This scheme leads to the equation

$$\tau^{-1} = k_f m_{\mathrm{OH}} \left[1 + \frac{(m_{\mathrm{i,i}+})(1 + K_1)}{((m_{\mathrm{i,o}+}) + m_{\mathrm{OH}})(1 + K_1) + K_1 K_2} \right] + \frac{k_r m_{\mathrm{OH}}}{((m_{\mathrm{i,o}+}) + m_{\mathrm{OH}})(1 + K_1) + K_1 K_2} \quad (12)$$

the most obvious feature of which is that it requires τ^{-1} to approach zero as $m_{\mathrm{OH}-}$ approaches zero. This does not appear to be consistent with the observed results. Similar schemes involving two protolytic equilibria also lead to equations that were qualitatively inconsistent with the observed results.

It is perhaps surprising that 2,2,1 should behave differently to the other three cryptands. This could arise in the following manner. Both the 2,1,1 and 2,2,1 cryptands may require inversion of the free nitrogen prior to proton transfer, as shown in Schemes II and III, because of the relatively smaller cavities, leading to stronger internal H bonding, etc. However, the proton transfer from the o,i$^+$ form of 2,2,1 should be considerably faster than that from 2,1,1. Thus it may be faster than the subsequent conformational change (i,o) → (i,i), leading to a more complex dependence of the rate upon $m_{\mathrm{OH}} + m_{\mathrm{CryH}}$, as shown in eq 11. Further ring expansion to the 2,2,2 and 2,2,2B may enable direct proton transfer from i,i$^+$ to OH$^-$, this again resulting in a simple linear dependence of τ^{-1} upon m_{OH} and m_{CryH}.

A more detailed discussion of the results would require additional information about the conformational equilibria of the ligands, such as that available for the macrobicyclic ammonium ions from the NMR studies of Park, Simmons, and co-workers.[24] Solvent deuterium isotope effects might also provide additional information on the nature of the rate-determining step for the various ligands. The use of ultrasonic absorption techniques has also provided evidence for rapid conformational changes in biofunctional macrocyclic ligands[25] and crown ethers,[26] occurring prior to complex formation with

metal ions, and such studies on cryptands may also prove fruitful.

References and Notes

(1) (a) Chemistry Department, University of Stirling, Stirling FK9 4CA, Scotland; (b) Max-Planck-Institut für Biophysikalische Chemie.
(2) C. J. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).
(3) J. M. Lehn, *Struct. Bonding (Berlin)*, **16**, 1 (1973).
(4) W. Simon, W. G. Morf, and P. C. Meier, *Struct. Bonding (Berlin)*, **16**, 113 (1973).
(5) J. M. Lehn, J. P. Sauvage, and B. Dietrich, *J. Am. Chem. Soc.*, **92**, 2916 (1970).
(6) J. M. Cohen, J. L. Dye, and A. I. Popov, *J. Phys. Chem.*, **79**, 1292 (1975).
(7) J. M. Ceraso and J. L. Dye, *J. Am. Chem. Soc.*, **95**, 4432 (1973).
(8) V. M. Loyola, R. G. Wilkins, and R. Pitzer, *J. Am. Chem. Soc.*, **97**, 7382 (1975); V. M. Loyola, R. Pitzer, and R. G. Wilkins, *ibid.*, **99**, 7185 (1977).
(9) B. G. Cox and H. Schneider, *J. Am. Chem. Soc.*, **99**, 2809 (1977).
(10) J. M. Lehn and J. P. Sauvage, *J. Am. Chem. Soc.*, **97**, 6700 (1975).
(11) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
(12) E. Kauffman, J. M. Lehn, and J. P. Sauvage, *Helv. Chim. Acta*, **59**, 1099 (1976).
(13) G. Anderegg, *Helv. Chim. Acta*, **58**, 1218 (1975).
(14) J. Chevey and J. M. Lehn, *J. Chem. Soc., Chem. Commun.*, 487 (1972).
(15) W. Knoche and G. Wiese, *Chem. Instrum.*, **5**, 91 (1973–1974).
(16) M. Križan and H. Strehlow, *Chem. Instrum.*, **5**, 99 (1973).
(17) H. Strehlow and J. Jen, *Chem. Instrum.*, **3**, 47 (1971).
(18) A. Albert and E. P. Serjeant, "The Determination of Ionization Constants", 2nd ed, Chapman and Hall, London, 1971.
(19) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions" 2nd ed, Butterworths, London, 1965.
(20) C. W. Davies, "Ion Association", Butterworths, London, 1962.
(21) M. Eigen, W. Kruse, G. Maas, and L. De Maeyer, *Prog. React. Kinet.*, **2**, 285 (1964).
(22) A. J. Kresge, *Acc. Chem. Res.*, **8**, 354 (1975).
(23) R. P. Bell, B. G. Cox, and B. A. Timimi, *J. Chem. Soc. B*, 2247 (1971).
(24) H. E. Simmons, C. H. Park, R. T. Uyeda, and M. F. Habibi, *Trans. N.Y. Acad. Sci.*, **32**, 521 (1970).
(25) P. B. Chock, F. Eggers, M. Eigen, and R. Winkler, *Biophys. Chem.*, **6**, 239 (1977).
(26) G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, *J. Am. Chem. Soc.*, **98**, 6905 (1976).
(27) See paragraph at end of paper regarding supplementary material.

