

Theoretical Studies of the Low-Lying States of Vinylidene^{1a}

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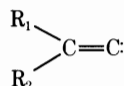
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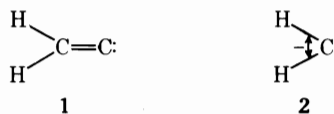
Abstract: The ground and excited states of vinylidene, H₂C=C:, were studied using generalized valence bond (GVB) and configuration interaction (GVB-CI) wave functions. We find that the ground state is the singlet state [¹A₁ (σ²)] with the methylene-like triplet [³B₂ (σπ)] lying 2 eV = 46 kcal higher. These states lead to CC bond lengths of 1.35 and 1.36 Å, respectively, slightly longer than a normal CC double bond. The ionization potential for singlet vinylidene (¹A₁) is calculated to be 10.8 eV (out of the π orbital). With extensive CI calculations we find a CC bond energy of D_e(H₂C=C) = 160 kcal/mol or including zero-point effects and estimates of additional correlation effects D₀(H₂C=C) = 162 kcal/mol. This leads to ΔH_f²⁹⁸(H₂CC:) = 100 kcal/mol. The dipole moment for the ground state is calculated to be 2.23 D (the methylene end negative), while the dipole moment for the ³B₂ excited state is 0.55 D.

I. Introduction

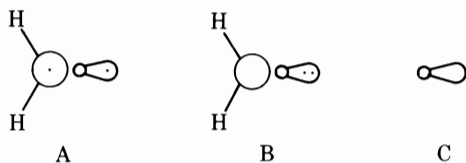
Stang and co-workers² have recently developed the use of vinylidenes formed from vinyl triflates as an effective re-



agent for the formation of methylenecyclopropenes. The reacting species appears to be a singlet state, although there is little information on its physical properties. The parent species **1** has so far not been observed, since intramolecular insertion into the CH bond to give acetylene is extremely fast. The objective of this paper is to provide some reliable information on the character of the states of **1** and its excitation energies and ionization potentials.



In describing the states of **1** it will be helpful to compare with the states of methylene, **2**. The two low-lying states of **2** are a triplet state, ³B₁ (σπ) (A) and a singlet state, ¹A₁ (σ²) (B), where the portion of A and B shown in C indicates an sp-hy-

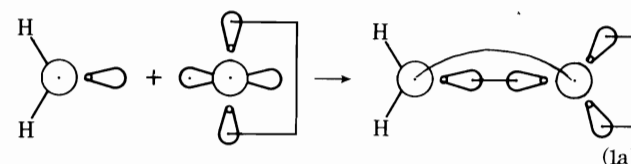


bridized nonbonding orbital (denoted as σ) in the plane of the molecule, and O indicates a nonbonding p orbital (denoted as π) perpendicular to the molecular plane; the dots indicate how many electrons are in each orbital. The ground state of methylene is ³B₁ (σπ) with a bond angle^{8,19-21} of ~135°; however, the ¹A₁ (σ²) state (bond angle 102.4°)¹⁷ is only 0.88 eV¹⁸ higher. The potential curves⁸ for CH₂ are shown in Figure 1. Note in particular that the difference in energy between ³B₁ (σπ) and ¹A₁ (σ²) decreases with θ (over the range shown) and that the ¹A₁ state is the lower state for θ < 90°.

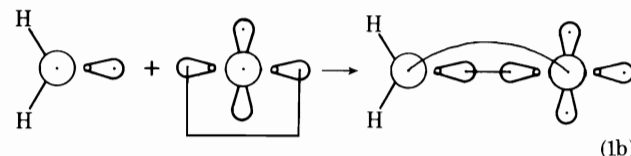
A crude estimate of the relative ordering of the lowest triplet and singlet states of **1** could be made by considering **1** to correspond to **2** with a very small θ (thinking of the CC double bond as two "banana" bonds, one might expect θ ~ 30–60°). Since the ¹A₁ (σ²) state of methylene is the ground state for θ < 90°, one would expect that vinylidene would have a singlet

ground state, as first suggested by Hoffmann and Gleiter³ on the basis of extended Hückel calculations. Indeed we find (vide infra) that the ground state of vinylidene is a singlet with the triplet state 46 kcal (2.0 eV) higher.

In qualitative considerations we will consider vinylidene to be composed of methylene and a carbon atom. Joining ground state methylene (³B₁) and ground state carbon atom (³P) gives ¹A₁ vinylidene (denoted as σ²) (eq 1a) and ³B₂ vinylidene

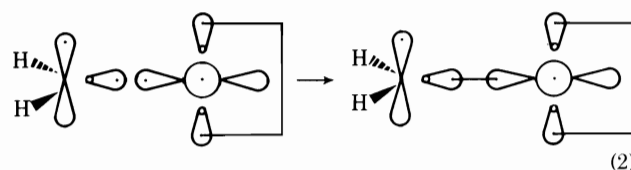


(denoted as σπ)⁵ (eq 1b). [Note that an orbital which is sym-



metric with respect to the molecular plane but antisymmetric with respect to the perpendicular plane passing through the CC axis is denoted as π.] The second configuration (σπ) also gives rise to a singlet state, ¹B₂.

In these calculations we emphasize the two lowest states, ¹A₁ (σ²) and ³B₂ (σπ); however, we also report excitation energies to a number of higher states including the ¹B₂ (σπ), ¹A₂ (ππ), and ³A₂ (ππ) states [see (eq 2) for the ππ configurations].



