Application of the Extended Hückel Molecular Orbital Method to the Properties of Vinyl Cations. Conformational Energies of Some 1-Cyclopropylvinyl Cations and a Comparison of SN2 Displacements at Saturated and Vinyl Carbon

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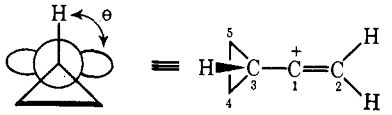
Abstract: The extended Hückel molecular orbital method developed by Hoffmann has been used to examine the predicted properties of a number of 1-cyclopropylvinyl cations. The calculations suggest that the ions in all cases are most stable in the linear, "bisected" conformation, and some indication of carbon–carbon hyperconjugation is found in one methyl-substituted derivative. In addition, a study of parts of the energy surfaces for attack of hydride ion upon ethane and ethylene supports the postulate that SN2 displacement is energetically more favorable at saturated than at vinyl carbon.

In this paper we report the results of an examination of some of our inferences about the preferred conformations of cyclopropylvinyl cations[2] through the use of the extended Hückel (EHT) molecular orbital method developed by Hoffmann.[3] We also describe a study of possible pathways for SN2 substitution at saturated and vinyl carbon centers. The serious approximations inherent in EHT calculations have been discussed,[4] as have the errors involved in using EHT calculations for charged species,[5] but we feel that the results of most of the calculations which have been reported appear to reflect fairly accurately the *relative* energies and other properties of molecules or conformations which are structurally similar to one another, although absolute values calculated for these properties are much more ambiguous.[6] The results on vinyl cation systems described below reinforce these notions.

Conformations of Cyclopropylvinyl Cations

Initially we examined the energies of some relatively specific conformations of cation **1**. Ideally, one would like to explore the variations in potential energy with respect to all the degrees of freedom of a given molecule. However, this is extremely expensive and, in any case, it is not clear that the energy will tend to reach a minimum at the correct bond lengths and angles, even for calculations more sophisticated than those of the extended Hückel type.[7] We have, therefore, limited our exploration to a small portion of the potential surface, and have fixed all bond lengths and other bond angles at standard[8] values.

We first investigated the dependence of the total energy of cation **1** on the relative orientation of the cyclopropane ring and the empty p orbital at the vinyl carbon carrying the formal positive charge. This appeared to be a reasonable place to begin because a similar calculation had been carried out previously, along with an analogous investigation of the conformations of the aliphatic cyclopropylcarbinyl cation.[9] Figure 1 shows the calculated potential curve depicting the energy change with respect to θ, the angle between the empty orbital and methine C–H bond. The calculated energy difference between the extreme conformations **1a** and **1b** is 6.67 kcal/mol. That this is a reasonable value is suggested by the fact that Hoffman[5a] has calculated an 8.86 kcal/mol energy difference between the analogous aliphatic cation conformers **2a** and **2b**, and Wiberg has estimated an 8 kcal/mol difference between **2a** and **2b** using Pople's self-consistent-field modification of the extended Hückel



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[2] (a) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 2115 (1969); (b) *ibid.*, **93**, 1925 (1971); (c) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970); (d) *ibid.*, **93**, 1941 (1971).

[3] (a) R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 2179, 3489 (1962); (b) R. Hoffmann, *ibid.*, **39**, 1397 (1963).

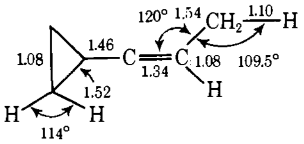
[4] See, for example, (a) M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970); (b) N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **92**, 3854 (1970); (c) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, pp 442–443.

[5] (a) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (b) T. Yonezawa, H. Nakatsuji, and H. Kato, *J. Amer. Chem. Soc.*, **90**, 1239 (1968).

[6] For some recent applications, see (a) R. Hoffmann, E. Heilbronner, and R. Gleiter, *ibid.*, **92**, 706 (1970); (b) W. Adam, A. Grimison, and R. Hoffmann, *ibid.*, **91**, 2590 (1969), and earlier papers.

[7] (a) G. A. Segal, *J. Chem. Phys.*, **47**, 1876 (1967); (b) K. B. Wiberg, *J. Amer. Chem. Soc.*, 90, 59 (1968).

