

Acknowledgments. The authors would like to express their appreciation to Professor G. M. Maggiora, Cary Chabalowski, Dr. James Petke, and Dale Spangler for many helpful discussions concerning this work. Also, partial support for the computing time needed for this work by the University of Kansas is gratefully acknowledged. This work was supported in part by a grant from The Upjohn Co., Kalamazoo, Mich.

References and Notes

- (1) G. E. Johnson, *J. Phys. Chem.*, **78**, 1512 (1974). See also R. W. Bigelow and G. E. Johnson, *J. Chem. Phys.*, **66**, 4861 (1977), and references cited therein.
- (2) M. Zander, *Ber. Bunsenges. Phys. Chem.*, **72**, 1161 (1968).
- (3) M. Witanowski, L. Stefaniak, H. Januszewski, and Z. Grabowski, *Tetrahedron*, **28**, 637 (1972).
- (4) L. E. Nitzsche, C. Chabalowski, and R. E. Christoffersen, *J. Am. Chem. Soc.*, **98**, 4794 (1976).
- (5) See T. D. Davis, R. E. Christoffersen, and G. M. Maggiora, *J. Am. Chem. Soc.*, **97**, 1347 (1974), and references cited therein.
- (6) R. E. Christoffersen, D. Spangler, G. M. Maggiora, and G. G. Hall, *J. Am. Chem. Soc.*, **95**, 8526 (1973).
- (7) J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.*, **51**, 5584 (1969); M. Hackmeyer and J. L. Whitten, *ibid.*, **54**, 3739 (1971).
- (8) The geometry used was essentially the same as that used for carbazole. See I. P. Batra, P. S. Bagus, E. Clementi, and H. Seki, *Theor. Chim. Acta*, **32**, 279 (1974). Two conformations of the additional methyl group were examined at the SCF level, i.e., one with one of the CH bonds perpendicular to the carbazole macrocycle ("staggered"), and the other with one of the CH bonds parallel to the carbazole macrocycle ("eclipsed"). The "staggered" form was found to be more stable, and was used throughout the subsequent CI studies.
- (9) Hartree atomic units are used throughout this paper unless otherwise specified. See H. Shull and G. G. Hall, *Nature (London)*, **184**, 1559 (1959).
- (10) J. D. Petke, R. E. Christoffersen, G. M. Maggiora, and L. L. Shipman, *Int. J. Quantum Chem.: Quantum Biol. Symp.*, **4**, 343 (1977).
- (11) J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, *J. Mol. Spectrosc.*, in press.
- (12) J. D. Petke, G. M. Maggiora, L. L. Shipman, and R. E. Christoffersen, *J. Mol. Spectrosc.*, to be published.
- (13) See, for example, L. Z. Stenkamp and E. R. Davidson, *Theor. Chim. Acta*, **44**, 405 (1977).
- (14) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
- (15) Nomenclature introduced by C. L. Perrin and G. A. Skinner, *J. Am. Chem. Soc.*, **93**, 3389 (1971).

The Vinylidene–Acetylene Rearrangement. A Self-Consistent Electron Pairs Study of a Model Unimolecular Reaction

Clifford E. Dykstra* and Henry F. Schaefer III†

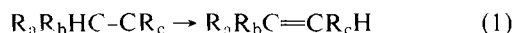
Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received April 7, 1977

Abstract: As a model for a potentially important pathway for the disappearance of carbenes and nitrenes, the unimolecular rearrangement of vinylidene into acetylene has been studied using the self-consistent electron pairs (SCEP) method. SCEP provides an accurate accounting of correlation effects by yielding a wave function equivalent to a configuration expansion including all singly and doubly substituted configurations relative to one reference determinant. A double- ζ (DZ) basis set of 24 contracted Gaussian functions was used to determine the equilibrium structures of vinylidene and acetylene and the transition state for the rearrangement pathway. A larger basis set of 42 functions including polarization (DZ + P) functions was then used to determine the energetics of the reaction, and the difference in energy between vinylidene and acetylene was found to be 40 kcal/mol. Polarization functions and the inclusion of correlation effects contribute about equally to lowering the rearrangement barrier from the DZ-SCF result of 26 kcal/mol to 8.6 kcal/mol (DZ + PSCEP). Other electronic states of vinylidene were investigated, and the 3B_2 ($5a_1 \rightarrow 2b_2$) state was found to be the lowest excited state with a vertical excitation energy of 11 500 cm^{-1} . Finally, SCEP calculations were performed on $\text{Li}^+-\text{C}_2\text{H}_2$ in an attempt to consider rearrangement through electrostatic interaction with a positive center.

