The lactones (Table XXVI) are quite strained. Considering the large energy difference between the cis and trans conformations of an ordinary ester, it is easy to understand why. Propiolactone has a strain energy of over 20 kcal/mol, and α-lactones are commonly seen only as reactive intermediates, rather than isolable species. Butyrolactone has a strain energy calculated to be 8.70 kcal/mol, and this may seem surprisingly high, considering that γ-hydroxy acids often spontaneously ring close to form γ-lactones. The driving force for such a ring closure is, however, not the stability (enthalpy) of the lactone so much as it is the large favorable translational entropy effect which results when the water molecule is also generated. While butyrolactones often close spontaneously, valerolactones usually do not, and the extra 1.5 kcal/mol in strain of the valerolactone over the butyrolactone shows why. The seven- and eight-membered ring lactones contain relatively high strain, and such molecules are normally not obtained spontaneously, and indeed, they are obtained with considerable difficulty, if at all, from most kinds of ring-closure reactions.

Acknowledgment. The authors are indebted to the National Science Foundation (Grant No. CHE 8918839) for support of this work.

Registry No. Formic acid, 64-18-6; acetic acid, 64-19-7; butyric acid, 107-92-6; valeric acid, 109-52-4; isovaleric acid, 503-74-2; pivalic acid, 75-98-9; butyl acetate, 123-86-4; methyl caproate, 106-70-7; propiolactone, 57-57-8; γ-butyrolactone, 96-48-0; δ-valerolactone, 542-28-9; ϵ-caprolactone, 502-44-3; heptanolactone, 539-87-7; methyl acetate, 79-20-9; ethyl formate, 109-94-4; β-butyrolactone, 3068-88-0; propionic acid, 79-09-4; methyl formate, 107-31-3; caproic acid, 142-62-1; heptanoic acid, 111-14-8; octanoic acid, 124-07-2; 2-ethylhexanoic acid, 149-57-5; ethyl acetate, 141-78-6; isopropyl acetate, 108-21-4; methyl valerate, 624-24-8; methyl heptanoate, 106-73-0; ethyl propionate, 105-37-3; ethyl pentanoate, 539-82-2; propyl pentanoate, 141-06-0; butyl pentanoate, 591-68-4; methyl pivalate, 598-98-1; ethyl pivalate, 3938-95-2; methyl isovalerate, 556-24-1; ethyl isovalerate, 108-64-5; methyl α-methylbutyrate, 868-57-5; ethyl α-methylbutyrate, 7452-79-1; *sec*-butyl butyrate, 819-97-6; *sec*-butyl pentanoate, 23361-94-6; isopropyl pentanoate, 18362-97-5; isobutyl pentanoate, 10588-10-0; formic acid dimer, 14523-98-9.

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Vinylidene and the Hammond Postulate

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Abstract: The potential energy barrier for the isomerization of vinylidene, $:C{=}CH_2$, to acetylene, $HC{\equiv}CH$, has been calculated by the quadratic configuration interaction method using a 6s6p3d2f,4s2p1d basis of atomic pair natural orbitals with extrapolation to the complete basis set limit (CBS-QCI/[...3d2f] APNO model). The calculated barrier ($\Delta E_e^{\ddagger} = 2.2 \pm 0.5$ kcal/mol) and energy change from vinylidene to acetylene ($\Delta E_0 = -43.9 \pm 0.5$ kcal/mol) are in excellent agreement with recent experimental values ($\Delta E_e^{\ddagger} = 2$ kcal/mol, and $\Delta E_0 = -44.1 \pm 0.7$ kcal/mol). In spite of the small barrier height for this strongly exothermic reaction, the transition state is located halfway between the reactant and product in apparent violation of the Hammond postulate. The potential energy surface for the isomerization can best be understood by considering two distinct processes. The location of the transition state is determined by the hydrogen migration, which has a significant barrier, whereas the exothermicity results from the conversion of the lone pair of vinylidene to a π bond in acetylene. Each of these processes individually satisfies the Hammond postulate.

I. Introduction

Over the years, there has been considerable interest in the chemistry of vinylidene, $:C{=}CH_2$, the simplest unsaturated carbene.[1,2] Theoretical studies have focused on the question of whether vinylidene actually exists as a stable species,[3-15] while numerous experimental studies have provided evidence for the participation of vinylidene as an intermediate in chemical reactions.[16-19] Lineberger and co-workers have recently observed vinylidene spectroscopically[20,21] and thus provided the definitive answer to the question of the existence of vinylidene. Nevertheless, there are several aspects to this problem that warrant further investigation.