A Study of the Vinyl Anion System. Rearrangements and Formation from H⁻ and Acetylene

Clifford E. Dykstra,* [1a] **A. J. Arduengo,**[1a] **and T. Fukunaga**[1b]

Contribution from the Department of Chemistry, University of Illinois, Urbana, Illinois 61801, and Contribution No. 2582 from the Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898. Received April 4, 1978

Abstract: As a model for nucleophilic attack on acetylenes, the formation of the vinyl anion $C_2H_3^-$ and its rearrangements have been studied with ab initio molecular wave functions. The calculations used an extended basis set of 31 contracted Gaussian functions. The vinyl anion equilibrium structure, rearrangement transition state structures, and the H⁻ + HC≡CH minimum energy reaction path were determined using the energies obtained from one-configuration self-consistent field wave functions. The relative energetics were also analyzed using well-correlated wave functions calculated from a self-consistent electron pairs (SCEP) method. Unlike the vinyl cation, the rearrangement barriers are high in energy, the lowest being 40 kcal. The activation energy of the H⁻ + HC≡CH reaction is found to be 16 kcal, and the stability of the vinyl anion relative to acetylene and H⁻ is 26 kcal. Correlation effects are important in the reaction energetics and the minimum potential energy reaction surface indicates that the vinyl anion is formed by attachment of H⁻ to the first carbon it encounters.

Introduction

In recent years, many chemists have explained chemical reactivity within the paradigm of frontier molecular orbitals, as suggested by Fukui and others.[2] One aspect of the frontier-orbital method which is often neglected is the direction of approach that reactants must assume, as dictated by the three-dimensional shapes of the most strongly interacting or-
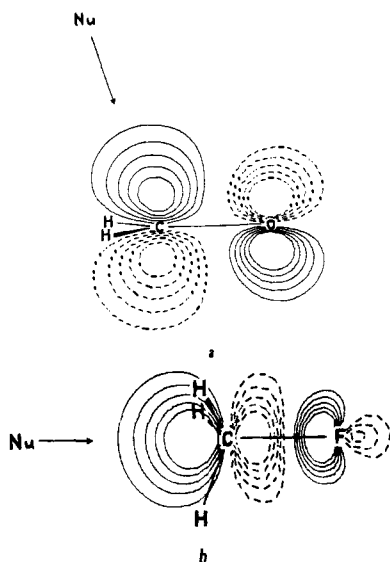
Figure 1. (a) Preferred approach direction of a nucleophile to a carbonyl.[2] (b) Trajectory assumed by reactants in an SN_2 reaction.[2]

Figure 2. Nucleophilic approach to an acetylene[2] as suggested by the predominance of *"endo-digonal"* closures in Baldwin's rules.

bitals. When considering the frontier orbital two-electron interaction, it is important that reactants approach one another along a path which maximizes orbital overlap and minimizes nuclear–nuclear repulsions (there is usually a dipole interaction which should also be considered). Thus reactants should approach along a path which allows the most strongly interacting orbitals to cross at points of highest amplitude.

Dunitz, Lehn, and Burgi[3b,c] have investigated the approach direction of a nucleophile to a carbonyl. Their results from both theoretical and structural work are in good agreement with what would be expected using the model of a nucleophile interacting with the π^* LUMO (lowest unoccupied molecular orbital) of a carbonyl (Figure 1a). The chemical literature is replete with investigations of the S_N2 reaction[4] and again the approach of the nucleophile is such that the nucleophilic HOMO (highest occupied molecular orbital) interacts most strongly with the electrophiles' LUMO (Figure 1b).

Recently, Baldwin[5] has proposed a set of empirical rules for predicting products of a variety of ring closure reactions. For ring closure by nucleophilic attack on various ethylenic centers, Baldwin's rules are in good accord with the theoretical expectations of nucleophilic attack on an ethylenic LUMO. In cases of nucleophilic addition to an acetylenic center, the Baldwin rules are predominated by closure of the *"endo-digonal"* type, suggesting nucleophilic approach to a carbon of the acetylene by first passing over one carbon and proceeding through the π^* node to the second (Figure 2). For nucleophilic addition to an acetylenic acceptor which is not highly perturbed, we anticipate that nucleophilic approach to the π^* of the acetylene should occur in much the same manner as for simple olefins. Furthermore, passage of the incoming nucleophile through the π^* node should require a substantial input of energy. At this point it is appropriate to mention that the position of the node in the acetylenic π^* is dependent upon electronic perturbations which may be present in the system. Thus, if C_1 in Figure 2 bore a strong electron-withdrawing substituent, the indicated approach direction would not necessitate the passage of the nucleophile through a π^* node.

