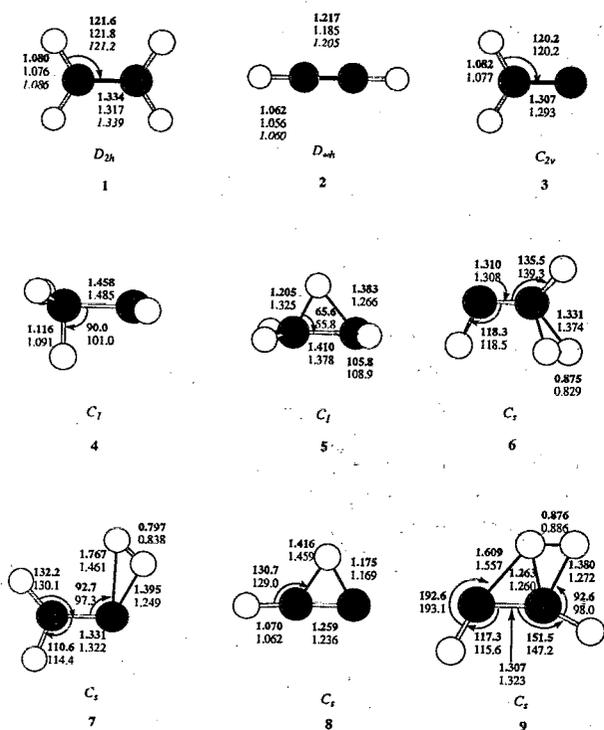


FIG. 1. Experimental (italics), MP2/6-31G** (bold), and RHF/6-31G* optimized geometries for the stationary points discussed in the text. All bond lengths are in Ångströms and all angles are in degrees.

of $\text{HCCH} + \text{H}_2$ and $\text{H}_2\text{CC} + \text{H}_2$ relative to ethylene are 41.7 and 87.5 kcal/mol,^{1(a)} respectively, which compare reasonably well with our best calculated values 37.0 and 81.0 kcal/mol.

Table I also lists the nature of the PES at each stationary point and it is important to note that although there are some structural differences between the RHF and MP2 structures (see below), the nature of the stationary points is not altered on going to a higher level of theory. Since the aim of this paper is to elucidate *qualitative* pictures of the mechanisms, the less-expensive RHF/6-31G* IRCs are used toward that end.

B. The ethylidene pathway

The MP4/6-311+G(*d,p*)/MP2/6-31G(*d,p*) potential energy profile for H₂ elimination in which ethylidene is an intermediate is displayed in Fig. 2(a). Ethylidene (4) is a local minimum on the ethylene PES, 74.2 kcal/mol higher in energy than ethylene. One CH bond on the methyl group is approximately perpendicular to the C-C bond. On going to a correlated wave function, the stability is decreased by 14 kcal/mol relative to RHF, and the angle that the eclipsing methyl CH bond makes with the carbene carbon increases. As one would expect from the Hammond postulate,¹¹ the MP2 TS for 1,2 hydrogen transfer (5) to give ethylidene is late (i.e., more ethylidene-like) relative to the RHF structure, although both methods predict that the hydrogen transfers along the top of the π bond.

Using MP4/6-31G** energies at RHF/6-31G* geometries, Raghavachari *et al.*^{3(b)} reported that the energy of