Although the formation of acetylene, $HC{\equiv}CH$, from vinylidene is strongly exothermic, the calculated geometry for the transition state is roughly halfway between the two,[15] in apparent violation of the Hammond postulate,[22] as first noted by Dykstra and Schaefer.[3] The geometry of this transition state shows very little variation with the level of theory used.[15] Such a well-defined transition state halfway between reactant and product is typical of reactions with large activation energies. However, it seems peculiar in the present case, since the barrier is very small and

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Table I. Calculated and Observed Geometries for the Isomerization of Vinylidene to Acetylene[a]

	vinylidene			transition state					acetylene	
method/basis set	R_{CC}	R_{CH}	∠HCH	R_{CC}	$R_{C_bH_b}$	$R_{C_bH_a}$	$R_{C_aH_a}$	∠CCH_b	R_{CC}	R_{CH}
AM1	1.304	1.102	112.9	1.266	1.068	1.393	1.338	166.9	1.195	1.061
RHF/STO-3G	1.305	1.079	117.9	1.249	1.074	1.445	1.209	178.1	1.168	1.065
RHF/DZ+P[b]	1.299	1.080	120.2	1.243	1.068	1.467	1.174	180.5	1.191	1.062
RHF/TZ+2P[b]	1.286	1.075	120.5	1.230	1.060	1.450	1.175	180.3	1.180	1.054
MP2/6-31G*	1.307	1.088	120.4	1.258	1.075	1.413	1.187	177.3	1.216	1.066
CCSD/DZ+P[b]	1.322	1.090	119.5	1.271	1.080	1.400	1.202	178.7	1.220	1.072
CCSD/TZ+2P[b]	1.300	1.081	120.0	1.251	1.067	1.386	1.201	178.6	1.201	1.061
experiment[c]									1.203	1.060

[a] Bond distances in angstroms and bond angles in degrees. [b] Reference 15. [c] Reference 44.

is sensitive to the level of theory employed.

In an attempt to resolve these apparent contradictions and obtain a more accurate value for the isomerization barrier, we have studied these species at several different levels of theory up to our complete basis set–quadratic configuration interaction atomic pair natural orbital CBS-QCI/[6s6p3d2f,4s2p1d] APNO model chemistry, which consistently gives energy differences to an accuracy of ±0.5 kcal/mol.[23-34]

II. Theoretical Methods

The accurate calculation of a potential energy surface requires convergence with both the one-electron basis set and the configuration interaction (CI) expansion. In our calculations, the former is accomplished by the CBS extrapolation.[23-34] To address the latter, we have recently modified our method[29-32] to include the quadratic CI (QCI) approach of Pople.[35] In this work the QCISD(T) procedure, which includes a noniterative evaluation of the contribution of triple excitations, has been used. This procedure is essentially the coupled cluster singles and doubles limit[36] (CCSD) with triple excitations correct through fourth order (i.e., CCSDT-1).[37]

For the present study, we have used our largest basis set, consisting of (14s9p4d2f,6s3p1d) Gaussian primitive functions contracted to [6s6p3d2f,4s2p1d] atomic pair natural orbitals.[29] This model is designated the CBS-QCI/[...3d2f] APNO model chemistry. In earlier work, we demonstrated that CBS extrapolations based on the asymptotic convergence of pair natural orbital expansions[23,24] achieved an accuracy of 0.1 kcal/mol for the individual second-order Møller–Plesset[38] pair correlation energies of atoms[23-26] and molecules.[27,28,30] A calibration study of the ionization potentials and electron affinities of the first-row atoms and the bond dissociation energies of the first-row diatomics and hydrides using the CBS-QCI/[...3d2f] APNO model chemistry gave a root mean square error of 0.5 kcal/mol for the total energy changes in these chemical processes.[30] This CBS model has also been applied to the calculation of the heat of formation of NH_3 from $N_2 + H_2$ (−8.8 kcal/mol calcd; −9.34 ± 0.01 kcal/mol obsd),[32] the heat of formation of singlet CH_2 (102.0 kcal/mol calcd; 101.8 ± 0.5 kcal/mol obsd),[33] and the bond dissociation energies of H–CCH (131.5 kcal/mol calcd; 131.3 ± 0.7 kcal/mol obsd)[31] and NF (76.1 kcal/mol calcd; 75.4 ± 0.5 kcal/mol obsd).[34] The small size of the barrier to isomerization of vinylidene and the sensitivity to the basis set used make this an obvious candidate for the application of our CBS-QCI/[...3d2f] APNO model.

We have also employed several lower levels of theory in order to establish the effects of the individual components of the calculated energy. These methods include the Austin Model 1 (AM1) semiempirical method of Dewar[39] and the restricted Hartree–Fock (RHF) and second-order Møller–Plesset (MP2) methods of Pople using STO-3G, 6-31G**, and 6–311+G** basis sets.[40] We have included Pople's more recent G1 model chemistry[41] as an intermediate level of theory. These calculations were performed with a modified version of the computer program Gaussian 90.[42] Since this paper was originally submitted, Smith, Smernik, and Radom have published[43] QCISD(T)/6-311++G(3df,2pd)//QCISD(T)/6-311G** calculations which fall between Pople's G1 model and our CBS-QCI/[...3d2f] APNO model.