The energetics of rearrangement of the vinyl anion are an important consideration for the nucleophilic attack on acety-' lene, because if the barriers are very small, distinguishing
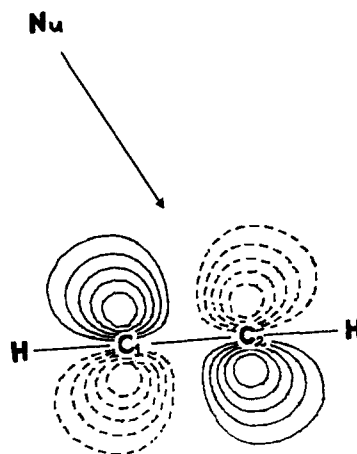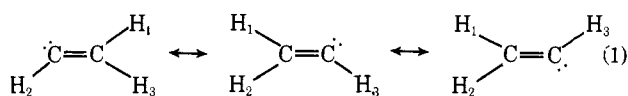
different reaction mechanisms may not be possible. If, for instance, H^- attaches to one carbon and has no barrier to moving to the second carbon, the mechanism is equivalent to direct attachment to the second carbon. The theoretical study of the classical C_{2v} (linear) and bridged structures of the vinyl cation by Weber, Yoshimine, and McLean[6] has demonstrated very minor energy differences, and rearrangement barriers less than 3 kcal. The orbital occupancy of the vinyl cation (linear C_{2v}) is

$$1a_1{}^22a_1{}^23a_1{}^24a_1{}^25a_1{}^21b_2{}^21b_1{}^2 \qquad (2)$$

In the vinyl anion, the occupancy for the linear C_{2v} structure is

$$1a_1{}^22a_1{}^23a_1{}^24a_1{}^25a_1{}^21b_2{}^21b_1{}^22b_2{}^2 \qquad (3)$$

The nature of the $2b_2$ orbital electron distribution will strongly affect the relative energies of the vinyl anion structures. Since the $2b_2$ is largely localized on the anionic carbon, the equilibrium structure of the anion is shifted from C_{2v} symmetry. The magnitude of the resulting rearrangement barrier has obvious implications on the stereoselectivity of nucleophilic addition to acetylene.

An accurate theoretical study of this prototype reaction requires the use of an adequate basis set to describe the negatively charged system. Careful attention must also be given to geometric changes occurring throughout the reaction. Furthermore, as was demonstrated for the vinyl cation[6] and the vinylidene–acetylene rearrangement,[7] correlation effects are important for critical energy determinations. Thus, we have examined the $C_2H_3{}^-$ system with ab initio self-consistent field (SCF) and correlated wave functions, as the first part of a study of nucleophilic reactions.

Theoretical Approach

A double ζ (DZ) basis set of Dunning-contracted[8] functions [carbon (9s5p/4s2p) and hydrogen (4s/2s)] was augmented with one diffuse s function on each center. This basis set (DZ*) of 31 contracted functions was used in all but two calculations. The diffuse s functions had an exponent of 0.05 on both hydrogen and carbon. This value is very roughly equal to the value obtained by using the even-tempered criterion of Raffenetti and Ruedenberg.[9] The inclusion of these functions was done to correct the most serious deficiency of the DZ basis, that is, describing H^-. The importance of the added hydrogen s function is seen from its Mulliken population of 1.003 in H^- (at the SCF level). The diffuse carbon s functions were included in order to preserve equivalency in the C and H bases.
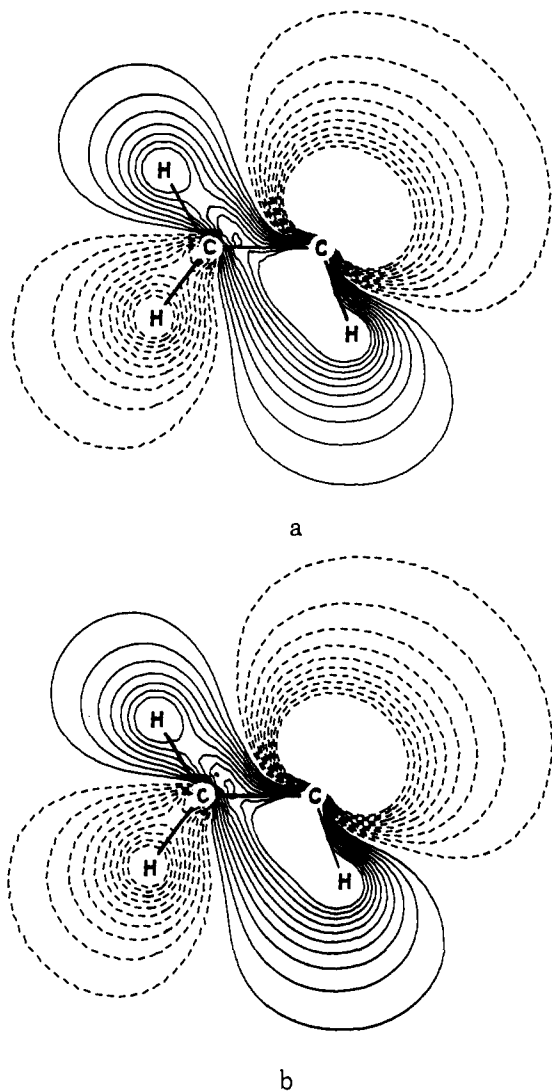
a

b

Figure 3. Highest occupied molecular orbital for the vinyl anion constructed from the SCF wave function with the DZ* basis (a) and the TZ basis (b).