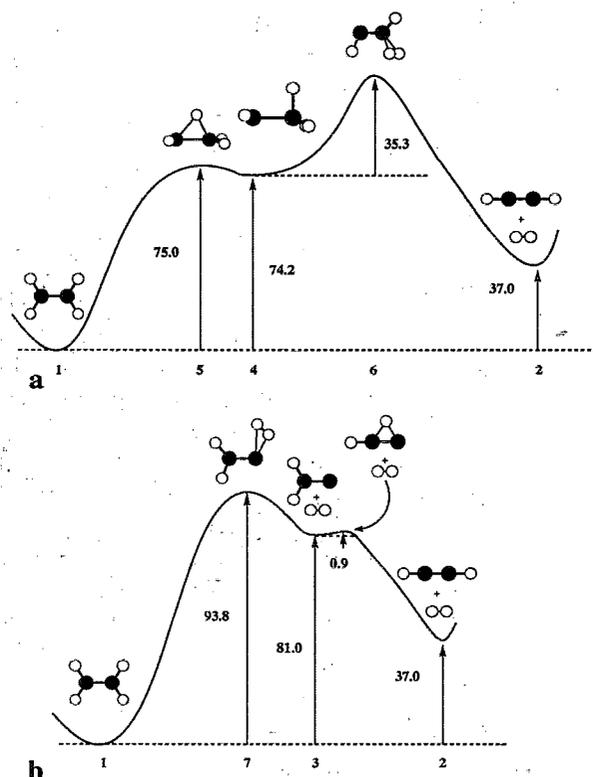


FIG. 2. A schematic representation of the potential energy surfaces of two of the three pathways for ethylene decomposition discussed in the text. The values given are relative enthalpies at 0 K calculated at the MP4/6-311+G**//MP2/6-31G** level of theory.

the ethylene \rightarrow ethylidene TS is *lower* than that of ethylidene. They therefore concluded that ethylidene does not exist as a true intermediate. However, when correlation is included in the geometry optimization, ethylidene is predicted to be a true intermediate (local minimum), albeit separated from decomposition to ethylidene by a small (0.8 kcal/mol) barrier.

The ethylidene intermediate is separated from the acetylene + H₂ products by a 35.3 kcal/mol barrier involving a C_7 transition state for 1,1 elimination (6). Although the HH bond is essentially formed by the time the TS is reached, based on the HH distance, the HCCH unit is significantly distorted from the final acetylene geometry. As a result, the TS is 72.5 kcal/mol higher in energy than $\text{HCCH} + \text{H}_2$. Thus the overall barrier height for this pathway is 109.5 kcal/mol. MP2/6-31G** [without ZPE corrections (Table I)] predicts an overall classical barrier height of 124.5 kcal/mol, which is in good agreement with the RHF/6-31G* value of 129.7 kcal/mol. It appears that the two TSs discussed so far (5 and 6) are well represented by RHF, but that ethylidene is not.

As noted in the Introduction, Lee and co-workers¹ observed that the exiting H₂ is rotationally hot. To understand more about this feature of the mechanism, intrinsic reaction coordinates (IRCs)¹⁰ were traced, at the RHF level of theory, starting from the $\text{CH}_3\text{CH} \rightarrow \text{HCCH} + \text{H}_2$ saddle point. Molecular structures along the IRC are shown in Fig. 3. Since the normal mode of the imaginary

TABLE I. Total (in hartrees) and relative (in kcal/mol) energies of the stationary points. Zero point energy corrections are in cm⁻¹. The relative energies are calculated relative to ethylene, with the exception of [CH₃CH → HCCH + H₂][†] and [H₂CC: → HCCH][†] which are relative to CH₃CH and H₂CC:, respectively (cf. Fig. 2).

		Total energies								
		1	2	3	4	5	6	7	8	9
		H ₂	C ₂ H ₂	H ₂ CC:	CH ₃ CH	[C ₂ H ₄ → CH ₃ CH] [†]	[CH ₃ CH → HCCH + H ₂] [†]	[C ₂ H ₄ → H ₂ CC: + H ₂] [†]	[H ₂ CC: → HCCH] [†]	[C ₂ H ₄ → HCCH + H ₂] [†]
RHF/6-31G* energy		-1.126 83	-76.817 83	-76.763 40	-77.922 37	-77.900 94	-77.824 96	-77.847 68	-76.737 17	-77.789 87
ZPE		1335 <i>i</i>	1710 <i>i</i>	1185 <i>i</i>	1086 <i>i</i>	1184 <i>i</i> , 1750 <i>i</i>
MP2/6-31G** energy		6.64	18.48	16.38	31.61	30.94	27.80	28.12	14.31	26.75
ZPE		520 <i>i</i>	1812 <i>i</i>	801 <i>i</i>	1069 <i>i</i>	900 <i>i</i> , 1702 <i>i</i>
MP4/6-311+G**		6.59	16.48	15.20	30.42	29.75	26.66	25.82	13.74	25.37
		-1.167 69	-77.141 82	-77.069 58	-78.261 90	-78.259 50	-78.199 66	-78.223 30	-77.065 78	-78.172 35
		Relative energies								
		2	3	4	5	6	7	8	9	9
		C ₂ H ₂	[CH ₃ CH → HCCH + H ₂] [†]	CH ₃ CH	[C ₂ H ₄ → CH ₃ CH] [†]	[C ₂ H ₄ → H ₂ CC: + H ₂] [†]	H ₂ CO: + H ₂	[H ₂ CC: → HCCH] [†]	[C ₂ H ₄ → HCCH + H ₂] [†]	[C ₂ H ₄ → HCCH + H ₂] [†]
RHF/6-31G*		54.6	61.1	68.6	82.1	115.5	88.8	16.5	151.8	151.8
RHF+ZPE		45.3	57.3	65.8	78.7	109.2	77.4	14.3	144.2	144.2
MP2/6-31G**		49.0	41.7	82.5	83.2	109.5	99.9	0.9	141.7	141.7
MP2+ZPE		39.2	38.0	80.1	80.1	102.5	88.8	-0.5	134.2	134.2
MP4/6-311+G**		46.8	39.1	76.7	78.2	100.9	92.1	2.4	132.9	132.9
MP4+ZPE		37.0	35.3	74.2	75.0	93.8	81.0	0.9	125.3	125.3