Gallo, Hamilton, and Schaefer[15] have already published a very careful and thorough study of the convergence of both the transition-state geometry and the energy with the basis set and the level of CI. They provide convincing evidence of geometry convergence to 0.002 Å for vinylidene and acetylene and 0.01 Å for the reaction coordinate of the transition state. They estimate that their best calculated value for the isomerization barrier, $\Delta E_e^* =$ 4.6 kcal/mol, would be reduced to 3.0 kcal/mol with the use of larger basis sets. The calculated harmonic vibrational frequencies for vinylidene[15] are just a few percent larger than Lineberger's experimental frequencies,[21] clearly demonstrating that theory and experiment are looking at the same species. The largest relative error occurs in the HCH rock, which is the reaction coordinate and thus highly anharmonic, but even this error is only 66 cm^{-1} (0.19 kcal/mol). The calculated changes in the zero-point energies of vinylidene and the transition state appear to be accurate to ±0.1 kcal/mol and clearly indicate a bound vibrational state for vinylidene in agreement with Lineberger's experimental observation

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Table II. Calculated and Observed Energy Changes[a] for the Isomerization of Vinylidene to Acetylene

method/basis set/geometry	$\Delta E_e^{\ddagger}$	ΔE_0
AM1	21.95	−58.06
RHF/STO-3G	29.32	−40.46
RHF/6-31G**	14.70	−31.22
RHF/TZ+2P	13.4[b]	−35.0[b]
CBS-RHF/[...3d2f]//CCSD/TZ+2P	12.10	−35.19
MP2/6-31G**	1.07	−48.66
MP2/6-311+G*//MP2/6-31G**	−0.94	−49.33
CBS-MP2/[...3d2f]//CCSD/TZ+2P	−2.96	−51.59
CCSDT-1/TZ-2P//CCSD/TZ+2P	4.6[b]	−42.1[b]
G1	2.86	−42.78
QCISD(T)/6-311++G(3df,2pd)//QCISD(T)/6-311G**	2.63[c]	−42.33[c]
QCISD(T)/[...3d2f]//CCSD/TZ+2P	2.72	−42.81
CBS-QCI/[...3d2f]//CCSD/TZ+2P	2.16	−43.91
experiment	2[d]	−44.1 ± 0.7[d,e]

[a] In kilocalories/mole. [b] Reference 15. [c] Reference 43. [d] Reference 21. [e] Reference 46 (upper bound).

of the 2 ← 0 transition.[21] On the basis of the observation of this transition, Lineberger infers a lower bound for the barrier of 1.3 kcal/mol and estimates the barrier height to be about 2 kcal/mol.

Using the accurate CCSD/TZ+2P optimized geometries of Gallo et al.,[15] we have performed CBS-QCI/[...3d2f] APNO calculations for vinylidene and the transition state. The results, combined with our previously reported calculations on acetylene,[31] allow us to reduce the uncertainty in the calculated energy changes for the vinylidene–acetylene isomerization process to 0.5 kcal/mol.

III. Results

The calculated geometries of the reactant (vinylidene), the transition state, and the product (acetylene) are given in Table I. We did not attempt to improve upon the CCSD/TZ+2P geometries of Schaefer,[15] but instead provide results from lower levels of theory for comparison. These calculations show that the geometries are fairly insensitive to the level of theory. Even the AM1 semiempirical theory[39] gives geometries which are in qualitative agreement with Schaefer's CCSD/TZ+2P ab initio results. This is rather surprising for the transition state, since the potential energy barrier, $\Delta E_e^{\ddagger}$, for the reaction is only 2 kcal/mol (Table II), indicating a very flat potential energy surface (Figure 1). The height of the calculated barrier is very sensitive to the level of calculation (Table II), but the position is not (Table I). Hence, we have an apparent contradiction of a well-defined transition state on a very flat potential.

A fairly large barrier is obtained unless electron correlation is included (Table II). Both the AM1 semiempirical surface and the RHF/STO-3G ab initio surface give barriers that are much too large. A larger basis set lowers the RHF barrier until the complete basis limit (12.1 kcal/mol) is reached. The convergence of the isomerization energy, ΔE_0, to the complete basis set RHF limit is more erratic, but in both cases the 6-31G** level basis set gives fairly good results.

The MP2 calculations converge smoothly to the complete basis set limit for both the activation barrier, $\Delta E_e^{\ddagger}$, and the isomerization energy, ΔE_0. Both the transition state and the acetylene product involve more crowding of electrons around the carbon–carbon bond and hence have larger correlation energies than vinylidene. Higher-order corrections reduce this correlation effect by about 5 kcal/mol in both cases. Although the barrier disappears at the MP2 level, it returns when the higher-order correlation effects are included.