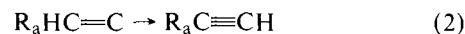
Introduction

Theoretical chemistry is in principle well suited to the study of organic free radicals and other highly reactive species. First of all, such species, while essential to any fundamental understanding of organic chemistry, tend to be very elusive in the laboratory. Theoretical methods, although often imprecise, are as well suited to evanescent species as to ordinary stable molecules. Equally important, the most intriguing unstable intermediates are usually rather small molecules, making them frequently susceptible to the more reliable of theoretical methods.¹

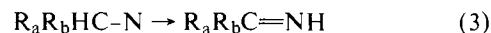
Carbenes² and nitrenes³ are certainly two of the most interesting classes of organic radicals. In the present paper we consider a type of unimolecular reaction which often leads to the disappearance of carbenes and nitrenes. This is the 1,2 hydrogen shift reaction,⁴ which for carbenes takes the form



and for vinylidenes



The reaction analogous to eq 1 for nitrenes is



The existence *at all* of the species on the left-hand side of eq 1–3 of course requires some barrier between reactants and products. Otherwise these types of carbenes and nitrenes would immediately convert to the more thermodynamically stable products on the right-hand side. However, the magnitude of these barriers (or activation energies) is of crucial importance, as it provides a measure of just how unstable these species are. Since one of the primary goals of much current experimental research is to elucidate reaction pathways, it is also important to have firm theoretical predictions of the transition state geometries for reactions such as 1–3.

The simplest prototypes for eq 1–3 are eq 4–6.



* J. S. Guggenheim Fellow, 1976–1977.

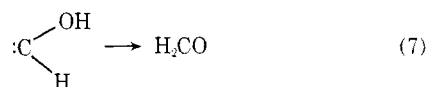


Since both methylcarbene⁵ and methylnitrene⁶ have triplet ground states, one can immediately predict that these two ground state isomerizations should not be typical. This is due to the fact that the lowest triplet state of ethylene (and presumably methylenimine as well) has a twisted equilibrium geometry and lies ~ 65 kcal⁷ above the $^1A_{1g}$ ground state. Thus, although the triplet reaction 4 is probably slightly exothermic,⁷ one does not have the large energy release normally associated with 1,2 hydrogen shifts, nor the expected product olefin structure. We see that the conventional aspects of eq 4 and 6 begin on excited potential energy surfaces.

However, the vinylidene rearrangement (eq 5) is qualitatively different, since $\text{CH}_2=\text{C}$ is expected to have a singlet ground state. Dewar and co-workers⁸ have predicted triplet vinylidene to lie 20.5 kcal above the lowest singlet state, and we qualitatively confirm their result in the present paper. Thus isomerization (eq 5) should proceed entirely along the singlet ground state potential surface. Hopefully it will serve as a prototype for the more general classes (eq 1-3) of singlet rearrangements.

Two other motivations for the present research should be mentioned. First, we have recently predicted^{9,10} that vinylidene is much more strongly bound (by ~ 40 kcal) to transition metal atoms than is the conventional π -bonded acetylene. The recently determined crystal structures^{11,12} of several transition metal vinylidenes are consistent with this hypothesis. However, remaining question marks are the precise energy difference and barrier between CH_2C and HCCH . In addition we report here model studies of the $\text{Li}^+-\text{C}_2\text{H}_2$ systems, in a rough attempt to simulate the presence of a partially charged transition metal atom.

A second motivation is our interest in a related reaction, the hydroxycarbene-formaldehyde rearrangement (eq 7). It has



recently been suggested¹³ that CHOH may play a role in the photodissociation^{13,14} of formaldehyde, a process which is not satisfactorily understood at present. Our prediction here of a low barrier for eq 5 implies that eq 7 may also have a low barrier, quite possibly making hydroxycarbene accessible from the higher vibrational levels of the formaldehyde S_0 ground state.