Figure 4. Vinyl anion equilibrium and rearrangement structures. The designation of the centers as H_A, H_B, etc., corresponds to that used in the tables. The linear rearrangement structure has H_A along the C_1-C_2 axis as given by the dashed line. The bridged rearrangement structure has H_C symmetrically located between C_1 and C_2 with H_A and H_B in equivalent positions.

Two test calculations were performed with a larger basis set formed by adding diffuse p functions (exponent = 0.05) to the carbons to form a triple-ζ (TZ) basis (for the valence electrons). For studying anion electron affinities, the DZ* basis may be insufficient; for B, C, N, O, and F atoms, an additional set of diffuse 2p functions, as in the TZ basis, would be necessary.[10] However, the focus of this work is on structure predictions and relative energies and not on electron affinities. In this regard, the SCF studies of Radom[11] have convincingly shown that 4-31G basis sets (nearly equivalent to DZ) can yield accurate structure predictions for anions. Thus, the DZ* basis should be sufficient for this work, and, as discussed below, the TZ basis results show little difference from the DZ* results. Finally, a recent study of the methyl anion[12] with a very complete basis set showed that optimum near-equilibrium geometries are changed only slightly when going from a self-consistent field (SCF) to a correlated treatment. Of course, correlation effects are important in the relative energetics.

Geometry optimizations were performed using SCF energies. For the vinyl anion equilibrium structure and the rearrangement transition structures, all geometrical parameters were optimized, including out of plane angles. The minimum potential energy path of the hydride plus acetylene reaction was determined by partia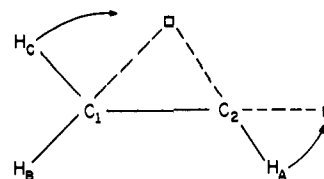l geometry optimization at a number of points along the reaction coordinate, followed by complete optimization at selected points. The reaction coordinate (ξ) was chosen as the difference of a given C–H bond length from its equilibrium value in the vinyl anion.

Correlation effects were included by using the method of self-consistent electron pairs[13] (SCEP). SCEP is an efficient iterative scheme which finds a variational wave function, equivalent to a configuration expansion that includes all singly and doubly substituted configurations, relative to a closed-shell reference configuration. A recent extension of SCEP used in this study is the inclusion of closed-shell quadruply substituted configurations.[14] By using approximate natural orbitals for the virtual orbital set, these configurations can account for a share of the size-consistency correction[15] to a singles and doubles (substituted) configuration wave function. The size-consistency error is the difference in the sum of particle energies (e.g., H^- and $HC\equiv CH$) and the energy of the total system in the separated limit when all are treated at the same level of substitution in the configuration expansion. In general, only a full configuration expansion will have a zero size-consistency error using variational treatments. However, by including higher order configurations, such as quadruple substitutions, we can more closely approach the full expansion result and minimize the size-consistency error. Size-consistency can be a minor or subtle correction, but should not be overlooked in a dissociation or formation process, such as that being investigated here.

The ease with which large numbers of configurations may be handled within the SCEP framework makes it an excellent method for this study. For the equilibrium vinyl anion, the symmetry is only C_s, and thus nearly 10 000 symmetry-adapted configurations (singles, doubles, and closed-shell quadruples) are included in the correlated DZ* basis wave functions. With SCEP, this and much larger expansions[16] are handled with only a relatively small amount of computer core. In all the SCEP calculations, the two lowest lying orbitals were held frozen to substitution. These orbitals are essentially carbon 1s atomic orbitals, and as shown for CH_3^-,[12] freezing these orbitals has a negligible effect on relative energies.

Results and Discussion

The canonical orbital energies at the vinyl anion equilibrium structure are given in Table I and the shape of the 7a' HOMO is given in Figure 3a. The different hydrogen and carbon

Table I. Vinyl Anion Orbital Energies

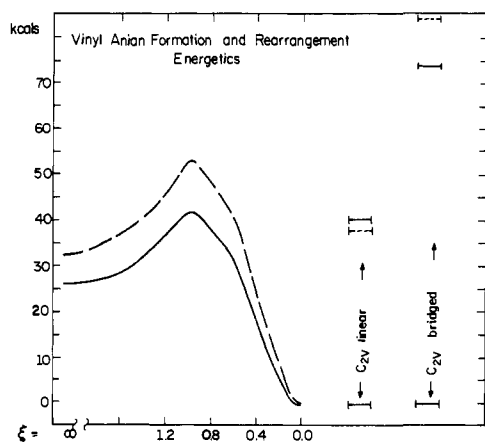| orbital	ϵ, au	orbital	ϵ, au
1a'	−10.9864	1a''	−0.1120
2a'	−10.9747	7a'	−0.0634 HOMO
3a'	−0.7596	8a'	0.2329 LUMO
4a'	−0.5095	9a'	0.2673
5a'	−0.3574	10a'	0.2828
6a'	−0.2771		