[8] Double-precision calculations were carried out on an IBM 360/75 computer. Fixed bond lengths and angles used are the following (distances in ångströms). The C_1–C_3 length of 1.46 Å was chosen to conform with the C–C bond length in methylacetylene. See "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11**, M147, M149 (1958); **No. 18**, S16s, S18s, M96s, M107s, M112s (1965).



[9] J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968).

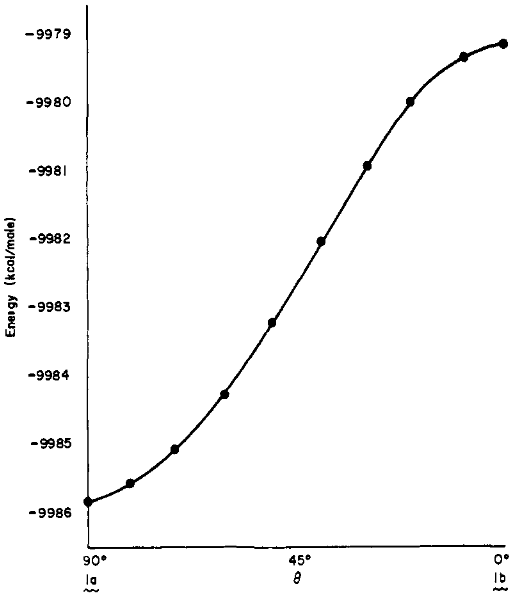


Figure 1. Calculated energy of the linear 1-cyclopropylvinyl cation as a function of cyclopropyl ring orientation.

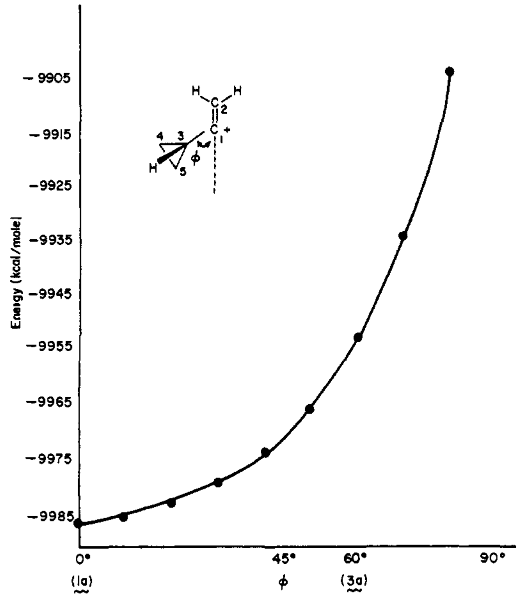
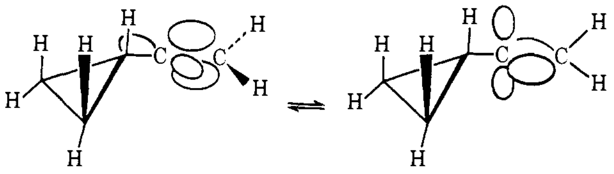
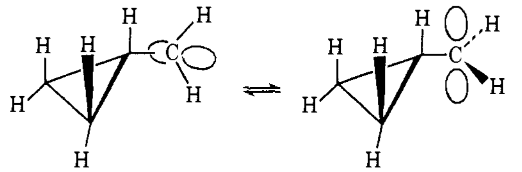


Figure 2. Energies calculated for the 1-cyclopropylvinyl cation as a function of bond angle φ.

method.[10] Recent experimental evidence indicates the barrier to rotation in **2a**–**2b** is about 14 kcal/mol.[11]



1a **1b**



2a **2b**

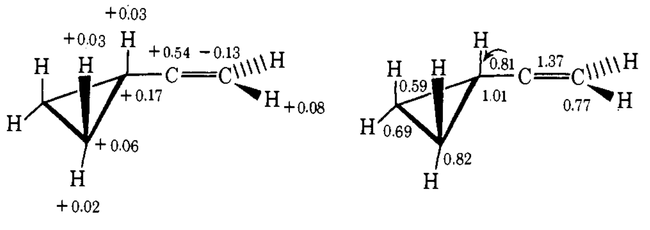
Although we have not employed iterative procedures for optimization of the parameters used in the calculations,[9] we have carried out some arbitrary variations to examine their effect on the relative energies of **1a** and **1b**. As one can see in Table I, moderate variation of Slater exponents and Coulomb integrals causes large changes in the absolute energies calculated, but relatively small fluctuations in the energy difference between the two extreme conformations. This reinforces our feeling that this difference may well provide an accurate picture of the real situation, and emphasizes the ambiguity of absolute total energy values calculated using this method.