There have been a number of previous theoretical studies¹⁵⁻¹⁹ of 1,2 hydrogen shifts in carbenes and most of them refer specifically to the singlet methylcarbene rearrangement (eq 4). These studies have ranged from purely qualitative¹⁵ to *ab initio*¹⁹ and have tended to focus on the question of stereoelectronic control of migration.²⁰ For the two studies in which numerical energetics were predicted, there seems to be little agreement. That is, Dewar¹⁸ predicts essentially no barrier at all for the singlet isomerization (eq 4), while Csizmadia¹⁹ suggests a sizable barrier, 27 kcal/mol.

Theoretical Aspects

A double ζ (DZ) Gaussian basis set of Dunning-contracted²¹ functions, carbon (9s 5p/4s 2p) and hydrogen (4s/2s), was used in the geometry optimizations. As selected geometries, calculations were performed with a larger double ζ plus polarization (DZ + P) set which included hydrogen p functions with an exponent of 1.0 and carbon d functions with an exponent of 0.75. Geometry optimizations were performed by cyclical optimization of individual structural parameters. Around the point of the barrier to rearrangement, the angle α (see

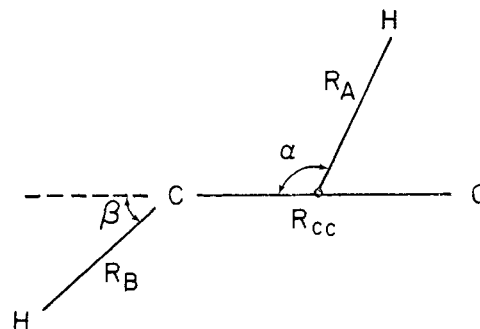


Figure 1. Structural parameters for the vinylidene-acetylene rearrangement.

Figure 1) was held fixed at various values and the remaining parameters were optimized.

Correlation effects were included in this study by use of the new self-consistent electron pairs (SCEP) method.²²⁻²⁴ SCEP is an iterative scheme which achieves computational efficiency through the use of a simple operator formalism. The (unnormalized) SCEP wave function has the following form:

$$\psi = \psi_0 + \sum_P \psi_P + \sum_{i,a} C_i^a \psi_i^a \quad (8)$$

ψ_0 is a closed-shell reference determinant and ψ_P is a doubly substituted function for an internal pair of electrons (e.g., in the $|i\rangle$ and $|j\rangle$ orbitals, occupied in ψ_0) with either singlet or triplet spin coupling. In all C_2H_2 calculations, the carbon 1s orbitals were frozen to substitution, so that there were 25 ψ_P s in the wave function. Each ψ_P implicitly includes all double excitations of the internal pair orbitals with external or virtual orbitals and is represented by a pair coefficient matrix, C_P , which can be given directly in terms of basis functions. An iterative approach which converges rapidly (owing to the use of sets of nonorthogonal external orbitals) is used to improve each C_P until all doubly excited configurations have zero (H-E) matrix elements with the total wave function, ψ . Singly excited configurations are included only after convergence of the ψ_P s (i.e., the doubly substituted configurations). This fixed- ψ_0 treatment²³ neglects the very small effect of the singles on the doubles. Since each ψ_P or C_P is processed individually, there is no explicit limit on the number of configurations which can be included in the expansion of the wave function, even for computer systems with limited memory. In fact, all calculations reported here were performed on the Harris Slash Four minicomputer²⁵ with 32K of 48-bit words, and the largest C_2H_2 calculation was equivalent to a configuration expansion over 8508 symmetry-adapted configurations. A further advantage of the method which has been recently incorporated into the SCEP computer program is that not all pairs need to be processed on each iteration. That is, some of the ψ_P s or C_P s are much closer to convergence on a given iteration than others and so can be skipped until, say, the last one or two iterations. Most of the SCEP calculations required 8 doubles iterations and typical computation times are given in Table I.