II. Computational Details

A. Basis Set and Geometries. Dunning's⁶ (4s2p/2s) contraction of Huzinaga's⁷ (9s5p/4s) primitive Gaussian basis was used in all calculations. Since polarization functions are known to be important in the singlet-triplet energy difference for methylene, we included one set of d polarization functions (α = 0.6769) on each carbon.⁸

The geometries considered maintained C_{2v} symmetry and used the following parameters: R_{CH} = 1.076 Å; ∠HCH =

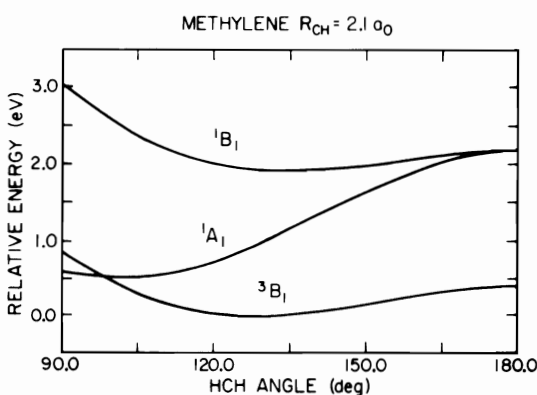


Figure 1. The energies of the electronic states of methylene as a function of bond angle (GVB-CI calculation of ref 8, plot courtesy of W. Wadt).

116.6° (based on ethylene).¹³ Since the most likely difference in geometry between the σ^2 and $\sigma\bar{\pi}$ states was expected to be in the carbon-carbon bond length, this parameter was optimized (using $R_{CC} = 1.25, 1.33,$ and 1.41 Å). The 1A_1 state was found to have an optimum bond length of 1.35 Å, while the 3B_2 state has a bond length of 1.36 Å. These optimum values were used in all subsequent calculations.

B. The GVB Calculations. To describe accurately the variation of the energy with bond length, we must carefully consider those bonds that are directly affected by the geometry modifications. The Hartree-Fock (HF) wave function for the 1A_1 state of vinylidene would have seven doubly occupied orbitals. Breaking the carbon-carbon bond to give 3B_1 methylene and 3P carbon atom requires HF wave functions consisting of five doubly occupied and four singly occupied orbitals. Thus the HF wave function for vinylidene cannot properly describe the dissociation of the CC bond.

The GVB wave function⁸ allows every electron to have its own orbital. For example, the doubly occupied π orbital of the HF wave function would be replaced by

$$\phi_{\pi}(1)\phi_{\pi}(2) \rightarrow \phi_{\pi}(1)\phi_{\pi r}(2) + \phi_{\pi r}(1)\phi_{\pi}(2) \quad (3)$$

allowing each electron to be in different (nonorthogonal) orbitals; these orbitals are all solved for self-consistently. For a molecule such as **1**, these GVB orbitals are found to be localized in pairs in the region of each of the bonds and to correspond qualitatively to the simple valence bond description of the molecule. However, to describe properly the dissociation of the CC bond of **1**, it is sufficient that only two HF pairs be correlated or split into pairs of nonorthogonal singly occupied orbitals. These two pairs correspond to the CC σ and π bonding pairs, which are clearly directly involved in breaking the CC bond. We also correlated the doubly occupied carbene σ orbital of the singlet state in order to make the treatment of the 1A_1 state consistent with our treatment of the 3B_2 state (in which the σ and $\bar{\pi}$ orbitals are each singly occupied, thereby leading to negligible correlation effects). Thus the GVB wave functions used for **1** have the form

$$\mathcal{A}\{\Phi_{cs}(\phi_{\sigma_1}\phi_{\sigma r} + \phi_{\sigma r}\phi_{\sigma_1})(\phi_{\pi_1}\phi_{\pi r} + \phi_{\pi r}\phi_{\pi_1}) \times (\phi_{\sigma_1}\phi_{\sigma_2} + \phi_{\sigma_2}\phi_{\sigma_1})\alpha\beta\alpha\beta\alpha\beta\}$$

for the 1A_1 (σ^2) state and

$$\mathcal{A}\{\Phi_{cs}(\phi_{\sigma_1}\phi_{\sigma r} + \phi_{\sigma r}\phi_{\sigma_1})(\phi_{\pi_1}\phi_{\pi r} + \phi_{\pi r}\phi_{\pi_1}) \times (\phi_{\sigma}\phi_{\bar{\pi}} - \phi_{\bar{\pi}}\phi_{\sigma})\alpha\beta\alpha\beta\alpha\beta\}$$

for the 3B_2 ($\sigma\bar{\pi}$) state, whereas, for example, the HF wave function of the 1A_1 state has the form

$$\mathcal{A}\{\Phi_{cs}(\phi_{\sigma_a}\phi_{\sigma_a})(\phi_{\pi}\phi_{\pi})(\phi_{\sigma_b}\phi_{\sigma_b})\alpha\beta\alpha\beta\alpha\beta\}$$

Here \mathcal{A} is the antisymmetrizer (determinant operator), each orbital is understood to have a different electron, and Φ_{cs} indicates the four doubly occupied orbitals corresponding to two C 1s pairs and two CH bond pairs. All orbitals are solved for self-consistently so that all orbitals of the 1A_1 state (including those in Φ_{cs}) differ from those of the 3B_2 state; however, there is a close correspondence as indicated by the identical notation. These GVB wave functions, with three pairs of singly occupied orbitals, are denoted as GVB(3).⁹ It is the GVB(3) wave function which was used in the geometry optimization.