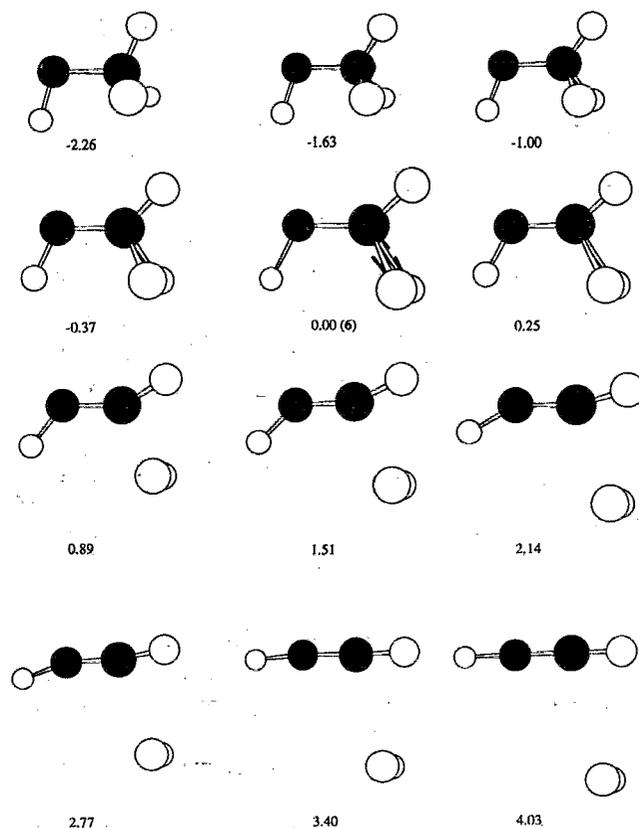


FIG. 3. Structures along the RHF/6-31G* IRC leading from ethylidene to acetylene and hydrogen, with their reaction coordinate values (s in bohr amu^{1/2}) given below. At the TS structure (6, $s=0.00$), the normal mode associated with the imaginary frequency (1710*i* cm⁻¹) is drawn. All structures have C₂ symmetry.

frequency has a' symmetry (Fig. 3, $s=0.00$), the reaction path retains C₂ symmetry. The exiting hydrogens are not in the symmetry plane, so the C₂ constraint prevents them from rotating around an axis parallel to the HCCH plane. Since the IRC is defined as the minimum energy path (MEP), infinite friction is applied to remove all excess kinetic energy (KE) as the system moves downhill. So, no actual rotation using excess kinetic energy is allowed. Nonetheless, one can infer potential rotational motions by examining structures and transverse vibrations along the IRC. For this path, one indication of possible rotational motion of the exiting H₂ is the lowest (599.7 cm⁻¹ at the RHF level) real mode at the TS (top structure in Fig. 4). This a'' mode is mostly H₂ rotation, and it is likely to be significantly populated since it is the lowest-lying vibrational mode. So it is possible that some of the excess KE is removed by the rotational motion of the leaving hydrogen molecule. As the reaction proceeds, this mode becomes one of the rotational degrees of freedom of the H₂ molecule, and the associated frequency drops sharply as shown in Fig. 4.¹² Due to the different symmetry of the reaction path (a') and the mode (a''), the energy released from the reaction itself cannot contribute to the rotational motion of H₂ through that mode (within the rigid rotor-harmonic oscillator approximation employed in this study).