The orbital occupancy for acetylene is, of course,

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 \quad (9)$$

For vinylidene, the closed-shell ground state has the occupancy

$$1a_1^2 2a_1^2 3a_1^3 4a_1^2 1b_2^2 1b_1^2 \quad (10)$$

In the bridged intermediate forms (Figure 1) which have only C_s symmetry, both electron configurations become

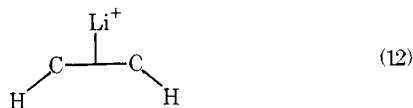
$$1a'^2 2a'^2 3a'^2 4a'^2 5a'^2 6a'^2 1a''^2 \quad (11)$$

Table I. Representative Computation Times (min)^a for a Single Point on the Vinylidene-Acetylene Potential Energy Surface

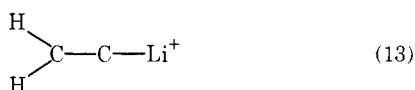
	DZ basis	DZ + P basis
Integrals calculation	8	40
SCF ^b	4	14
SCEP	39	220
Total	51	274

^a Calculations performed on the Harris Slash Four minicomputer and times given are total elapsed time. This minicomputer is ~27 times slower than the CDC 7600. ^b Time required for six or seven SCF iterations, which were typically required for convergence when beginning with an SCF set of orbitals from a nearby geometry.

In the Li⁺-C₂H₂ calculations, the DZ + P basis for C₂H₂ and a basis of 10s 4p Gaussian functions contracted to 5s 2p functions for Li²⁶ were used, giving a total of 53 functions. As a rough model for the interaction of C₂H₂ with Li⁺, structures analogous to the vinyl cation forms studied by Weber, Yoshimine, and McLean²⁷ were used. The first of these was the "bridged form" where the optimum geometrical parameters of C₂H₂ with $\alpha = 90^\circ$ were used. That is, the bridging hydrogen of the $\alpha = 90^\circ$ vinylidene structure was positioned to be symmetric with respect to the vinylidene terminal hydrogen and Li⁺ was placed symmetrically (C_{2v}) between the carbons (12). The "vinylidene form" consists of the optimized vinyli-



dene geometry for the carbons and hydrogens with Li⁺ assumed collinear with the carbons (13).



The Li distance was optimized using SCF energies. SCEP was used at the optimum Li distance with the energetically lowest two orbitals frozen to substitution, giving 36 ψ_{ps} in the wave function. An equivalent configuration expansion would include 10 419 symmetry-adapted configurations for the bridged form and 11 020 for the vinylidene form. (Since the current SCEP program does not take advantage of symmetry, a comparison can also be made with the equivalent number of configurations in C₁ symmetry, which is 36 856.)

Results and Discussion

Ground State Surface. Optimized geometrical parameters for C₂H₂ are given in Table II. Spectroscopically determined equilibrium acetylene bond lengths²⁸ are 1.203 Å for the carbon-carbon distance and 1.060 Å for the carbon-hydrogen distance, which compare with the DZ SCEP lengths of 1.230 and 1.071 Å, respectively. The theoretical bond distances are somewhat longer than experiment because when correlation effects are included a more complete basis set including polarization functions (which typically shorten bond length predictions) is necessary for a more precise agreement.^{1,29} However, these structural parameters are sufficiently close to the true values that we may expect the geometrical features (e.g., the transition state structure) of the potential energy surface to be reliably predicted.

The carbon-carbon bond length for vinylidene was determined to be 1.342 Å, typical of a C-C double bond. The carbon-hydrogen bond distance of 1.096 Å is somewhat longer than for acetylene and the HCH angle of 117.9° is typical of

Table II. Optimized Structures of C₂H₂^a

α	R_{CC}	R_A	R_B	β
Vinylidene	1.342	1.553	1.096	58.94
90°	1.294	1.150	1.078	6.18
93°	1.292	1.153	1.078	4.93
96°	1.290	1.168	1.079	4.17
98°	1.289	1.176	1.079	3.89
101°	1.286	1.195	1.080	3.75
Acetylene (= 180°)	1.230	1.685	1.071	0

^a DZ-SCEP energies were used to optimize structures at fixed values of α . Lengths are in angstroms and angles are in degrees. See Figure 1 for a definition of the five geometrical parameters.

HCH angles in methylene carbons, for instance, ketene.³⁰ A previous ab initio vinylidene geometry optimization by Hopkinson, Yates, and Csizmadia³¹ using an uncontracted C(7s 3p), H(3s) basis set and one configuration SCF wave functions predicted a C-C length of 1.290 Å, a C-H length of 1.074 Å, and an HCH angle of 119°. The difference between these values and the results given here is almost entirely due to the inclusion of correlation effects in the present work. Not surprisingly, tests on nonplanar structures confirm that ground state vinylidene is planar.