Although the GVB(3) wave function is adequate for describing the geometry and excitation energies of vinylidene, accurate bond strengths require inclusion of all electron correlation effects that are present in the molecule but missing in the separated species. This requires close attention to small correlation effects not included in the GVB(3) wave function. In order to include all possible correlations that might affect the CC bond energy, we increased the complexity of our GVB(3) wave function by also correlating the orbitals corresponding to the two CH bonding pairs. This GVB(5) wave function allows us to account for any differential correlation in the CH pairs between vinylidene and methylene. From previous studies on ethylene,^{10a} it was found that accurate CC bond strengths required the inclusion of two additional correlating orbitals for each of the CC bond pairs. For example, the GVB pair (eq 3) can be written as

$$\phi_{\pi_1}\phi_{\pi r} + \phi_{\pi r}\phi_{\pi_1} = C_1\phi_{\pi_1}\phi_{\pi_1} + C_2\phi_{\pi_2}\phi_{\pi_2} \quad (4)$$

in terms of orthogonal functions ϕ_{π_1} and ϕ_{π_2} , referred to as *natural orbitals*.^{8b,10b} With only a little additional effort, we can replace the GVB pair (eq 4) with

$$\sum_{i=1}^P C_i\phi_{\pi_i}(1)\phi_{\pi_i}(2) \quad (5)$$

leading to a total of P natural orbitals per pair. The first two terms of eq 5 correspond to the usual GVB terms and can be thought of as allowing correlation of the motions of the electrons, so that when one electron is on the left the other tends to be on the right (note the left side of eq 4). This is referred to as *left-right correlation*. The additional two important correlations of the bond pair are: (i) *in-out correlation* (when one electron is near the bond midpoint, the other tends to stay further from the bond midpoint); and (ii) *side-to-side correlation* (when one electron is on the starboard side of the molecule, the other tends to be on the port side; this is also referred to as angular correlation). These additional correlation effects become important mainly for the bond being broken, and hence the CH bonds were described with the usual two GVB orbitals. For the 1A_1 state we found that in-out correlation is of some importance in the σ lone pair and hence three natural orbitals ($P = 3$ in eq 5) were used for this pair. Thus for the 1A_1 state for five correlated pairs of orbitals are described with $4 + 4 + 2 + 2 + 3 = 15$ natural orbitals; this wave function is denoted as GVB(5/15) and in order to distinguish the normal GVB(5) wave function ($P = 2$ in eq 5 for all pairs), this latter wave function is denoted as GVB(5/10). For the 3B_1 state the non-bonding pair of electrons uses only two orbitals (ϕ_{σ} and $\phi_{\bar{\pi}}$), leading to GVB(5/14) for the description corresponding to GVB(5/15) for 1A_1 .

C. CI Calculations. Three different levels of CI wave functions were used. In the bond length determinations a full GVB(3)-CI was carried out. This utilized all configurations with six or more electrons distributed among the six GVB orbitals (CC $\sigma\sigma^*$, CC $\pi\pi^*$, LP $\sigma\sigma^*$). This results in 50 spatial configurations (104 determinants) for 1A_1 and 27 spatial configurations (65 determinants) for 3B_2 .

In determining the CC bond energy we carried out considerably more extensive CI calculations [referred to as

GVB(5/15)-CI] designed to include a consistent level of correlation effects for both vinylidene and the separated molecules (i.e., CH₂ and C). The following scheme for the CI is based on the principles developed by Harding and Goddard¹⁰ from the extensive analysis of GVB-CI wave functions of a number of molecules. To account for all correlation effects about the CC σ and π bonds, we allowed up to quadruple excitations within the set of eight orbitals ($\sigma\sigma_1^*\sigma_2^*\sigma_3^*\pi\pi_1^*\pi_2^*\pi_3^*$) describing the four electrons of the CC bond, with the restriction that there be no excitations between the σ and π sets. To these configurations we added another set to account for correlation effects available to separated molecules, but not normally utilized in vinylidene. This set involved all five pairs of GVB orbitals: A = CC($\sigma\sigma^*$); B = CC($\pi\pi^*$); C = CH(1)($\sigma\sigma^*$) + CH(2)($\sigma\sigma^*$); D = LP($\sigma\sigma_1^*\sigma_2^*$) or LP($\sigma\pi$) for singlet or triplet, respectively. Double excitations within sets A, B, and D and single excitations within set C were allowed, all simultaneously (with the restriction that no quintuple or higher excitations be included); however, no excitations between sets were allowed. In addition, all single excitations from the dominant configurations¹¹ were included, and we allowed all excitations from the doubly occupied CC σ into the three π virtuals (π^* , π_2^* , π_3^*). This CI led to 166 spatial configurations (296 spin eigenfunctions) for the ¹A₁ state and 136 spatial configurations (542 spin eigenfunctions) for the ³B₂ state. Although these CI wave functions contain only a small number of configurations, they include the equivalent of enormous sized CI's because we have optimized the shapes of the correlating orbitals. For example, with our basis the set of all double excitations would lead to 62 000 determinants despite leaving out the numerous triple and quadruple excitations we find to be important.

The CI calculations for the IP's were based on similar principles as follows. For the ²B₁ (σ^2) state we used the GVB orbitals of the ¹A₁ (σ^2) state, and for all other states we used the GVB orbitals of the ³B₂ ($\sigma\pi$) state. The CI calculations were then carried out as for the ground state except that CI excitations were based on the dominant configurations¹¹ of the various ion states.

III. The GVB Orbitals

A. The ¹A₁ (σ^2) State. The ground state GVB(5) orbitals are shown in Figure 2. We find that the orbitals localize in different regions and have the basic character of valence bond wave functions.