The parameters used to obtain the data presented in Figure 1 were those which appeared to give the most reasonable charge distributions.[12] The charge distributions and overlap populations calculated for the most stable conformation **1a** are illustrated in Scheme I. As would be expected, the charge distribution in the less stable conformer **1b** indicates less charge delocalization (Scheme II).

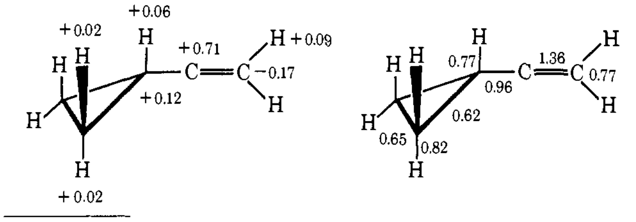
Table I. Effect of Parameter Variation on Energies Calculated for the 1-Cyclopropylvinyl Cation (**1**)

Atom	Orbital	Slater exponent	Coulomb integral	E_{1a}	E_{1b}	ΔE
H	1s	1.2	−13.06			
C	2s	1.625	−19.44	−9985.79	−9979.12	6.67
	2p	1.625	−10.67			
H	1s	1.0	−13.60			
C	2s	1.625	−21.01	−10516.62	−10512.13	4.49
	2p	1.625	−11.27			
H	1s	1.2	−13.60			
C	2s	1.625	−21.01	−10590.86	−10583.97	6.89
	2p	1.625	−11.27			
H	1s	1.0	−13.06			
C	2s	1.625	−19.44	−9913.89	−9909.52	4.37
	2p	1.625	−10.67			

Scheme I. Charge Distribution and Overlap Populations Calculated for the Most Stable Conformation of the 1-Cyclopropylvinyl Cation (**1a**)



Scheme II. Charge Distribution and Overlap Populations Calculated for the Less Stable Conformation of the 1-Cyclopropylvinyl Cation (**1b**)



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[10] K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

[11] D. S. Kabakoff and E. Namanworth, *J. Amer. Chem. Soc.*, **92**, 3235 (1970).

[12] These are the values used by J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

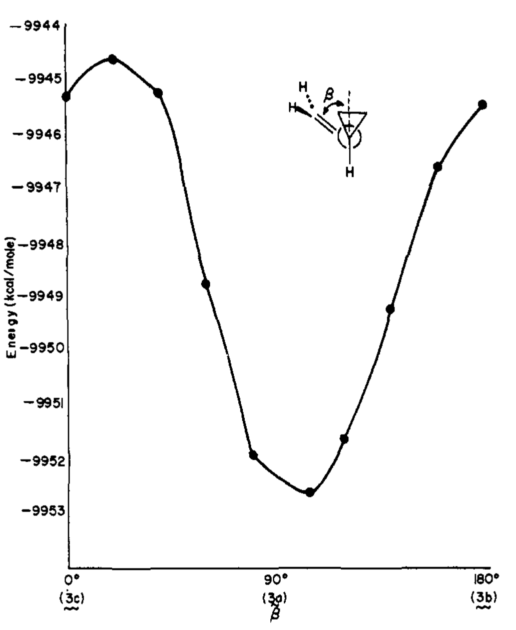
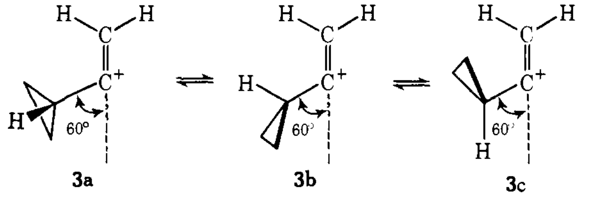


Figure 3. Calculated energies of the 1-cyclopropylvinyl cation as a function of twist angle β with φ fixed at 60°.