Our best estimates, obtained from our CBS-QCI/[...3d2f] APNO calculations, for the classical barrier ($\Delta E_e^{\ddagger}$ = 2.16 ± 0.5 kcal/mol) and the vinylidene to acetylene isomerization energy (ΔE_0 = −43.91 ± 0.5 kcal/mol) are consistent with earlier calculations using finite basis sets and are in excellent agreement with the experimental results of Lineberger[20,21,45] ($\Delta E_e^{\ddagger}$ = 2 kcal/mol and ΔE_0 = −47.4 ± 4.0 kcal/mol) and Field[46,47] ($-\Delta E_0 \leq 44.4 \pm 0.3$ kcal/mol). The overlap of the two experimental ranges gives ΔE_0 = −44.1 ± 0.7 kcal/mol. Our CBS-QCI/[...3d2f] result for ΔE_0 includes vibrational zero-point energies calculated from scaled RHF/6-31G* harmonic vibrational frequencies.[41] The zero-point correction to the isomerization barrier calculated by this procedure agrees to 0.1 kcal/mol with the CCSD/TZ+2P result reported by Schaefer and should be of comparable accuracy for the correction to the isomerization energy. We have accomplished our first goal of refining the calculated energy changes for this reaction. Now we shall examine the peculiar nature of this potential energy surface.

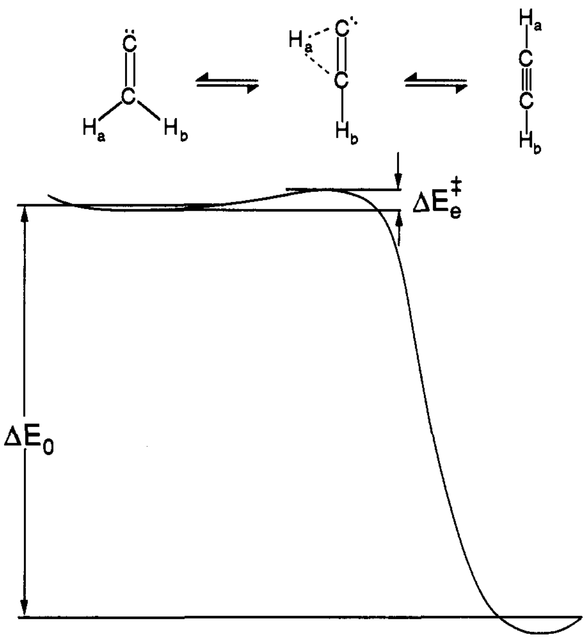

Figure 1. The potential energy along the reaction path for the isomerization of vinylidene to acetylene. The classical reaction barrier, $\Delta E_e^{\ddagger}$, does not include changes in the zero-point energy. The isomerization energy, ΔE_0, does include the zero-point energy corrections.

In order to provide a quantitative framework to discuss the behavior of the potential energy surface for the vinylidene isomerization, we have determined the reaction path and the energy profile along this path at several levels of theory (Figure 2). Once the stationary points on the surface were located, the transition

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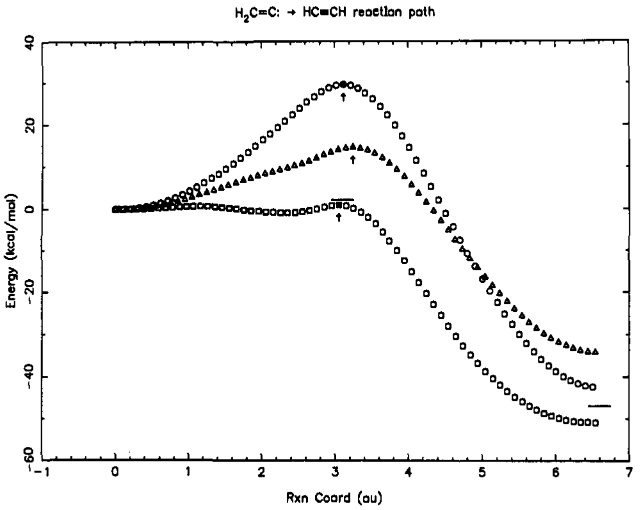

Figure 2. Calculated energy profiles along the reaction path for the isomerization of vinylidene. Results at the RHF/STO-3G (circles), RHF/6-31G** (triangles), and MP2/6-31G** (squares) levels of theory are shown. The calculated CBS-QCI/[...3d2f] APNO energies of the reactant, transition state, and product are indicated by horizontal lines. The position of the transition state is indicated by arrows.