In the σ system there are three different bonding pairs. The first pair (Figure 2A) corresponds to the CC σ bond; one orbital centered on the central carbon is hybridized ($sp^{1.59}$)¹² toward the terminal carbon, while the other orbital centered on the terminal carbon is hybridized ($sp^{1.78}$) toward the central carbon. The other two pairs (Figures 2C and 2D) correspond to CH σ bonds—one centered on the upper hydrogen and the other on the lower hydrogen. The two pairs are identical and consist of two orbitals—one centered on the hydrogen is essentially spherical with some delocalization toward the central carbon, while the other is an sp^2 -type orbital (actually $sp^{1.88}$) centered on the central carbon and hybridized toward the hydrogen.

The other pair of orbitals in the σ system corresponds to the doubly occupied lone-pair orbital on the terminal carbon, (Figure 2B). The orbitals of this pair have the hybridization $sp^{0.63}$. Thus they are mainly s-like with high overlap as appropriate for singlet paired orbitals.

The π system consists of a p orbital centered on each carbon and hybridized toward the other carbon (Figure 2E). The overlaps and energy lowerings for these pairs are summarized in Table I.

B. The ³B₂ ($\sigma\pi$) State. Some of the GVB orbitals for the ³B₂

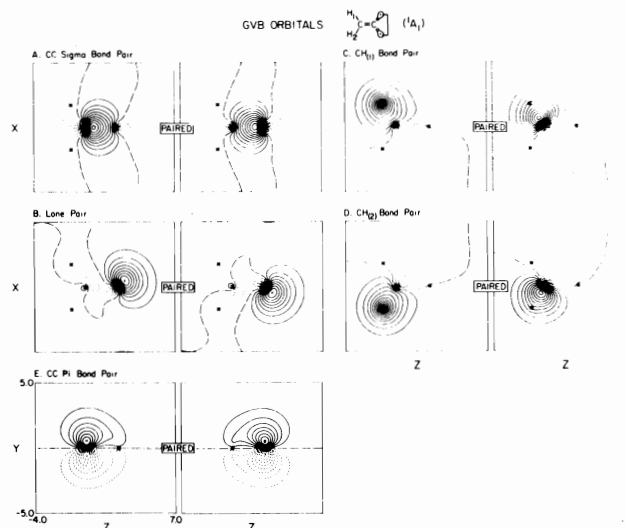


Figure 2. GVB orbitals for the ¹A₁ state of vinylidene, based on the GVB(5/15) wave function. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au. The same conventions are used for all plots.

Table I. GVB Pair Information

State	Energy, hartree	Pair	Overlap	Energy lowering, hartree
¹ A ₁ (σ^2)	-76.87130	CC- π	0.6593	0.0323
		CC- σ	0.8889	0.0148
		CH-left	0.8450	0.0142
		CH-right	0.8450	0.0142
		Lone Pair	0.7170	0.0272
³ B ₂ ($\sigma\pi$)	-76.79152	CC- π	0.6445	0.0333
		CC- σ	0.9043	0.0106
		CH-left	0.8460	0.0141
		CH-right	0.8460	0.0141

state are shown in Figure 3. The bonding pairs corresponding to the CH bonds and the CC π bond are not shown, since they are essentially identical with the corresponding ¹A₁ orbitals.

The CC σ bond (Figure 3A), however, shows greater delocalization toward the terminal carbon than was present in the ¹A₁ case. The orbital on the terminal carbon is $sp^{0.45}$ hybridized, while the orbital on the central carbon is $sp^{1.66}$. This is due to the change in the lone pair from a singlet-coupled pair to triplet-coupled orbitals. As can be seen, the triplet pair of orbitals (the “methylene” orbitals) now have the character of a singly occupied p_x orbital (Figure 3C) and a singly occupied $sp_z^{1.8}$ orbital (Figure 3B).

IV. Discussion

A. Heat of Formation. Since our GVB(5/15)-CI wave function for vinylidene is sufficiently correlated to describe accurately the breaking of the carbon-carbon bond to give ³B₁ methylene and ³P carbon atom, we expect the calculated carbon-carbon bond strength, $D_e(\text{H}_2\text{C}=\text{C}\cdot)$, to be fairly accurate, probably about 6–10 kcal low. The energies of H₂C=C \cdot , H₂C \cdot , and C are shown in Table II and lead to an energy difference of $D_e(\text{H}_2\text{C}=\text{C}\cdot) = 159.6$ kcal/mol. The HF wave function leads to a bond strength 55 kcal/mol smaller, but even including the dominant electron correlation effects as in GVB(3)-CI leads to a bond energy 23 kcal/mol too weak.

Since an experimental determination of the bond energy would include the difference in zero-point energies of the molecule and fragments, it is necessary to correct D_e for the zero-point vibrational energies. Estimating the vibrational

Table II. Total Energies, Bond Energies, and Excitation Energies for the 1A_1 and 3B_2 States of Vinylidene^g

	$^1A_1 (\sigma^2)$	$^3B_2 (\sigma\pi)$	Bond energy 1A_1	Excitation energy $^3B_2-^1A_1$
HF	(76.77135) 76.77066	(76.7220) ^a 76.7195 ^a	(104.6) ^{b,e} 104.1 ^{b,e}	(31.0) 32.1
GVB(3)	(76.82882) 76.82951	(76.75808) 76.75911	(128.8) ^{b,f} 129.3 ^{b,f}	(44.4) 44.2
GVB(5/10)	76.85744	76.7855 ^a	129.2 ^{c,f}	45.1
GVB(5/14)	76.87130	76.79152	137.9 ^{c,f}	50.1
GVB(3)-CI	(76.84695)	(76.78734)	(140.2) ^{b,f}	(37.4)
GVB(5/14)-CI	76.88407	76.81089	159.6 ^{d,f}	45.9