Figure 5. Potential curve for the formation of the vinyl anion. The energies of structures along the reaction path are plotted relative to the vinyl anion equilibrium energy. The dashed lines are SCF results and the solid lines are the SCEP results. The reaction coordinate, ξ, is defined in the text. While complete geometry optimizations were only performed at infinite separation and at $\xi \leq 1.15$ (see Table V), partial optimizations and SCF energies predict the rapid fall-off to the infinite separation energy. On the right of the figure, the relative energies of the rearrangement structures are plotted.

Table II. Atomic Net Charges in the Vinyl Anion from the Mulliken Populations

	SCF	SCEP
H_A	+0.0359	+0.0637
C_2	−0.7190	−0.8376
C_1	−0.2895	−0.1611
H_C	+0.0252	+0.0136
H_B	−0.0526	−0.0785

Table III. Vinyl Anion Optimized Structures[a]

	equilibrium	C_{2v} linear	C_{2v} bridged[b]
R_{C-C}	1.367	1.331	1.375
R_{C-H_B}	1.097	1.103	1.108
$\angle CCH_B$	125.8	125.4	127.4
R_{C-H_C}	1.087	1.103	1.303
$\angle CCH_C$	121.4	125.4	58.2
R_{C-H_A}	1.112	1.056	1.108
$\angle CCH_A$	109.9	180	127.4

[a] Bond lengths are in ångstroms, angles in degrees. [b] Optimization at the SCF level leads to a nonplanar structure with a dihedral angle of 120.0°.

centers are defined in Figure 4 and their net populations are presented in Table II. Essentially all of the negative charge is located on the carbons and there is little difference between the SCF and SCEP treatments. On the basis of the Mulliken populations,[17] the diffuse functions added to better describe the negatively charged system are particularly important on the carbon centers. SCF and SCEP test calculations with the TZ basis were performed at the equilibrium geometry. As shown in Figure 3b, the shape of the 7a′ HOMO is changed slightly by inclusion of the diffuse p functions on the carbons, and in the region of greatest electron density, at the anionic carbon, the structure of the orbital remains the same.

As indicated in Figure 4, the two C_{2v} rearrangement transition structures were formed by moving H_C toward C_2 (C_{2v} bridged) or by moving H_A to be collinear with C_1 and C_2 (C_{2v} linear). All independent structural parameters were then optimized and the results are given in Table III. To ensure a complete optimization, all structures were tested for nonplanarity. At the SCF level, the C_{2v}-bridged structure's energy was lowered when H_C was allowed to bend out of the plane of the molecule. Optimization of this dihedral angle yielded a value of 120.0° and reoptimization of the H_C bond length in this C_s symmetry structure gave $R_{C-H_A} = 1.307$ Å, only slightly different from the planar value of 1.303 Å.

The orbital occupancy of the C_{2v}-bridged structure is

$$1a_1{}^2 2a_1{}^2 3a_1{}^2 1b_2{}^2 4a_1{}^2 5a_1{}^2 1b_1{}^2 2b_2{}^2 \qquad (4)$$

and the orbital energy of the $2b_2$ is only −0.021 61 au. The orbital energy of the C_{2v}-linear HOMO ($2b_2$) is actually positive[18] and it is clear that the vinyl anion HOMO is very much destabilized in either of the C_{2v} rearrangement structures. Thus, the rather large rearrangement barriers given in Table IV are not surprising. Correlation effects are about 10% of the relative energies, but are important qualitatively. The nonplanar C_{2v}-bridged structure is about 5 kcal lower in energy than the planar structure at the SCF level. However, correlation effects bring the energies much closer together, with the planar structure actually lower in energy than the nonplanar structure.

Previous ab initio studies of the $C_2H_3{}^-$ system have been performed by Lehn et al.[19] and Streitwieser and co-workers.[20] Lehn et al. used a triple-ζ basis set and a limited geometry

optimization to predict the the C_{2v}-linear rearrangement barrier is 39 kcal. This is quite close to the 37.9 kcal SCF result obtained here and thus is another indication that the DZ* basis is sufficient for the energetics being studied. Streitwieser's calculations are particularly interesting because the C_{2v}-linear barrier was studied with several basis sets: a minimum basis set (MBS), a double-ζ set, and a double-ζ set with carbon d polarization functions. While there were major differences in predicted structures and energies between the MBS results and the other two calculations, the net effect of including carbon d functions with the double-ζ basis was only to lower the barrier from 35.7 to 35.0 kcal.