states were verified to be first-order saddle points and the local minima were identified as such by a harmonic frequency analysis. We have used the conventional definition of the reaction path (i.e., following the minimum energy path from the transition state to the reactant or product).[48-51] The mass-weighted reaction path, or intrinsic reaction coordinate (IRC), is the appropriate coordinate for consideration of molecular dynamics or kinetics and is readily available through the program Gaussian 90.[42,52] The IRC clearly demonstrates the near invariance of the position of the transition state on the reaction path (Figure 2). Our results above suggest that the MP2/6-31G** energy profile along the IRC in Figure 2 should be qualitatively similar to the energy profile of the exact potential energy surface. However, the very shallow local minimum (0.9 kcal/mol below vinylidene) between vinylidene and the transition state disappears at higher levels of theory.[43]

The Hammond postulate was originally formulated to describe the energy profile along the reaction coordinate (Figure 1 of ref 22); and thus Figure 2 clearly violates the Hammond postulate. Although it has been suggested that the Hammond postulate should be interpreted as applying to the overlap of the transition state wave function with those of the reactant or product,[53,54] this interpretation removes all connection with reaction dynamics and kinetics, and hence we feel that it is more useful to try to understand why there is a breakdown using the conventional interpretation.

IV. Discussion

The apparent contradictions presented by the isomerization of vinylidene to acetylene can be easily understood if we consider a simple idealized model of the hybrid atomic orbitals involved in the bonding (Figure 3). The 120° HCC angle of vinylidene (Table I) indicates sp^2 hybridization for the methylene carbon. This angle has already opened to 180° in the transition state (Table I), indicating that the hybridization of this carbon is sp in both the transition state and the acetylene product. The hybridization of the carbon bearing the vinylidene lone pair is clearly sp in vinylidene and acetylene, but should be sp^2 in the transition state since it is beginning to bond to the migrating hydrogen while still holding the lone pair (Figure 3).

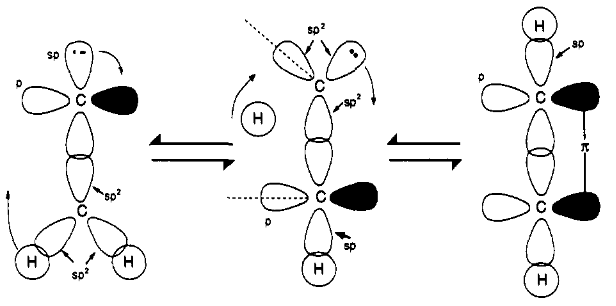

Figure 3. An idealized hybrid atomic orbital description of the isomerization of vinylidene. The π orbitals perpendicular to the plane of the molecule have been omitted. The hybridization of the methylene carbon has been selected to be consistent with the H–C–C angle for the nonmigrating hydrogen from Table I. The hybridization of the lone pair carbon has been selected to be consistent with the number of atoms and lone pairs associated with this atom.

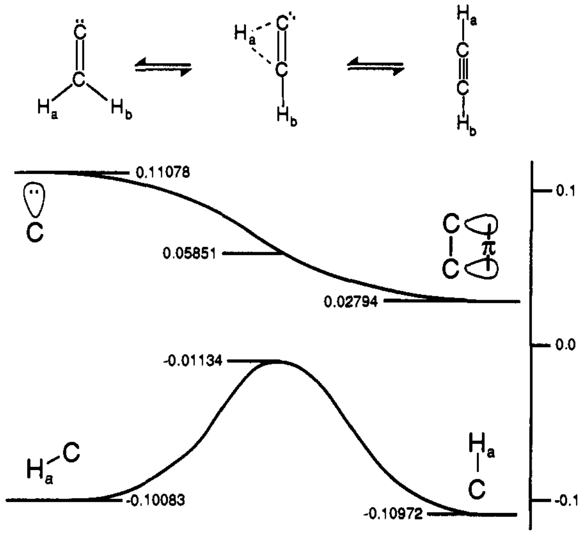

Figure 4. An idealized molecular orbital energy level diagram for the migrating C–H bond orbital and the lone pair orbital during the vinylidene isomerization. Both of these idealized orbital energies satisfy the Hammond postulate individually, but their sum does not.

Note that in the transition state the migrating hydrogen is closer to the terminal carbon atom (Table I), but midway between the hybrid AOs of the two carbon atoms (Figure 3). The energy of the MO representing this migrating C–H bond is clearly a maximum in the transition state (Figure 4). This explains the fact that the geometry of the transition state is so well defined and relatively independent of the level of theory employed. Since the migration of the hydrogen breaks one C–H bond but creates another, the process is neither significantly exothermic nor endothermic.[55] According to the Hammond postulate,[22] the transition state for such a reaction should be midway between reactant and product as in Figure 4.

The second part of the vinylidene isomerization reaction is the migration of the lone pair MO of vinylidene to form the second π bond of acetylene (Figure 3). The C–C bond length of the transition state is almost exactly halfway between the length of the C–C double bond in vinylidene and the length of the C–C triple bond in acetylene (Table I). This indicates that the formation of the new π bond is well under way in the transition state and thus the energy of this MO should also be about halfway between the vinylidene lone pair energy and the acetylene π bond energy (Figure 4). The "transition state" for the lone pair migration must then be more like vinylidene than acetylene. Thus the energy of

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(51) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(52) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

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(54) Cioslowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 6756.