It is possible that the energy released as the reaction

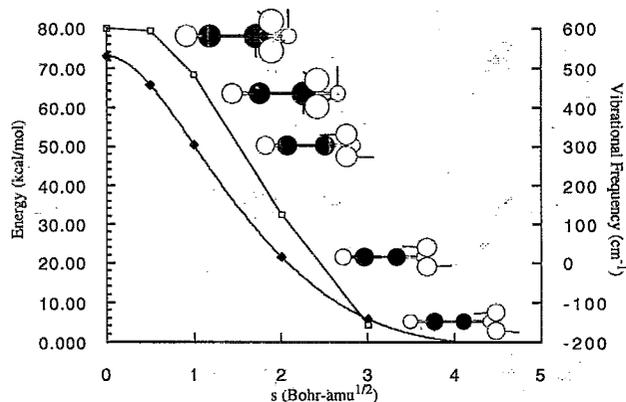


FIG. 4. A plot of energy vs reaction coordinate [(dark squares) left y axis] of the IRC shown in Fig. 3, and the associated a'' frequency along the IRC [(open squares) right y axis]. Also shown are plots of the normal mode associated with each frequency.

proceeds can be transferred into transverse normal modes of the same symmetry, i.e., the reaction coordinate (s) and an a' mode (k) can couple. To investigate this possibility, the s,k coupling constants $B_{s,k}$ (Ref. 13) were calculated at the points shown in Fig. 4. No appreciable coupling was found between the reaction coordinate and any of the normal modes. The reaction path curvature (κ), given by¹³

$$\kappa = \left(\sum_k^{3N-7} B_{s,k}^2 \right)^{1/2},$$

peaks at 0.32 just off the TS ($s=0.04$). Thus, the majority of the energy released from the reaction coordinate is apparently converted to H₂-translational energy.

C. The vinylidene pathway

The MP4/6-311+G(d,p)/MP2/6-31G(d,p) pathway for H₂ elimination involving vinylidene as an intermediate is displayed in Fig. 2(b). Vinylidene + H₂ lies 81 kcal/mol higher in energy than ethylene. It is formed from ethylene by a 1,1 elimination via a planar TS [7; the RHF normal mode is shown in Fig. 5 ($s=0.00$)]. The TS is very distorted from C_{2v} symmetry, a path that is symmetry forbidden, and, as for 6, the HH bond is essentially formed at the saddle point structure. The distortion from C_{2v} symmetry is more pronounced for the MP2/6-31G** TS than for the RHF/6-31G* structure. The correlated TS structure is again further into the product channel. The barrier to hydrogen elimination is 93.8 kcal/mol. Since this first H₂-elimination step has the highest barrier along the path shown in Fig. 2(b), this barrier also corresponds to the net energy requirement for this path. MP2 and RHF predict net activation energies of 102.5 and 109.2 kcal/mol, respectively.

As was the case with the ethylidene pathway, the vinylidene reaction path has a' symmetry, and the corresponding IRC (Fig. 5) does not reveal any rotational motion of H₂ until the associated vibrational modes are considered (Fig. 6). In this case, the lowest (a'') vibrational mode is almost pure H₂ rotation at the onset of

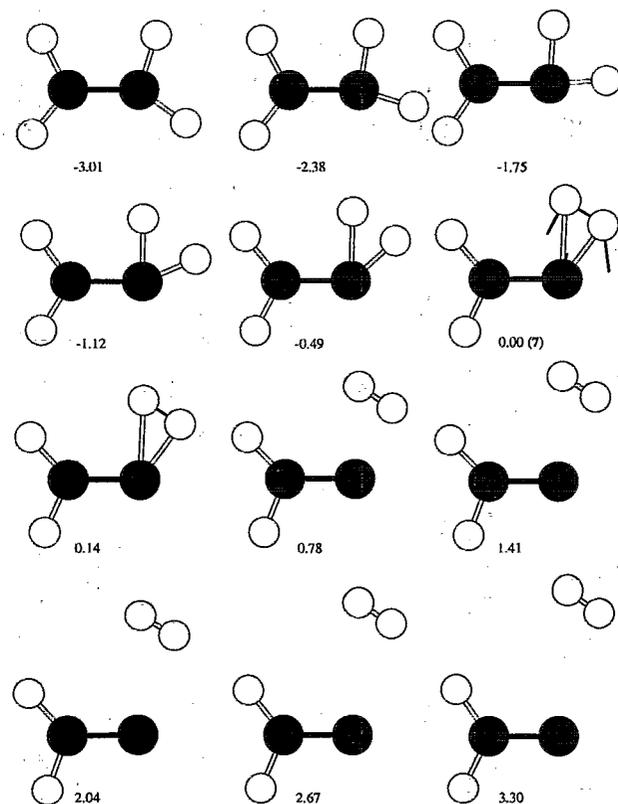


FIG. 5. Structures along the RHF/6-31G* IRC leading from ethylene to vinylidene and hydrogen, with their reaction coordinate values (s in bohr amu^{1/2}) given below. At the TS structure (7, $s=0.00$) the normal mode associated with the imaginary frequency (1185i cm⁻¹) is drawn. All structures have C_s symmetry.