The formation of the vinyl anion was studied by optimizing structures at fixed R_{C-H_B} distances. This approach assumes that the two acetylene hydrogens move to a trans configuration upon interaction with H^-. It is also conceivable that they could be cis to each other as in the interaction with a cation,[7,21] and the incoming H^- would be in the H_C position (Figure 4) of the product. However, by performing a complete geometry optimization, we automatically allow for this possibility. Even at distances where the energy of the system becomes very close to the energy at the infinite separation limit, test calculations always placed the H_A hydrogen on the same side of the carbons as the incoming hydrogen. Since the C_{2v}-bridged rearrangement barrier is very high and vinylidene lies about 40 kcal above acetylene,[7] the remaining formation process, which places the incoming H^- on the anionic carbon, can be ignored.

The results from points where full geometry optimizations were performed are given in Table V and represented in Figure 5. The reaction coordinate is defined as the difference between the R_{CH_B} distance and the equilibrium distance in the vinyl anion. A simple parabolic fit of the energies at $\xi = 0.85$, 1.0, and 1.15 predicts the barrier to be at $\xi = 0.98$ with an energy of 42 kcal relative to the vinyl anion minimum. The separated limit energy is found to be 26 kcal above the vinyl anion and thus the activation energy barrier for the addition process is 16 kcal.

Comparison of SCF and SCEP relative energies shows the importance of including correlation effects. Without electron correlation, the predicted relative energy at $\xi = 0.2$ would be increased to about 10 kcal, and at $\xi = 1.0$ it would be 53 kcal.
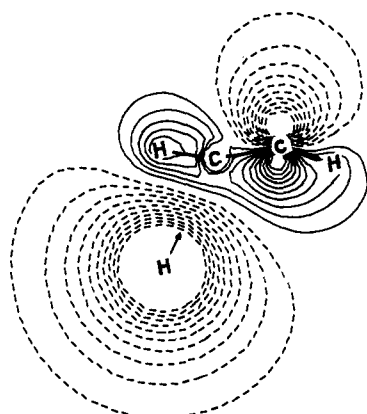
Table IV. Vinyl Anion Rearrangement Energies

	E_{SCF}, au	E_{SCEP}, au	ΔE_{SCF}, kcal	ΔE_{SCEP}, kcal
equilibrium	−77.337 17	−77.527 30		
C_{2v} linear	−77.276 77	−77.463 07	37.9	40.3
C_{2v} bridged	−77.202 78	−77.409 31	84.3	74.0
C_{2v} bridged; nonplanar	−77.210 28	−77.405 91	79.6	76.2

Table V. Formation of the Vinyl Anion[a]

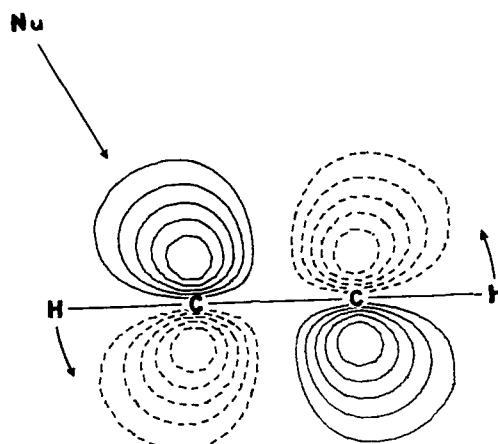| reaction coordinate ζ	R_{CH_B}	R_{CC}	$\angle CCH_B$	R_{CH_C}	$\angle CCH_C$	R_{CH_A}	$\angle CCH_A$	E_{SCF}, au	E_{SCEP}, au	ΔE_{SCEP},[b] kcal
0.2	1.297	1.361	125.5	1.082	124.3	1.111	110.0	−77.321 60	−77.516 72	6.64
0.6	1.697	1.333	128.0	1.075	133.6	1.100	116.2	−77.272 32	−77.476 70	31.75
0.85	1.947	1.303	127.4	1.068	143.1	1.090	126.1	−77.257 09	−77.464 36	39.49
1.0	2.097	1.277	128.0	1.062	146.8	1.088	127.8	−77.252 63	−77.460 68	41.80
1.15	2.247	1.253	126.4	1.055	158.9	1.070	151.5	−77.261 56	−77.466 27	38.29
∞[c]		1.200		1.054	180	1.054	180	−77.285 28	−77.486 14	25.83

[a] Bond lengths are in ångstroms, angles in degrees. [b] Relative to equilibrium structure. [c] Independent calculations on H⁻ and HCCH. The experimental acetylene equilibrium structure is $R_e(CH) = 1.060$ and $R_e(CC) = 1.203$.[22]

Figure 6. The HOMO at $\xi = 1.15$ (TZ basis).

Figure 7. The preferred approach direction of a nucleophile to an acetylene[2] accompanied by a trans motion of the acetylenic hydrogens.