The location and characterization of the saddle point (or transition state) is a critical problem owing to its central role in simple kinetic theories³² and mechanistic discussions.¹⁵⁻²⁰ In the region of the potential surface near the barrier, three distances and the angle, β , were optimized for five selected values of α . Table II shows that the C-C length changes smoothly in this region while the C-H length r_B of the terminal hydrogen varies little. Interestingly, this terminal hydrogen is very nearly collinear with the carbons, a result not anticipated from Hammond's postulate.³³ Another feature of the surface is that at the transition state, which occurs essentially at $\alpha = 98^\circ$, the second hydrogen is close to being symmetrically located between the carbons, and indeed serves as a bridging hydrogen center. This transition state structure is sketched in Figure 2.

It is interesting to compare the C₂H₂ barrier structure with the bridged vinyl cation, C₂H₃⁺, structure determined by Weber, Yoshimine, and McLean.²⁷ In terms of the structural parameters as defined here, they found $R_{CC} = 1.210$ Å, $R_B = 1.073$ Å, $R_A = 1.276$ Å, $\beta = 0.9^\circ$ at $\alpha = 90^\circ$. Thus, except for the difference in C-C bond lengths, the bridged vinyl cation equilibrium structure which Weber et al.²⁷ find to be 1-2 kcal more stable than the classical vinyl cation structure is quite analogous to C₂H₂ at the rearrangement barrier. Clearly, protonation of C₂H₂ dramatically stabilizes the bridged structure, a point considered more fully below.

The total energies for the two basis sets and for SCF and SCEP wave functions are given in Table III and the relative energies are summarized in Table IV. The DZ SCF energy difference between vinylidene and acetylene is essentially the same as obtained in analogous calculations of Csizmadia and co-workers.³¹ In addition the DZ SCF barrier (26 kcal) predicted for reaction(s) is essentially indistinguishable from the 27 kcal predicted by Csizmadia¹⁹ for the methylcarbene rearrangement (eq 4).

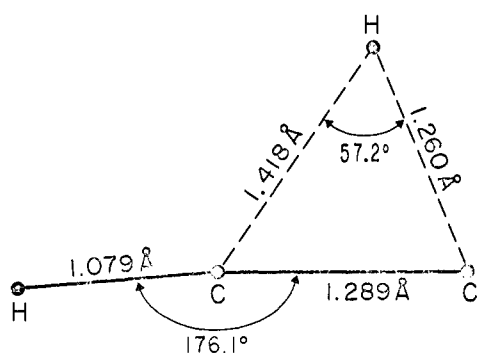
Correlation effects lower the barrier by about 8 kcal and stabilize acetylene relative to vinylidene. However, polarization functions, even with a one-configuration wave function, are important for the vinylidene structure and absolutely necessary to describe the system at the barrier. The lowering of the barrier with the inclusion of polarization functions is around 10 kcal and is roughly additive with the correlation effect lowering. For the vinylidene-acetylene energy difference, correlation and polarization effects tend to cancel indicating

Table III. Calculated Energies (hartree Atomic Units) for the Different Optimized Structures of C₂H₂

α	DZ-SCF	DZ-SCEP	DZ + P-SCF	DZ + P-SCEP
Vinylidene	-76.740 19	-76.904 62	-76.775 94	-77.018 06
90°	-76.701 79	-76.877 49		
93°	-76.700 37	-76.876 58		
96°	-76.699 24	-76.876 07	-76.753 18	-77.004 87
98°	-76.698 72	-76.876 05	-76.752 44	-77.004 37
101°	-76.698 58	-76.876 58		
Acetylene	-76.797 10	-76.977 38	-76.829 27	-77.081 73

Table IV. C₂H₂ Energetic Summary (kcal)

	Rearrangement barrier	Vinylidene-acetylene energy differences
DZ-SCF	26.0	35.7
DZ-SCEP	17.9	45.7
DZ + P-SCF	14.7	33.5
DZ + P-SCEP	8.6	40.0