product formation and remains virtually unchanged as the reaction proceeds, though the magnitude of the associated frequency drops. Again, it is likely that excess energy is disposed of through H₂ rotation. As for the ethylidene case, the reaction coordinate and the H₂-rotational normal mode are of different symmetries and energy released from the reaction can thus not be transferred to the latter (within the rigid rotor-harmonic oscillator approxima-

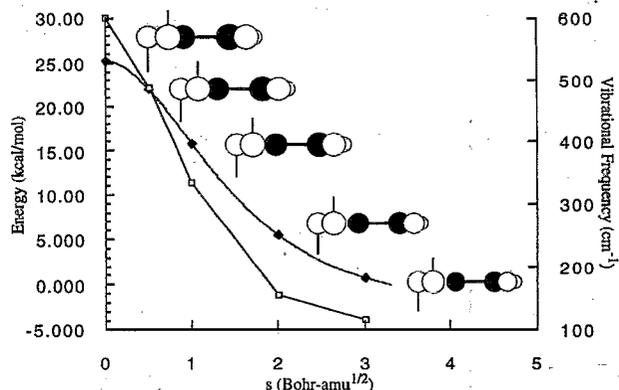


FIG. 6. A plot of energy vs reaction coordinate [(dark squares) left y axis] of the IRC shown in Fig. 7, and the associated a'' frequency along the IRC [(open squares) right y axis]. Also shown are plots of the normal mode associated with each frequency.

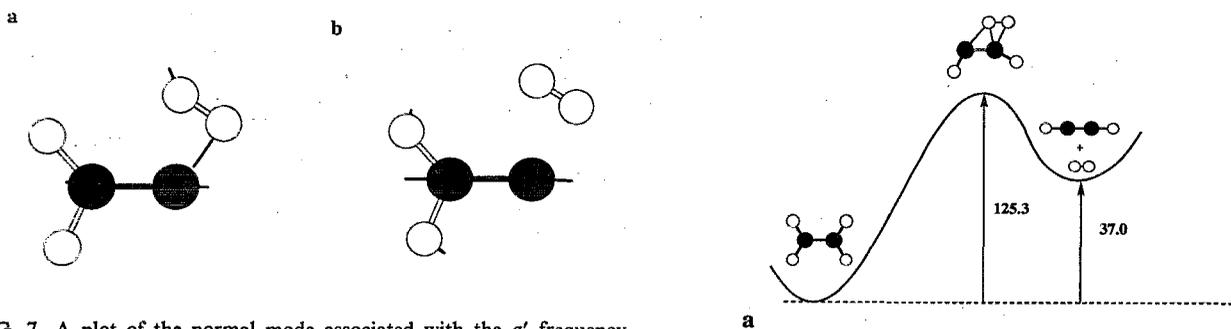


FIG. 7. A plot of the normal mode associated with the a' frequency shown to be strongly coupled with the reaction coordinate at $s=0.06$ [(a) 1911 cm^{-1}], but not at $s=0.50$ [(b) 1806 cm^{-1}].

tion). However, the vinylidene mechanism differs from the ethylidene mechanism in that around the TS, there is some coupling ($B_{s,k}=1.45$; $\kappa=1.53$) between the reaction coordinate and an a' mode [Fig. 7(a)]. As can be seen from Fig. 7(a), this mode has some (in-plane) H₂ rotational character as well as a slight C=C stretch character. As the reaction proceeds, this mode becomes predominantly C=C stretch [Fig. 7(b)] and all H₂ rotational character is lost. In addition, $B_{s,k}$ decreases to 0.01. Nevertheless, it appears that early in the reaction some of the reaction energy released can contribute to H₂ rotational motion.