The second TZ test point was the $\xi = 1.15$ geometry. The SCF energy was −77.263 04 au vs. −77.261 56 au with the DZ* basis, for a difference of 0.001 48 au or only 0.93 kcal. At the equilibrium geometry, the SCF energies were E(TZ) = −77.340 46 and E(DZ*) = −77.337 17, and the energy lowering at equilibrium is 0.003 29 au or 2.06 kcal. Correlation energies are little changed with the TZ basis at the two test points. The total change in relative energies is a raising of the energy of the $\xi = 1.15$ geometry by only 2.0 kcal.

The structural results in Table V show that the barrier to formation of the vinyl anion occurs at a point far along the reaction coordinate, that is, close to the product. Furthermore, partial geometry optimization beyond $\xi = 1.4$ indicates that the H_A-CC-H_C structure very quickly approaches that of isolated acetylene. Interestingly, the angle that the incoming H⁻ makes with the C-C axis is roughly constant, around 126°. As anticipated on the basis of nucleophilic attack on an acetylenic π^*, the incoming H⁻ attaches directly to the first carbon. The structure of the 7a′ HOMO at $\xi = 1.15$ (near the transition state) is given in Figure 6 and shows how the H⁻ orbital interacts to produce the $C_2H_3^-$ HOMO of Figure 3.

Finally, a comparison of the relative energetics shows the activation energy for the formation process to be substantially lower than either the C_{2v}-linear or C_{2v}-bridged rearrangement barrier. Figure 7 represents the preferred approach direction of a nucleophile to an acetylene with the trans motion of the acetylenic hydrogens. This trajectory also maintains a nucleophile-C-C angle of about 126°, which is close to that observed in the product. While this approach direction is clearly the minimum energy path when the nucleophile is hydride and the acetylene is unperturbed, changes in the nature of the nucleophile and acetylene substitution might be expected to cause changes in the preferred approach direction. Our continuing studies in this area hope to correlate any dependencies of approach direction on nucleophile structure and acetylene substitution.

References and Notes

(1) (a) University of Illinois; (b) E. I. du Pont de Nemours and Co.
(2) (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **42**, 3399 (1969); (b) K. Fukui, "Theory of Orientation and Stereoselection", Springer-Verlag, Heidelberg, 1970; (c) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971); (d) K. Fukui, "23rd International Congress of Pure and Applied Chemistry", Vol. 1, Butterworth, London, 1971, p 84; (e) L. Salem *J. Am. Chem. Soc.*, **90**, 543, 553 (1968); (f) L. Salem. *Chem. Br.*, **5**, 449 (1969); (g) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press,

New York, N.Y., 1970: (h) K. N. Houk, *Acc. Chem. Res.*, 11, 361 (1975); (I) C. L. Llotta, *Tetrahedron Lett.*, 519, 1975.

(3) (a) The orbital contours were constructed using an extended version of the program by W. L. Jorgensen (PSI/77) and represent cross sections of a particular MO at five contour levels. The extended Hückel wave functions for the π* or σ* are presented in each case. For methyl fluoride the hydrogen contributions were not plotted to maintain clarity. (b) H. B. Bürgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, 30, 1563 (1974). (c) H. B. Bürgi, J. M. Lehn, and G. Wipff, *J. Am. Chem. Soc.*, 96, 1956 (1974).

(4) (a) W. Th. A. M. Van der Lugt and P. Ros, *Chem. Phys. Lett.*, 4, 389 (1969); (b) G. Berthier, D.-J. David, and A. Veillard, *Theor. Chim. Acta*, 14, 329 (1969); (c) A. Dedieu and A. Veillard, *Chem. Phys. Lett.*, 5, 328 (1970); (d) J. J. C. Mulder and J. S. Wright, *ibid.*, 5, 445 (1970); (e) N. L. Allinger, J. C. Tai, and F. T. Wu, *J. Am. Chem. Soc.*, 92, 579 (1970); (f) C. D. Ritchie and G. A. Chappell, *ibid.*, 92, 1819 (1970); (g) J. P. Lowe, *ibid.*, 93, 301 (1971); (h) *ibid.*, 94, 60 (1972).

(5) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

(6) J. Weber, M. Yoshimine, and A. D. McLean, *J. Chem. Phys.*, 64, 4159 (1976).

(7) C. E. Dykstra and H. F. Schaefer, *J. Am. Chem. Soc.*, 100, 1378 (1978).

(8) T. H. Dunning, *J. Chem. Phys.*, 53, 2823 (1970).

(9) R. C. Raffenetti, *J. Chem. Phys.*, 59, 5936 (1973).

(10) T. H. Dunning and P. J. Hay, "Modern Theoretical Chemistry", Vol. 3, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.

(11) L. Radom, "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.

(12) C. E. Dykstra, M. Hereid, R. R. Lucchese, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, 67, 4071 (1977).

(13) (a) W. Meyer, *J. Chem. Phys.*, 64, 2901 (1976); (b) C. E. Dykstra, H. F. Schaefer, and W. Meyer, *ibid.*, 65, 2740 (1976); (c) C. E. Dykstra, Program No. 346, QCPE, Bloomington, Ind., 1977.