(55) The dissociation energy (ref 45) of an sp-hybridized C–H bond in acetylene (131 kcal/mol) is somewhat greater than that of an sp^2-hybridized C–H bond in ethylene (110 kcal/mol).

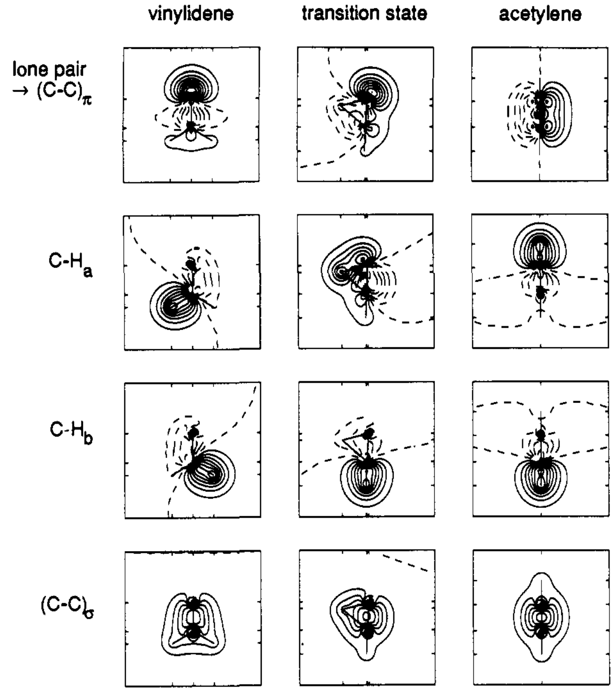

Figure 5. Contour maps of the four ab initio molecular orbitals in the plane of vinylidene, the transition state, and acetylene. The C–H bond orbitals have been localized. The C–C σ bond is the canonical orbital, but the migrating C–H bond and the lone pair have been rotated by 22.5° (see Figure 6) in the transition state.

the lone pair orbital would appear to obey the Hammond postulate, which states that for an exothermic reaction, the transition state should more closely resemble the reactant than the product.

The vinylidene isomerization is then the sum of two separate process: the hydrogen migration and the π bond formation. Each process individually satisfies the Hammond postulate (Figure 4). However, the sum of the two simultaneous processes appears to violate the Hammond postulate (Figure 1 and Figure 2). We conclude that, at least in this case, *the Hammond postulate should be applied to the energies of individual orbitals or bonds*, but not to the total energy directly. The behavior of the total energy must be deduced by application of the Hammond postulate to each of the separate processes individually and then considering the sum of the energy changes from the separate processes. Although we have not yet examined additional examples, this generalization of the Hammond postulate to reactions with complex or concerted mechanisms seems so natural and obvious that we would be very surprised if it did not turn out to be generally applicable.

The calculated MOs of the reactant, transition state, and product (Figure 5) are consistent with the above AO hybridization scheme. The $C\text{-}H_a$ bond orbital of vinylidene has moved with H_a in the transition state and shows a weak bonding interaction to both carbons. The lone pair orbital of vinylidene has begun to form the π bond in the transition state, but also alters the weak bonds of the two carbons to H_a. The π bond that is perpendicular to the plane of the molecule has been omitted from Figure 5, since it does not participate in the reaction. The C–C σ bond and the nonmigrating C–H bond are also largely unaffected by the isomerization. Only the migrating C–H bond and the carbon lone pair show major changes during the reaction. These changes are consistent with our idealized AO hybridization picture. In particular, we note that the directions of the local maxima for these orbitals indicate that lone pair carbon uses sp^2 hybrid orbitals in the transition state. However, there is a subjective element in the calculated MOs of Figure 5.

Since the SCF wave function is invariant to unitary transformations among the occupied MOs, we are free to select any such transformation that proves useful in conceptualizing the isomerization process. We have therefore elected to localize the canonical orbitals representing the C–H bonds in both vinylidene and acetylene. This seems straightforward and unambiguous.

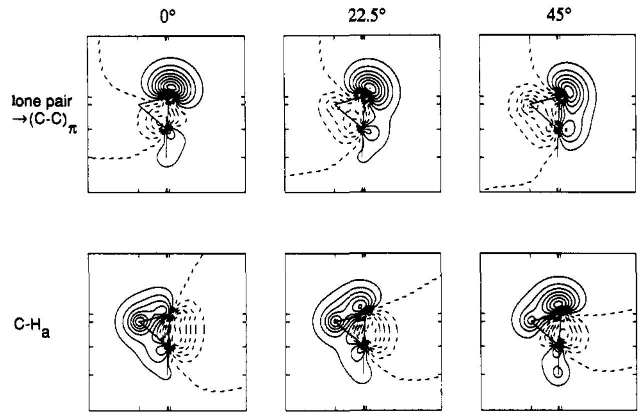

Figure 6. The effects of unitary transformations (rotations by 0°, 22.5°, and 45°) on the ab initio molecular orbitals representing the migrating C–H bond and the lone pair in the transition state for the vinylidene isomerization.