**Figure 2.** Transition state structure for the vinylidene-acetylene isomerization.

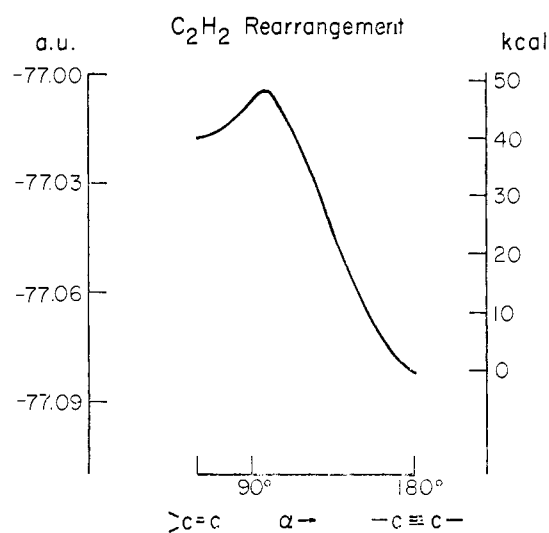
that the DZ SCF calculation can give a reasonable value. That, however, is not surprising since it is well known¹ that DZ SCF wave functions are quite appropriate for *equilibrium* structures of organic molecules. The finally determined rearrangement barrier is 8.6 kcal/mol, a low value which is consistent with an experimentally postulated³⁴ fast rearrangement. In light of the striking similarity of reactions 4 and 5 at the DZ SCF level, we can also predict with some confidence that the barrier height for the singlet methylcarbene isomerization should as well be in the range 5–10 kcal. This important prediction is possible because of the expected uniformity of correlation effects within closely related chemical entities. For the same reasons, we expect the hydroxycarbene-formaldehyde barrier to be considerably less than the ~50 kcal reported by Altman.³⁵

Excited States. The excited states of vinylidene were studied using the DZ basis since the inclusion of polarization functions should not greatly change the relative energies of the lowest valence states.^{1,30} Vertical excitation energies given in Table V were determined from one-configuration SCF results and correlation effects should slightly increase these energies owing to relatively greater electron correlation in the closed shell ground state. Orbital energies given in Table VI suggest that the lowest excited state would result from promoting a 1b₁ electron into the 2b₂ virtual orbital. However, the 5a₁ orbital is energetically close to the 1b₁ orbital, and the lowest excited state is, in fact, a ³B₂ arising from the 5a₁ → 2b₂ promotion. The singlet-triplet separations of the B₂ and A₂ states have a relationship similar to n → π* and π → π* carbonyl states.³⁰ That is, an in-plane electron promotion (e.g., a₁ → b₁, π → π*, σ → σ*) typically produces larger separations of the resulting singlet and triplet states than opposite type promotions (e.g., b₁ → b₁, n → π*, π → σ*).

Table V. Vinylidene Vertical Excitation Energies^a

Excitation	State	State energy, au	Excitation energy, cm ⁻¹
5a ₁ → 2b ₂	¹ B ₂	-76.5969	31 500
1b ₁ → 2b ₂	¹ A ₂	-76.6588	17 900
1b ₁ → 2b ₂	³ A ₂	-76.6728	14 800
5a ₁ → 2b ₂	³ B ₂	-76.6969	9500
g.s.	¹ A ₁	-76.7402	

^a One-configuration SCF results.

**Figure 3.** Energetics of the C₂H₂ rearrangement as determined from DZ + P-SCEP results.

The fairly large ³B₂-³A₂ separation, about 6000 cm⁻¹, tends to ensure that even with a more accurate treatment, the ³B₂ state is the lowest excited state. Studying the rearrangement of carbenes such as reaction 1 is complicated because excited potential energy surfaces are usually involved. To be sure that an excited state surface is not, say, thermally accessible in the vinylidene rearrangement, the equilibrium geometry of the ³B₂ state was determined. Since SCEP has not been fully extended to open-shell systems, the configuration interaction (CI) approach developed in the program BERKELEY³⁶ by Lucchese et al. was used to include correlation effects in the ³B₂ state energy. The DZ basis was used and all singly and doubly substituted configurations relative to the ³B₂ SCF reference configuration were included in the wave function. The 1a₁ and 2a₁ orbitals were frozen to substitution. The ³B₂ (CI) energy at the ground equilibrium geometry was -76.8529 for a vertical of 11 500 cm⁻¹. Optimization of the structure of the ³B₂ state gave a C-C bond length of 1.353 Å, a C-H bond length of 1.097 Å, and an H-C-H angle of 118.0°. The CI energy at the equilibrium structure was -76.8531. It seems clear that the excited state structure is nearly the same as the ground state. Furthermore, since the lowest point on the potential surface of the ³B₂ state is more than 32 kcal above the ground state and more than 23 kcal above the ¹A' transition state,