The predicted barrier for vinylidene isomerization is roughly the same as that for ethylidene (0.9 kcal/mol), indicating an extremely short lifetime for vinylidene. Schaefer and co-workers¹⁴ have estimated this barrier to be ~ 3 kcal/mol using larger basis sets and coupled cluster energies (CCSDT-1), indicating that vinylidene indeed is a stable intermediate.

D. The 1,2 H₂ elimination

Raghavachari *et al.*^{3(b)} reported an RHF C_s structure with two imaginary frequencies as a possible stationary point in the 1,2-elimination pathway (9). Figure 8 shows the normal modes associated with the two imaginary frequencies calculated at the RHF/6-31G* level of theory. At the MP2 level of theory, the structure remains a second order TS. Since no attempts to further explore the 1,2-elimination region of the PES (e.g., to find a C_1 TS) have been reported to our knowledge, the RHF/6-31G* surface around 9 was explored in the following fashion: An IRC was traced starting from 9, by displacing the geometry

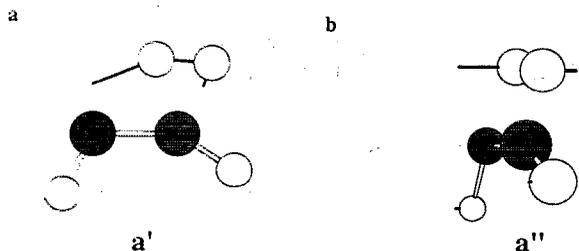


FIG. 8. A plot of the normal modes associated with the two imaginary frequencies [(a) $1750i\text{ cm}^{-1}$, a' ; (b) $1184i\text{ cm}^{-1}$, a''] of 9, calculated at the RHF/6-31G* level of theory.

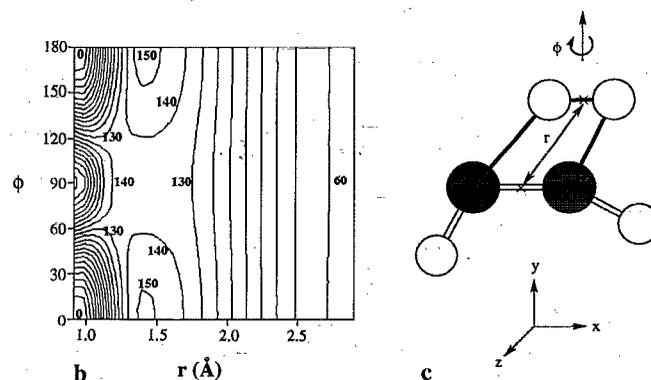


FIG. 9. (a) A schematic representation of a *constrained* section of the potential energy surface corresponding to the last pathway for ethylene decomposition discussed in the text. The values given are relative enthalpies at 0 K calculated at the MP4/6-311+G**//MP2/6-31G** level of theory. (b) A plot of the twist potential generated from the C_s IRC. The units are kcal/mol, Ångstroms, and degrees for the energy, distance (r), and angle, respectively. The contours increment by 10 kcal/mol and range from 0 ($r=0$, $\phi=0$) to 220 ($r=0$, $\phi=90$) kcal/mol. Selected contours are labeled. (c) Definitions of the orientation and parameters associated with the construction of the twist potentials are discussed in the text.

along the a' imaginary frequency, in the direction of both ethylene and acetylene+H₂. Thus the reaction path, displayed qualitatively in Fig. 9(a) is C_s throughout. The barrier at this level of theory is 151.8 kcal/mol {125.3 at the highest computational level [Fig. 9(a)]}.

The distance between the bond midpoint of the exiting H₂ and that of the two carbon atoms [r cf. Fig. 9(c)] was chosen as a suitable reaction coordinate and monitored along the IRC. Nineteen points along the IRC, corresponding to r increments of ~ 0.10 Å in the range $r=0.9$ – 2.5 and 0.20 Å for $r=2.5$ – 2.9 , were chosen. For each such point along the IRC, a twist potential was generated by rotating the two exiting hydrogens out of the molecular plane in 10° increments around an axis parallel to the y axis [see Fig. 9(c) for axis definitions] and passing through the HH bond midpoint. The PES thus generated is displayed in Fig. 9(b), while Fig. 9(a) corresponds to the $\phi=0^\circ$ path. Not surprisingly, the energy dependence on the rotation angle ϕ decreases considerably as r is increased, and