Table III. Calculated SCF Orbital Energies[a]

orbital	vinylidene	transition state	acetylene	carbon
C–C π	−0.41409	−0.43335	−0.41111	−0.43905 (2p)
C:	−0.46189	−0.44735	−0.41111	
C–H	−0.62896	−0.56174	−0.68239	
C–H	−0.73015	−0.77875	−0.76863	−0.70629 (2s)
C–C σ	−1.05937	−1.10476	−1.03047	
C 1s	−11.23838	−11.25267	−11.23833	−11.32305 (1s)
C 1s	−11.30083	−11.28639	−11.24215	
sum	−51.64156	−51.51462	−51.56838	−25.93678
E(SCF)	−76.79918	−76.77982	−76.85482	−37.69359

[a] In hartrees.

However, the separation of the migrating C–H bond from the migrating lone pair in the transition state is somewhat ambiguous and therefore subjective. The canonical orbitals for the transition state ($\theta = 0°$ in Figure 6) isolate the bonding to the migrating hydrogen in one orbital, since the other MO has a node passing through this hydrogen. However, this migrating hydrogen MO also has considerable C–C π character (Figure 6). If we rotate this pair of transition state MOs by 45°, the C–C π bonding becomes isolated in the lone pair MO, but the bonding to the migrating hydrogen is distributed equally between the two MOs. We therefore elected to include the compromise picture obtained with a rotation by 22.5° in Figure 5.

Our simple idealized AO hybridization scheme in Figure 3 seems clearly justified by the actual calculated MOs in Figure 5. Unfortunately, our idealized MO energy level diagram in Figure 4 is not on such firm ground. It is rather frustrating that, although such orbital energy level diagrams have proven enormously useful in the interpretation of chemical reactions, no firm connection with ab initio electronic structure calculations has been established. The calculated SCF orbital energies (Table III) describe the ionization potentials very well,[56] but do not add up to the calculated total energy and thus must be interpreted with caution. Although the SCF eigenvalue associated with one of the C–H bonds shows a pronounced increase in energy in the transition state and appears to justify this part of Figure 4, the sp-hybridized lone pair of vinylidene increases in energy as it becomes a pure p-hybridized π bond of acetylene. The individual calculated SCF orbital energies are dominated by changes in hybridization. The total energy is largely unaffected, since the C–C σ bond and the C–H bond acquire the s character that has been lost by the lone pair. A possible justification for diagrams such as Figure 4 is offered by comparison of the molecular SCF orbital energies with the corresponding atomic hybrid orbital energies. Table IV gives the adjusted orbital energies $\epsilon_i' = \epsilon_i(C_2H_2) - \epsilon_i(C_{hybrid})$ computed with the 6s6p3d2f APNO basis set. These orbital energies indicate

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(56) Koopmans, B. *Physica* **1934**, *1*, 104.

Table IV. Calculated Changes[a] in Molecular Orbital Energies Relative to Atomic Hybrid Orbitals

orbital	vinylidene	transition state	acetylene
C:	−0.461 89	−0.447 35	−0.411 11
C hybrid	+0.572 67 sp	+0.505 86	+0.439 05 p
ϵ_i'	0.110 78	0.058 51	0.027 94
C–H	−0.628 96	−0.561 74	−0.682 39
C hybrid	+0.528 13 sp^2	+0.550 40	+0.572 67 sp
ϵ_i'	−0.100 83	−0.011 34	−0.109 72

[a] In hartrees.

the effect on bonding of the removal of a particular electron, assuming that the hybridization will adjust to fully occupy the low-energy 2s orbital. We have used these orbital energies to construct Figure 4. The effects of electron correlation (not included in Figure 4) would lower the energies of the transition state and product relative to vinylidene (Table II). We fully recognize the lack of rigor in that our orbital energies do not sum to the calculated total energy. Nevertheless, we believe that Figure 4 offers a very useful interpretation of the calculated potential energy surface for the isomerization of vinylidene to acetylene.