^a These values were estimated from a higher level GVB calculation. Errors in such estimates for HF are expected to be about 0.001 hartree high for the 3B_2 state and 0.002 h high for the 1A_1 state. ^b HF [or GVB(1)] for CH_2 (3B_1), $E = -38.9202$. ^c GVB(3) for CH_2 (3B_1), $E = -38.9483$. ^d GVB(3)-CI for CH_2 (3B_1), $E = -38.92647$. ^e HF [or GVB(1)] for C (3P), $E = -37.6845$. ^f GVB(2) for C (3P), $E = -37.7033$. ^g The values for 1A_1 are at $R_{CC} = 1.35 \text{ \AA}$ and the values for 3B_2 are at $R_{CC} = 1.36 \text{ \AA}$ unless in parentheses (in which case $R = 1.33 \text{ \AA}$). Total energies are in hartree atomic units and should be negative; energy differences are in kilocalories per mole.

Table III. Vibrational Frequencies (in cm^{-1}) Used in Zero-Point Energy Calculation

Vibration	H ₂ CC estimated	H ₂ C exptl
CH a ₁	3062	2960
b ₂	3131	3200
CH ₂ a ₁	1393	1114
b ₂	1023	
b ₁	946	
CC a ₁	1623	
Total zero-point energy, kcal/mol	31.96	20.80

frequencies for vinylidene based on the average frequencies of ethylene¹³ as shown in Table III and using the experimental values for methylene,¹³ we calculate a zero-point correction of 5.6 kcal/mol. Thus we calculate the bond dissociation energy for vinylidene to be

$$D_0(H_2C=C:) = 154.0 \text{ kcal/mol.}$$

For comparison, similar calculations on ethylene by Harding and Goddard¹⁰ lead to $D_0(H_2C=CH_2) = 161 \text{ kcal/mol}$ as compared with the experimental value¹³ of 170 kcal/mol, and lead to $D_0(H_2C=O) = 168.7 \text{ kcal/mol}$ as compared with the experimental value of 176.2 kcal/mol. On the other hand, similar calculations on single bonded systems such as H_3C-CH_3 , H_3C-OH , $HO-OH$ lead to errors of the order of 1-4 kcal. On the average, this type of calculation leads to errors of about 4 kcal per bond. Consequently we assume our calculated bond strength for vinylidene to be about 8 kcal too weak, leading to

$$D_0(H_2C=C:) = 162 \text{ kcal/mol.}$$

Using the experimental values¹³ for the heat of formation of methylene (3B_1) and carbon atom (3P) and the theoretical D_0 , we calculate the heat of formation for vinylidene as

$$\begin{aligned} \Delta H^\circ_f(H_2C=C:) &= 92.2 + 169.6 - 154.0 \\ &= 107.8 \text{ kcal/mol} \end{aligned}$$

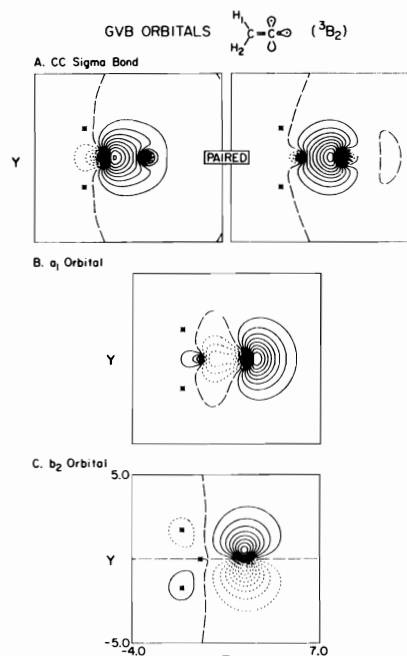
or including the above corrections based on the above comparisons of theory and experiment leads to

$$\Delta H^\circ_f(H_2C=C:) = 100 \text{ kcal/mol}$$

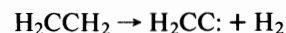
Correcting¹³ to 298 K leads to

$$\Delta H^\circ_f{}^{298} = \Delta H^\circ_f - 0.2 \text{ kcal/mol}$$

The above ΔH_f of 100 kcal/mol for vinylidene is 46 kcal/

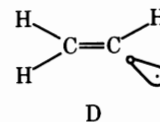
**Figure 3.** GVB orbitals for the 3B_2 state of vinylidene, based on the GVB(5/14) wave function.

mol above that of its isomer acetylene. The process



is predicted to be endothermic by 87.5 kcal/mol.

There is currently considerable uncertainty in the heat of formation of vinyl radical D, estimates ranging¹⁴ from ΔH_f^{298}