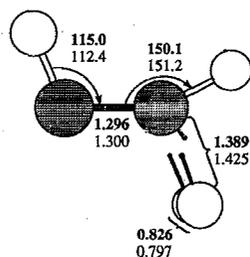


FIG. 10. MP2/6-31G** (bold) and RHF/6-31G* optimized geometry of structure 10 (bond lengths are in Ångstroms and angles in degrees). The RHF normal modes associated with the a' imaginary frequency ($1466i$ cm⁻¹) are also shown.

at small values of r ($r < 1.25$ Å), the energy increases as ϕ approaches 90°. Note that since the two rotating H's are both closer to the same C in 9, $\phi = 90^\circ$ produces a structure that is qualitatively similar to 6. For $r = 1.404$ Å (corresponding to 9), the twist potential becomes a single well, with a minimum energy of 134 kcal/mol at $\phi = 90^\circ$. This may be compared with the RHF/6-31G* value for 6 of 129 kcal/mol, and an r value of 1.724 Å. A search for a TS was initiated starting from $r = 1.40$ Å, $\phi = 90^\circ$ and resulted in the TS ($\nu_i = 1466i$ cm⁻¹) shown in Fig. 10. This C_s structure is merely an isomer of 6, only 0.9 kcal/mol higher in energy (2.9 kcal/mol at the highest level of theory).¹⁵ Thus, it seems likely that one of the two imaginary modes (a') connects ethylene with HCCH and hydrogen, whereas the other one [a'' [see Fig. 8(b)]] leads toward the ethylidene part of the surface.

The question of H₂ rotation for the 1,2-elimination case is rather obvious, since the a'' downhill direction (presumably leading toward ethylidene) clearly has strong H₂-rotational character [Fig. 8(b)]. So it appears that an exiting H₂ from the 1,2 elimination initially following the a' reaction path can break symmetry and pick up transverse rotational character around the hilltop region of the reaction path. Depending on the amount of transverse rotation that is picked up, the reaction either proceeds along an a' -like path (i.e., little a'' character), or diverts toward the ethylidene region. Note that this high energy route is accessible in the photochemical experiments of Lee *et al.*¹

IV. SUMMARY

Theoretical calculations on three pathways for ethylene decomposition are presented. The structures (Fig. 1) and energetics (Table I) of stationary points along the paths were calculated at various levels of theory.

One pathway [Fig. 2(a)] involves the formation of the ethylidene intermediate (with a very short lifetime) via a 1,2 hydrogen shift, followed by a 2,2 H₂ elimination. The activation energy and exothermicity for that path are 109.5 and 72.5 kcal/mol, respectively. At the TS, the lowest real vibrational frequency has some H₂ rotational character, a feature that increases as the reaction proceeds (Fig. 4), indicating that excess energy can be removed from the reaction via H₂ rotation. Because this vibrational mode and the reaction coordinate (Fig. 3) have different symmetries,

the potential energy released from the reaction coordinate cannot contribute to H₂ rotation (within the rigid rotor-harmonic oscillator approximation).

Another pathway [Fig. 2(b)] involves the formation of vinylidene through a 1,1 H₂ elimination from ethylene with a barrier of 93.8 kcal/mol, which is also the activation energy. Like ethylidene, vinylidene is predicted to have a very small isomerization barrier (0.9 kcal/mol) and hence a very short lifetime. The endothermicity for this path is 56.8 kcal/mol. Though the two breaking C-H bonds which produce the exiting H₂ are quite different, an IRC (Fig. 5) does not reveal any H₂-rotational character due to unequal repulsion of the two H's by the rest of the atoms. However, two vibrational modes are found that can contribute to H₂ rotation. One, the lowest real vibrational mode has a'' symmetry (and is thus uncoupled from the a' reaction path), and remains virtually pure H₂ rotation throughout the latter part of the reaction (Fig. 6). The other mode is a' (Fig. 7) and shows some coupling to the reaction coordinate early on in the reaction [Fig. 7(a)] a feature that decreases quickly as the reaction proceeds [Fig. 7(b)].

A true transition state for the direct 1,2 elimination of H₂ from ethylene was not found despite an extensive search. A second order transition state (a stationary point with two imaginary frequencies) was found. Results from a partial mapping of the potential energy surface (PES) surrounding this point (Fig. 9) reveals that one of the imaginary frequencies leads to the ethylene and acetylene reactants and products, respectively, whereas the other one leads to the ethylidene part of the surface. Both paths clearly lead to substantial HH rotation.