Table VI. Vinylidene Orbital Energies^a

Orbital	ϵ_i , au	Orbital	ϵ_i , au
3b ₁	0.469	1b ₁	-0.406
8a ₁	0.432	5a ₁	-0.457
3b ₂	0.419	1b ₂	-0.619
7a ₁	0.296	4a ₁	-0.734
6a ₁	0.266	3a ₁	-1.059
2b ₁	0.141	2a ₁	-11.256
2b ₂	0.062	1a ₁	-11.332

^a Improved virtual orbitals [W. J. Hunt and W. A. Goddard, *Chem. Phys. Lett.*, **3**, 414 (1969)] were used for virtual orbital energies.

Table VII. A Comparison of Two Forms of Li⁺-C₂H₂

	SCF	SCEP
Optimized distance between Li and the C-C bond midpoint		
Bridged form	2.36 Å	
Vinylidene form	3.45 Å	
Energy		
Bridged form	-84.080 12 au	-84.351 12 au
Vinylidene form	-84.067 84 au	-84.322 67 au
Energy difference	7.7 kcal	17.9 kcal

excited state potential surfaces are not likely to be important in the thermal rearrangement.

The Interaction of Li⁺ with C₂H₂. The results of the calculations done on the Li⁺-C₂H₂ system are given in Table VII. It can be seen that the bridged form is more stable and that correlation effects are more important in the bridged form. This is consistent with the results of Weber et al.,²⁷ who found the bridged form of C₂H₃⁺ to be more stable by a few kilocalories. A study of Be and Be⁺ with acetylene by Swope and Schaefer³⁷ showed that formation of a π complex was almost completely due to electrostatic effects. In C₂H₃⁺ the positive charge is nearly equivalently distributed onto the three hydrogen centers.²⁷ However, in Li⁺-C₂H₂, the partial charge on the lithium center is about 0.8, so that the π -complex electrostatic interaction is greater, and therefore the bridged structure is stabilized by several more kilocalories than in the vinyl cation. Clearly, in going from a charged center to a neutral center, the stability of the vinylidene complex will increase as the electrostatic interaction is reduced. The unanswered point in this analysis is the barrier to rearrangement from bridged to vinylidene complex. In the vinyl cation where the electrostatic interaction is apparently reduced by delocalization of the positive charge, the barrier is quite small, about 1 kcal.²⁷ If we construe this to mean that a small but not dominant electrostatic interaction is necessary for a low barrier, then formation of a stable vinylidene complex is most probable for a neutral system where the metal center has, at least in the bridging position, a partial positive charge. In view of this, it is interesting to realize that the experimentally observed vinylidene transition metal complexes^{11,12} were formed with acetylenes substituted with electron-withdrawing groups, which promote π back-bonding and electron transfer away from the metal.³⁸

Acknowledgments. We very much thank Mr. Robert Lucchese for his assistance in using the CI program BERKELEY³⁶ which was used in calculations on vinylidene excited states.

This work was supported, in part, by the National Science Foundation (Grants GP-41509X and GP-39317) and acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