= 62-71 kcal/mol. Using our $\Delta H_f^\circ = 100 \text{ kcal/mol}$ for H_2CC we find that these estimates lead to a bond energy $D_0(H_2CC-H)$ for vinyl of 90-81 kcal/mol, respectively, while the CH bond of ethylene¹⁵ is 101.5-110.5 kcal/mol. The latter bond energy should be compared with $D(H-CH_2) = 109.7$ and $D(H-C_6H_5) = 107 \text{ kcal/mol}$, suggesting that

$$\Delta H_f(H_2CCH) \approx 69 \text{ kcal/mol}$$

B. The Singlet-Triplet Splitting. As expected, we find that the singlet has a considerably lower energy, 45.9 kcal/mol,

Table IV. Excitation Energies and Dominant Configurations for Vinylidene^c

State	Excitation energy, eV	Dominant configurations ^a						Energy lowering ^b	
		CC bonds				Lone pair		GVB(5/15)-CI	GVB(3)-CI
		σ	σ^*	π	π^*	a ₁	b ₂		
¹ A ₁ ($\pi^2\sigma^2$)	0.0	2	0	2	0	2	0	0.0202	0.0234
		2	0	0	2	2	0		
		2	0	2	0	0	2		
		1	1	1	1	2	0		
³ B ₂ ($\pi^2\sigma\bar{\pi}$)	1.99	0	2	2	0	2	0	0.0076	0.0087
		2	0	0	2	1	1		
		2	0	1	1	1	1		
		1	1	1	1	1	1		
¹ B _N ($\pi^2\sigma\bar{\pi}$)	4.64	0	2	2	0	1	1	0.0061	0.0065
		2	0	0	2	1	1		
		1	1	1	1	1	1		
		0	2	2	0	1	1		
³ A ₂ ($\pi\sigma^2\bar{\pi}$)	3.15	2	0	1	0	2	1	0.0153	0.0103
		2	0	1	2	0	1		
		0	2	1	0	2	1		
		1	1	0	1	2	1		
¹ A ₁ ($\pi\sigma^2\bar{\pi}$)	3.54	2	0	1	0	2	1	0.0178	0.0106
		2	0	1	2	0	1		
		0	2	1	0	2	1		
		1	1	0	1	2	1		
³ A ₁ ($\pi\pi^*\sigma^2$)	5.14	2	0	1	1	2	0	0.0184	0.0227
		2	0	1	1	0	2		
		0	2	1	1	2	0		
		2	0	1	1	1	1		
⁵ B ₂ ($\pi\pi^*\sigma\bar{\pi}$)	5.53	2	0	1	1	1	1	0.0086	0.0086
		0	2	1	1	1	1		

^a The CH orbitals and the additional CC σ and π correlating orbitals are not shown, since their occupations remain the same for the dominant configurations. ^b The energy lowering is defined as the increase in energy resulting from deletion of the configuration without readjusting the remaining configurations. ^c All configurations with energy contribution greater than or equal to the $\sigma^2 \rightarrow \sigma^*\pi^2$ configuration were included.

Table V. Contributions to the Dipole Moment of Vinylidene Based on the GVB(5/15) Wave Function^a

State	Core (1s)		CH bonds				CC bond				Lone pair				Total		
	x	z	Left		Right		σ		π		σ (a ₁)		$\bar{\pi}$ (b ₂)		x	z	z
			x	z	x	z	x	z	x	z	x	z	x	z			
³ B ₂ ($\sigma\bar{\pi}$)	0.0	0.0	0.587	0.284	-0.587	0.284	0.0	-0.353	0.0	0.116	0.0	-0.640	0.0	0.091	0.0	-0.218	-0.554
¹ A ₁ (σ^2)	0.0	0.0001	0.592	0.261	-0.592	0.261	0.0	0.036	0.0	0.189	0.0	-1.626			0.0	-0.878	-2.232

^a All quantities in atomic units unless stated otherwise; 1 au = 2.541 765 D.

than the triplet state (see Table IV).¹⁶ The large ³B₂-¹A₁ splitting is consistent with experimental observations² that the only reactive species is a singlet state.

In methylene the triplet state is 41.5 kcal/mol below the singlet state for an HCH bond angle of 180°, 20.8 kcal/mol below for an angle of 135°, and nearly degenerate for ~100°. That is, two electrons in the nonbonding a₁ orbital are favored for small bond angles; hence for bond angles <90° the singlet state is below the triplet. In vinylidene the carbon is double-bonded to another carbon; this double bond is equivalent to reducing the bond angle to an angle <<90° and hence leads to a singlet ground state.

C. Dipole Moments. In GVB wave functions, the orbitals are unique and have clear valence bond characteristics which make it useful to analyze properties such as dipole moments in terms of orbital contributions. In order for the dipole moment to be independent of origin, we associate with the electron of each orbital a unit nuclear charge centered at the nucleus on which the orbital is centered (in the VB model). This leads to the results shown in Table V.

In the ¹A₁ ground state we see that the largest contribution comes from the lone pair on the terminal carbon, which is po-

larized strongly *away* from the carbon. (The CH pairs are also polarized away from the central carbon.) This polarization is partially compensated by the π system, which is polarized toward the central carbon. Hence the total dipole moment for the ¹A₁ state is 2.232 D, pointing toward the "carbene" carbon.

In the ³B₂ state, unlike ¹A₁, the CC σ bond is strongly polarized toward the terminal carbon. All other orbital contributions are approximately the same except for the diminished polarization of the now singly occupied a₁ orbital. Thus the overall dipole moment is 0.554 D, only one-quarter of the moment of the ¹A₁ state.