¹(a) B. A. Balko, J. Zhang, and Y. T. Lee, *J. Chem. Phys.* **97**, 935 (1992); (b) A. Stolow, B. A. Balko, E. F. Cromwell, J. Zhang, and Y. T. Lee, *J. Photochem. Photobiol. A* **62**, 285 (1992); (c) E. F. Cromwell, A. Stolow, M. J. J. Vrakking, and Y. T. Lee, *J. Chem. Phys.* **97**, 4029 (1992).

²E. M. Evleth and A. Sevin, *J. Am. Chem. Soc.* **103**, 7414 (1981).

³(a) K. Raghavachari, M. J. Frisch, J. A. Pople, and P. v. R. Schleyer, *Chem. Phys. Lett.* **79**, 408 (1981); (b) **85**, 145 (1982).

⁴K. Raghavachari and J. A. Pople, *J. Am. Chem. Soc.* **101**, 91 (1978).

⁵P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* **28**, 213 (1973) (d exponent for C=0.8).

⁶R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.* **72**, 4244 (1980).

⁷R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980) (d exponent for C=0.626, p exponent for H=0.75, and exponent for the diffuse sp shell for C=0.0438).

⁸M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, Jr., *J. Comput. Chem.* **14**, 1347 (1993).

⁹M. J. Frisch, M. Head-Gordon, H. B. Schlegel, K. Raghavachari, J. S. Binkley, C. Gonzalez, D. J. DeFrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. Martin, L. R. Kahn, J. J. P. Stewart, E. M. Fluder, S. Topiol, and J. A. Pople, GAUSSIAN88, Carnegie Mellon Quantum Chemistry, Pittsburgh, PA

¹⁰(a) K. Ishida, K. Morokuma, and A. Komornicki, *J. Chem. Phys.* **66**, 2153 (1977); (b) K. Muller, *Angew. Chem. Int. Ed. Engl.* **19**, 1 (1980); (c) M. W. Schmidt, M. S. Gordon, and M. Dupuis, *J. Am. Chem. Soc.* **107**, 2585 (1985); (d) B. C. Garrett, M. J. Redmon, R. Steckler, D. G. Truhlar, K. K. Baldrige, D. Bartol, M. W. Schmidt, and M. S. Gordon, *J. Phys. Chem.* **92**, 1476 (1988); (e) K. K. Baldrige, M. S. Gordon, R. Steckler, and D. G. Truhlar, *J. Phys. Chem.* **93**, 5107 (1989); (f) the IRC was initiated by displacing the TS geometry along the normal mode of the imaginary frequency so as to lower the

energy by 0.0001 hartree (0.0005 for 9). The step size for the IRC was 0.01 amu bohr^{1/2} (0.05 amu bohr^{1/2} for 9).

¹¹G. S. Hammond, J. Am. Chem. Soc. 77, 334 (1955).

¹²The observation that the vibrational frequency becomes imaginary was probed further as follows. "Jumps" off the IRC were taken by distorting the geometry along the normal mode associated with the imaginary frequency and IRCs were initiated. Although these jumps were taken so as to lower the energy by 1×10^{-6} hartrees, only at $s=4.03$ did this result in a decrease in energy (presumably due to a very flat transverse PES). The C₁ IRC thus initiated resulted mainly in distancing the exiting H₂ and in little further distortion from C_s symmetry. However, the frequency did become real again. It should be noted that this bifurcation takes place rather late along the MEP. In reality, the reaction has very likely deviated considerably from the MEP earlier due to both excess energy and energy released from the downhill motion along the reaction path.

¹³W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. 72, 99 (1980). Briefly,

$$B_{s,k} = L_s \cdot \left(\frac{\partial L_k}{\partial s} \right),$$

where L_s and L_k are the normal mode associated with the reaction coordinate and mode k , respectively. In this study, the derivative of mode k with respect to the reaction coordinate is calculated by numerical differencing.

¹⁴M. M. Gallo, T. P. Hamilton, and H. F. Schaefer III, J. Am. Chem. Soc. 112, 8714 (1990). This paper provides a good review of previous calculations of vinylidene and the rearrangement to acetylene.

¹⁵The nature of this new TS was confirmed by following an IRC to ethylidene. Since the ethylidene minimum is C₁ and that of the TS in Fig. 10 is C_s, the C_s IRC will naturally bifurcate. This bifurcation point was explored as described in Ref. 12. The resulting C₁ IRC leads directly to ethylidene.