References and Notes

- H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.
- M. Jones and R. A. Moss, "Carbenes", Vol. I and II, Wiley, New York, N.Y., 1973, 1975.
- W. Lwowski, "Nitrenes", Interscience, New York, N.Y., 1970.
- A. Nickon, F. Hagan, R. Weglein, K. Matsuo, and H. Yogi, *J. Am. Chem. Soc.*, **96**, 5264 (1974); S. S. Olin and R. M. Venable, *J. Chem. Soc., Chem. Commun.*, 104 (1974); M. Pomerantz and T. H. Whiterup, *J. Am. Chem. Soc.*, **95**, 9577 (1973); M. B. Sohn and M. Jones, *ibid.*, **94**, 8280 (1972); L. A. Paquette and G. H. Birnberg, *ibid.*, **94**, 164 (1972); D. H. White, P. B. Condit, and R. G. Bergmann, *ibid.*, **94**, 1348 (1972); D. F. Eaton, R. G. Bergman, and G. S. Hammond, *ibid.*, **94**, 1351 (1972).
- J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **96**, 4196 (1974); V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974).
- D. R. Yarkony and H. F. Schaefer, *J. Am. Chem. Soc.*, **96**, 5974 (1974).
- R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys.*, **9**, 75 (1975). The energy difference between triplet methylcarbene and ground state ethylene has been estimated as 80 kcal; see V. Staemmler, *Theor. Chim. Acta*, **35**, 309 (1974).
- N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).
- W. C. Swope and H. F. Schaefer, *Mol. Phys.*, **34**, 1037 (1977).
- B. R. Brooks and H. F. Schaefer, *Mol. Phys.*, **34**, 193 (1977).
- R. M. Kirchner and J. A. Ibers, *J. Organomet. Chem.*, **82**, 243 (1974); *Inorg. Chem.*, **13**, 1667 (1974).
- A. N. Nesmeyanov, G. G. Aleksandrov, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, and Y. T. Struchkov, *J. Organomet. Chem.*, **110**, C36 (1976).
- P. L. Houston and C. B. Moore, *J. Chem. Phys.*, **65**, 757 (1976).
- R. S. Lewis, K. Y. Tang, and E. K. C. Lee, *J. Chem. Phys.*, **65**, 2910 (1976); K. Y. Tang and E. K. C. Lee, *Chem. Phys. Lett.*, **43**, 232 (1976).
- H. C. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).
- O. S. Tee and K. Yates, *J. Am. Chem. Soc.*, **94**, 3074 (1972).
- R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Am. Chem. Soc.*, **90**, 1485 (1968).
- N. Bodor and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9103 (1972).
- J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Am. Chem. Soc.*, **97**, 5217 (1975).
- For an interesting experimental study of this point, see E. P. Kyba and C. W. Hudson, *J. Am. Chem. Soc.*, **98**, 5696 (1976).
- T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970); T. H. Dunning and P. J. Hay in "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.
- W. Meyer, *J. Chem. Phys.*, **64**, 2901 (1976).
- C. E. Dykstra, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, **65**, 2740, 5141 (1976).
- C. E. Dykstra, Ph.D. Thesis, University of California, Berkeley, Calif., 1976.
- A. L. Robinson, *Science*, **193**, 470 (1976); W. G. Richards, *Nature (London)*, **266**, 18 (1977).
- S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); J. E. Williams, unpublished; P. K. Pearson, W. J. Hunt, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.*, **58**, 5358 (1973).
- J. Weber, M. Yoshimine, and A. D. McLean, *J. Chem. Phys.*, **64**, 459 (1976).
- G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand-Reinhold, Princeton, N.J., 1966.
- H. F. Schaefer, "Critical Evaluation of Chemical and Physical Structural Information", D. R. Lide and M. A. Paul, Ed., National Academy of Sciences, Washington, D.C., 1974, pp 591-602.
- C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, **98**, 401, 2689 (1976).
- A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971).
- For a contemporary view of transition state theory, see W. H. Miller, *Acc. Chem. Res.*, **9**, 306 (1976).
- G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
- H. D. Hartzler, "Carbenes", Vol. II, R. A. Moss and M. Jones, Ed., Wiley, New York, N.Y., 1975, p 52.
- J. A. Altmann, I. G. Csizmadia, K. Yates, and P. Yates, *J. Chem. Phys.*, **66**, 298 (1977).
- R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope, and H. F. Schaefer, *J. Comput. Phys.*, in press.
- W. C. Swope and H. F. Schaefer, *J. Am. Chem. Soc.*, **98**, 7962 (1976).
- NOTE ADDED IN PROOF: A reliable theoretical study of the spectroscopy of vinylidene has recently appeared: J. H. Davis, W. A. Goddard, and L. B. Harding, *J. Am. Chem. Soc.*, **99**, 2919 (1977).