D. Ionization Potentials. Since the methylene and ethylene ionization potential are comparable, we can expect several lower positive ion states for vinylidene. We carried out CI calculations (vide supra) for these states, leading to the results in Table VI and Figure 4 (all vertical ionizations). The first ionization is out of the π system, leading to ²B₁ at 10.8 eV, just 0.3 eV above the corresponding IP of ethylene.¹⁷ The second ionization potential (the ²A₁) is at 11.3 eV, and results from ionization of the $\bar{\pi}$ electron of the ³B₂ state (or the σ orbital of ¹A₁). The analogous ionization in methylene is at 11.4 eV.¹⁷

Table VI. Ionization Potentials and Dominant Configurations [GVB(5/15)-CI(2)] for Vinylidene

State	Ionization potential, eV	Dominant configurations ^a										Energy lowering, hartree	
		CH bonds			CC bonds						Lone pair		
		a ₁	b ₂	b ₂ [*]	σ	σ ₁ [*]	π̄	π	π ₁ [*]	π ₂ [*]	a ₁		b ₂
² B ₁ (πσ ²)	10.82	2	2	0	2	0	0	1	0	0	2	0	0.0212 0.0106 0.0065
		2	2	0	2	0	0	1	0	0	0	2	
		2	1	1	2	0	0	1	0	0	2	0	
² A ₁ (π ² σ)	11.28	2	2	0	2	0	0	2	0	0	1	0	0.0229 0.0133 0.0065
		2	1	0	2	0	0	2	0	0	1	1	
		2	2	0	2	0	0	1	1	0	1	0	
⁴ A ₂ (ππ̄σ)	12.26	2	1	0	2	0	0	1	0	1	1	0	0.0097 0.0076 0.0070
		2	2	0	1	1	0	0	1	0	1	1	
		2	2	0	2	0	0	0	0	1	1	1	
² A ₂ (ππ̄σ)	13.76	2	2	0	2	0	0	1	0	0	1	1	0.0084 0.0080 0.0070
		2	1	1	2	0	0	1	0	0	1	1	
		2	2	0	1	1	0	0	1	0	1	1	
² A ₂ (ππ̄σ)	15.72	2	2	0	2	0	0	1	0	0	1	1	0.0128 0.0089 0.0073
		2	2	0	2	0	1	1	0	0	1	0	
		2	1	1	2	0	0	1	0	0	1	1	
² B ₂ (π ² π̄)	16.24	2	2	0	1	0	0	1	0	0	2	1	0.0349 0.0233 0.0161
		2	2	0	2	0	0	2	0	0	0	1	
		1	2	0	2	0	0	2	0	0	1	1	
		2	2	0	2	0	0	0	2	0	0	1	

^a The following orbitals are not shown because they do not change occupancy in the dominant configurations: a₁ CH*, σ₂^{*}, π₃^{*}, lone pair a₁^{*}.

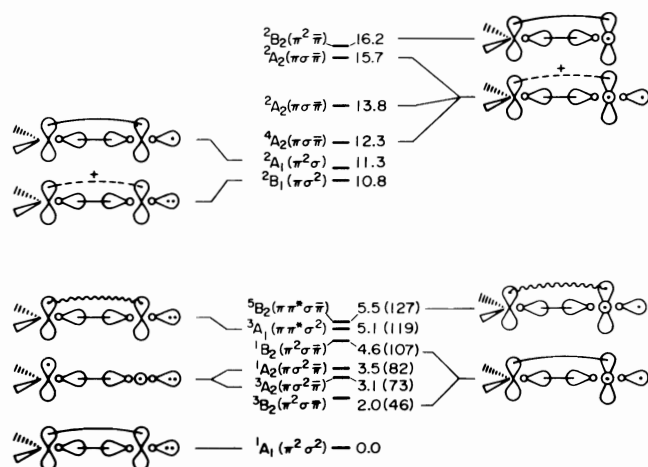


Figure 4. Electronic states of vinylidene and vinylidene cation. Energies in electron volts; the numbers in parentheses are excitation energies in kilocalories per mole (1 hartree = 27.2116 eV = 627.5096 kcal/mol).

Ionization of an electron in the π system of the ³B₂ state leads to a ⁴A₂ ion at 12.3 eV and two ²A₂ ions at 13.8 and 15.7 eV. Finally, ionization of the σ electron of the ³B₂ state yields a ²B₂ ion at 16.2 eV. We should emphasize here that of the ion states in Figure 4, only the first two are obtained by direct ionization from the ground state.

On the basis of the IP and in analogy with ethylene, we expect the first Rydberg transition (3s) to be at 7.4 eV (compared with 7.1 eV for ethylene).¹⁷

E. Higher Excited States. We have also carried out self-consistent GVB(3) and GVB(3)-CI calculations on each of a number of higher excited states of vinylidene. These results are given in Table VII. Note that GVB(3)-CI leads to a ¹A₁ (π²σ²)-³B₂ (π²σπ̄) separation of 38.5 kcal or 7.4 kcal smaller than the extensive GVB(5/14)-CI. This indicates an inade-

quacy in the GVB(3)-CI description of ¹A₁ and hence all excitation energies in Table VII are referenced to the open shell ³B₂ state. The resulting energy diagram is included in Figure 4.

There are five important configurations for the low-lying neutral states: (i) π²σ², leading to the ¹A₁ ground state; (ii) π²σπ̄, leading to the ³B₂ and ¹B₂ states at 45.9 and 107.1 kcal/mol, this is an excitation from the σ nonbonding orbital to the π̄ nonbonding orbital; (iii) πσ²π̄, leading to the ³A₂ and ¹A₂ states at 72.6 and 81.7 kcal/mol, this is an excitation from the π bond orbital to the π̄ nonbonding orbital; (iv) ππ*σ², leading to the ³A₁ state at 118.6 kcal, this configuration also leads to a much higher ¹A₁ state (not calculated); and (v) ππ*σπ̄, leading to a ⁵B₂ state at 127.5 kcal and higher singlet and triplet states (not calculated). The energy relationships of these states are given in Figure 4.