In order to further test the central role of the vinylidene lone pair in our analysis of the apparent violation of the Hammond postulate, we have examined the vinyl carbenium ion, $H_2C{=}CH^+$, in which the lone pair has been protonated and thus excluded from participation in the isomerization to the protonated acetylene form. This reaction should obey the conventional form of the Hammond postulate, since only one orbital (the migrating hydrogen) is involved. The stationary points on the surface were located, the transition states were verified to be first-order saddle points, and the local minima were identified as such by a harmonic frequency analysis. The mass-weighted minimum energy path (i.e., the IRC) was then followed from the transition states to the local minima. At the RHF/STO-3G level, the protonated acetylene form is a saddle point 18.1 kcal/mol above the protonated vinylidene form (Figure 7). If the basis set is increased to 6-31G**, the acetylene form becomes a local minimum 6 kcal/mol above the vinylidene form, and the transition state moves about $^1/_4$ of the way to the vinylidene form. As the basis set is increased and electron correlation is included, the energy of the acetylene form continues to lower until it is below the vinylidene form and the transition state continues its journey to the vinylidene form of the ion (Figure 7). As the transition state approaches the protonated vinylidene structure, the barrier becomes very small (0.18 kcal/mol at the MP2/6-31G** level). This is precisely the behavior predicted by the Hammond postulate! The behavior of the vinyl carbenium ion (Figure 7) is completely consistent with our interpretation of the vinylidene isomerization (Figure 4). Just as for neutral vinylidene, the MP2/6-31G** results for the protonated species are in qualitative agreement with single-point calculations at a much higher level of theory.[57] The ACPF/[6s5p3d2f,4s3p2d] ANO isomerization energy of Lindh, Rice, and Lee[57] is included in Figure 7.

Since a partition of the total energy into orbital energies cannot be unique, neither ab initio nor semiempirical methods can offer a rigorous interpretation of the source of the changes in the total energy. Their usefulness must instead rest on the insight they provide. The above ab initio description of the vinylidene isomerization is straightforward and directly connected to the changes in bonding, but its real strength is the interpretation it provides for the peculiar behavior of the potential energy surface: (1) the apparent violation of the Hammond postulate; (2) the shape of the lone pair orbital; (3) the very small barrier to isomerization; (4) the near invariance of the transition-state geometry; (5) the position of the migrating hydrogen; (6) the position of the nonmigrating hydrogen; (7) the length of the C–C bond. If one attributes[53] the first three observations to the similarity of the transition-state lone pair orbital to the vinylidene lone pair orbital (Figure 5), then observations 4–7 remain unexplained.

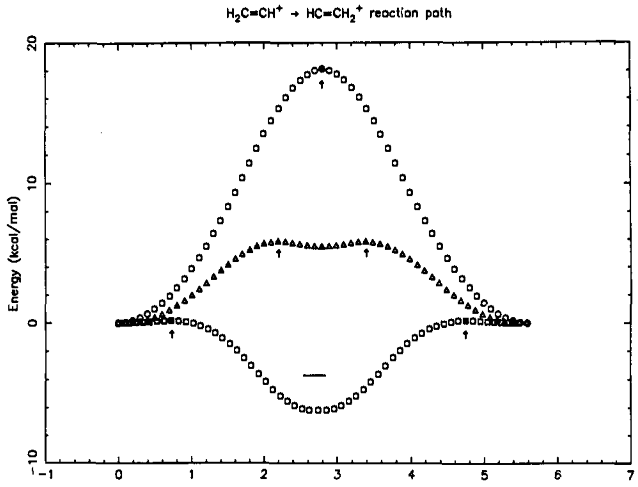

Figure 7. Calculated energy profiles along the reaction path for the isomerization of protonated vinylidene. Results at the RHF/STO-3G (circles), RHF/6-31G** (triangles), and MP2/6-31G** (squares) levels of theory are shown. The calculated ACPF energy difference (ref 57) between the reactant and product is indicated by a horizontal line. The position of the transition state is indicated by arrows.

V. Conclusions

The calculated CBS-QCI/[...3d2f] APNO barrier ($\Delta E_e^\ddagger = 2.2 \pm 0.5$ kcal/mol) and isomerization energy change ($\Delta E_0 = -43.9 \pm 0.5$ kcal/mol) are in excellent agreement with recent experimental values ($\Delta E_e^\ddagger = 2$ kcal/mol, and $\Delta E_0 = -44.1 \pm 0.7$ kcal/mol). There is no doubt that both experimentally and computationally vinylidene is a stable species with a bound vibrational state.

Although the formation of acetylene, $HC{\equiv}CH$, from vinylidene is strongly exothermic, the calculated geometry for the transition state is roughly halfway between the two, in apparent violation of the Hammond postulate. The geometry of this transition state shows very little variation with the level of theory used. Such a well-defined transition state halfway between reactant and product is typical of reactions with large activation energies. However, in the present case, the barrier is very small and is sensitive to the level of theory employed.

The potential energy surface for the isomerization can best be understood by considering two distinct processes. The location of the transition state is determined by the hydrogen migration, which has a significant barrier, whereas the exothermicity results from the conversion of the lone pair of vinylidene to a π bond in acetylene. Each of these processes individually satisfies the Hammond postulate.

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Registry No. Vinylidene, 2143-69-3.

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[57] Lindh, R.; Rice, J. E.; Lee, T. J. *J. Chem. Phys.* **1991**, *94*, 8008.