(14) C. E. Dykstra, *J. Chem. Phys.*, 68, 1829 (1978).

(15) J. A. Pople, R. Seeger, and R. Krishan, *Int. J. Quantum Chem.*, S11, 1490 (1977).

(16) C. E. Dykstra, *J. Chem. Phys.*, 68, 4244 (1978).

(17) (a) R. McWeeny and B. T. Sutcliffe, "Methods of Molecular Quantum Mechanics", Academic Press, New York, N.Y., 1969; (b) R. Mulliken, *J. Chem. Phys.*, 23, 1833, 2343 (1955).

(18) Typically, a positive orbital energy indicates an unbound electron. However, by including correlation effects such an electron may actually be bound.

(19) J. M. Lehn, B. Munsch, and Ph. Millie, *Theor. Chim. Acta*, 16, 351 (1970).

(20) J. E. Williams and A. Streitwieser, *J. Am. Chem. Soc.*, 97, 2634 (1975).

(21) W. C. Swope and H. F. Schaefer, *Mol. Phys.*, 34, 1037 (1977).

(22) G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. III, Van Nostrand-Reinhold, Princeton, N.J., 1966.

On the Thermal Reaction of Vinylcyclopropylidene to Cyclopentenylidene. An Exploration of the Electronic Hypersurface

W. W. Schoeller*[1a] and U. H. Brinker[1b]

Contribution from the Fakultät für Chemie, Universität Bielefeld, D 48 Bielefeld, West Germany, and the Lehrstuhl für Organische Chemie II, Ruhr-Universität, D 463 Bochum, West Germany. Received November 10, 1977

Abstract: The reaction of vinylcyclopropylidene to cyclopentenylidene represents a second type of carbene–carbene rearrangement. The quantum mechanical investigation of its singlet state $^1(\sigma^2)$ by the MINDO/3 method reveals that the reaction is initiated by a π-complex formation between the double bond and the empty p atomic orbital at the carbene site. The two electrons occupying the σ orbital do not participate in this interaction. A nonclassical carbene is formed in an intermediate stage. In this species electron density is shifted from the initial double bond toward the carbene site. The nonclassical carbene is relatively unstable toward deformation to cyclopentenylidene. Electron-donating substituents at the double bond of vinylcyclopropylidene should enhance the rate of π-complex formation. In contrast to vinylcyclopropylidene are the corresponding hetero analogues, vinylazirinylidene and vinyloxiranylidene, which should be less reactive under nucleophilic attack, because the p AO at the carbene site is partially filled with electron density supplied by its electron-rich neighbor atom.

Compared with vinylcyclopropane **1**, which undergoes thermal rearrangement to cyclopentene at temperatures around 300 °C,[2] vinylcyclopropylidene **2** (X = CH$_2$) reacts much more readily. Its rearrangement takes place at temperatures even as low as −78 °C.[3,4] From **2** (X = CH$_2$) competitive vinylallenes **3** and cyclopentadienes **5** are formed. While
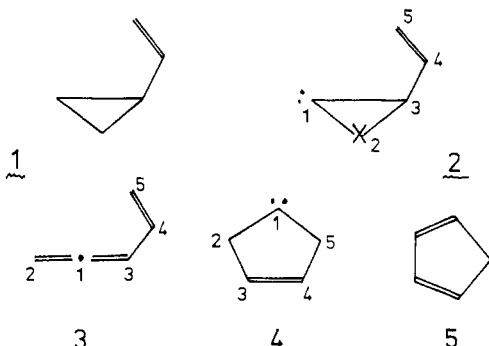
the former can be explained by cleavage of the X$_2$C$_3$ bond and subsequent allene formation as has been discovered earlier for cyclopropylidenes,[4,5] the latter is believed to originate from

a carbene–carbene rearrangement. In this rearrangement the initially generated carbene **2** induces a skeletal reorganization to yield a new carbene **4** in which the carbene carbon has kept its identity.[6] In a second step **4** then undergoes rapid 1,2-hydrogen shift to form cyclopentadienes **5**.[7]

For the vinylcyclopropane–cyclopentene rearrangement, which proceeds only at elevated temperatures, mechanistic studies favor a stepwise reaction sequence involving the intermediacy of a biradical.[2e,f] In contrast, the facile rearrangement of vinylcyclopropylidenes to cyclopentadienes at temperatures below 0 °C might well point to a concerted pathway which benefits from favorable electronic interaction in the transition state. This raises the interesting question of just how the presence of the carbene site might influence the stereochemical course of a 1,3-sigmatropic rearrangement which is obviously unfavored for the concerted vinylcyclopropane–cyclopentene isomerization. It must be the presence of the carbene (carbenoid) which is responsible for the dramatic difference in temperature (≈400 °C) at which these two structurally closely related reactions proceed. The easier rearrangement of vinylcyclopropylidene **2** (X = CH$_2$) might be the result of an interaction of the empty p orbital of the carbene with the double bond to form a π complex.

© 1978 American Chemical Society