The separation between the ³B₂ and ¹B₂ states (2.7 eV) is somewhat larger than that found in methylene (1.9 eV at ∠HCH = 135°). This is reasonable, since in the simplest description this energy difference is just twice the exchange integral between the open-shell orbitals (denoted as σ and π̄),²²

$$E(^1B_2) - E(^3B_2) = 2K_{\sigma\pi} \quad (5)$$

This exchange integral is a function of the hybridization of the σ orbital and for CH₂ increases from 2K = 1.8 eV at 180° to 1.9 at 135° to 2.2 at 90°.

On the other hand, the exchange integral between the π and π̄ orbitals of the πσ²π̄ configuration is much smaller (0.4 eV), since the π and π̄ orbitals tend to be on different carbon centers and since the p_xp_y atomic exchange integral is less than the sp exchange integral. The result of the big difference in exchange splittings between B₂ (π²σπ̄) and A₂ (πσ²π̄) is that ³B₂ is below ³A₂, whereas ¹A₂ is below ¹B₂. Thus the first excited singlet and triplet states correspond to *different* configurations.

Table VII. Calculated Excitation Energies for Vinylidene^c

	GVB(3/PP)	GVB(3)-CI	GVB(5/15)-CI
³ B ₂ → ¹ A ₁ ^a	-44.67	-37.38	-45.9
³ B ₂ → ¹ B ₂	58.77	61.19	(61.2) ^b
³ B ₂ → ³ A ₂	15.81	26.67	(26.7) ^b
³ B ₂ → ¹ A ₂	24.45	35.80	(35.8) ^b
³ B ₂ → ³ A ₁	56.21	72.69	(72.7) ^b
³ B ₂ → ⁵ B ₂	66.00	81.56	(81.6) ^b

^a The GVB(3/PP) total energies for the ¹A₁ and ³B₂ states are -76.829 95 and -76.758 77, respectively. The GVB(3)-CI energies are -76.847 87 and -76.788 30, respectively. ^b Only the ¹A₁ and ³B₂ states were calculated using self-consistent orbitals in the GVB(5/15)-CI description. We assume that the excitation energy to the other open-shell states with respect to the ³B₂(σπ) states will be approximately the same for GVB(3)-CI and GVB(5/15)-CI. ^c All values are for R_{CC} = 1.36 Å. Energy differences are in kilocalories per mole.

The ³A₁ (ππ*σ²) state was found at 5.14 eV (119 kcal), which is only slightly higher than the corresponding ππ* triplet state of ethylene, 4.6 eV. In addition, GVB-CI calculations predict a low-lying quintet state, ⁵B₂ (ππ*σπ), corresponding to a double excitation, π → π* and σ → π̄, from the ground state. This state is predicted to be 5.53 eV (127 kcal) above the ground state, or approximately 1.6 eV below the sum of the constituent excitations, ³(π → π*) and ³(σ → π̄). The extra stability derives from the large exchange interactions between the high spin coupled orbitals.

F. Comparison to Other Calculations. The first theoretical consideration of the spin state of vinylidene was by Hoffmann³ in 1968, who suggested that the singlet state may be the ground state (based on extended Hückel calculations). In 1972, Dewar and co-workers²⁴ applied the semiempirical MINDO/2 method to vinylidene and predicted a singlet ground state.

The MINDO/2 calculations lead to a ΔH_f of 104.1 kcal/mol, in surprisingly good agreement with our value of 100 kcal/mol. The agreement for the (open shell) excited states is much worse. For the ³B₂ (σπ) and ¹B₂ (σπ) states we find ΔH_f = 146 and 207 kcal/mol, respectively, whereas MINDO/2 leads to ΔH_f = 124.6 and 151.3 kcal/mol, respectively. Thus for excitation energies MINDO/2 leads to

$$E[{}^3\text{B}_2(\sigma\pi)] - E[{}^1\text{A}_1(\sigma^2)] = 20.5 \text{ kcal/mol}$$

whereas we find 45.9 kcal/mol, and

$$E[{}^1\text{B}_2(\sigma\pi)] - E[{}^3\text{B}_2(\sigma\pi)] = 26.7 \text{ kcal/mol}$$

whereas we find 61 kcal/mol.

An additional problem with the MINDO/2 calculations is that the ¹B₂ state is apparently predicted to be the lowest excited singlet state (S₁). The GVB-CI results show clearly that the large exchange interaction, K_{σπ}, in the B₂ states, pushes the ¹B₂ state above both the ³A₂ and ¹A₂ states. Thus we find the lowest excited singlet and triplet states of vinylidene to correspond to different orbital occupancies (configurations).

Large discrepancies between ab initio and MINDO/2 are also found in the calculated geometries. MINDO/2 leads to CC bond lengths of 1.265, 1.263, and 1.267 Å for the ¹A₁ (σ²), ³B₁ (σπ), and ¹B₁ (σπ) states, respectively, while we found 1.35, 1.36, and 1.36 Å, respectively. Similar GVB-CI calcu-

lations on ethylene^{10a} lead to R_{CC} = 1.353 Å, in good agreement with the experimental result, 1.339 Å.

V. Summary

We find the ground state of vinylidene is the singlet state (¹A₁) with the methylene-like triplet at 2.0 eV. The lower ionization potentials are close to the values expected from the corresponding ionizations of ethylene or methylene.

We find the carbon-carbon bond dissociation energy for vinylidene to be 162 kcal/mol, as compared with a dissociation energy of 169.9 kcal/mol for ethylene.

The dipole moment is found to be 0.554 D for the ³B₂ state and 2.232 D for the ¹A₁ (ground) state.

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References and Notes

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- (12) Hybridization was determined by Mulliken population analysis of the GVB orbitals.
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