These calculations provide some support for our deductions concerning the stabilization of cation **1** (and presumably of the transition state leading to **1**) by the cyclopropyl group adjacent to the ionization center, and about the mechanism by which this stabilization occurs.[2] We next sought to examine the probability that the configuration of the cation at the ionization center is linear. In this case, all bond distances were fixed at the standard values, as in the previous calculation, as were all bond angles except the $C_2C_1C_3$ angle φ (Figure 2). This angle was varied in the most stable conformer **1a**; the method clearly predicts a minimum at the linear structure (Figure 2). It is amusing that if the angle φ is set at 60°, and the cyclopropyl ring rotated about the C_1–C_3 bond as was done for the linear ion (Figure 1), the 0 and 90° rotamers **3a** and **3b** have the same *relative* stability as do **1a** and **1b**; *i.e.*, they are still predicted to differ in energy by 7 kcal/mol (Figure 3). The calculations therefore suggest that a cyclopropyl group stabilizes an adjacent charge placed initially in a p orbital to about the same extent (energetically) that it stabilizes such a charge placed in an sp^2 hybrid orbital.



3a **3b** **3c**

The charge distribution and overlap populations calculated for the "bent" cation in its most stable conformation (**3a**) indicate more electron delocalization (*vide infra*) from the vinyl hydrogen trans to the "empty" orbital than from the cis hydrogen (Scheme III). This is in general agreement with other "trans" interactions in ethylenes, *e.g.*, elimination of HX from CRH=CHX.[13] A similar kind of "trans" effect has been noted in Hoffmann's calculations.[5a]

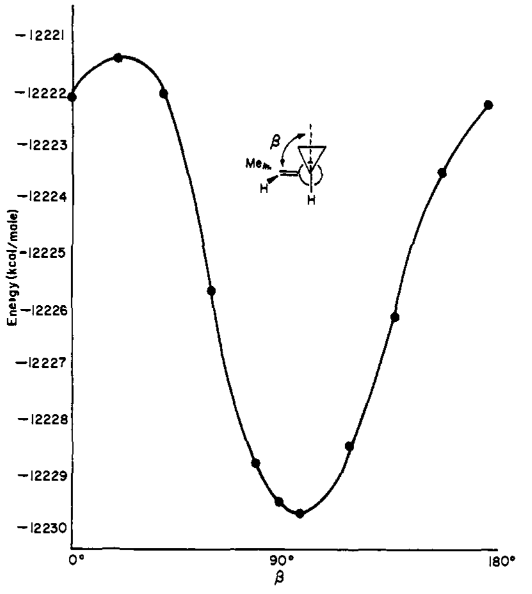
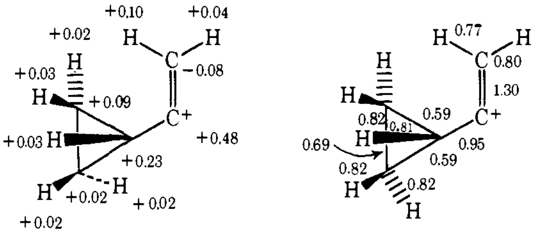


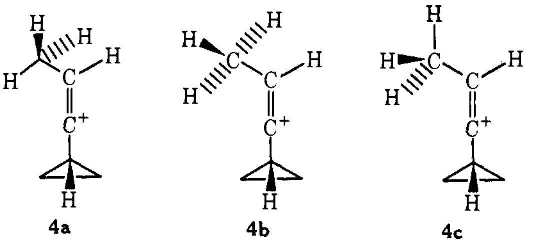
Figure 4. Energies calculated for the "*trans*"-1-cyclopropylpropenyl cation as the orientation of the ring is varied.

We also used the extended Hückel method to study the 1-cyclopropylpropenyl cation, **4**.[14a] The bond lengths and angles were fixed as before,[8] and the Slater exponents and Coulomb integral values were those used for calculations on the parent ion.[12] Again, for the linear configuration, the "bisected" conformation is calculated to be 6.72 kcal/mol more stable than the 90° rotamer. Rotation of the vinyl methyl group does not affect this relative energy difference at all (<0.05 kcal/mol). However, the energy of the "bisected" conformation is lowest when one methyl hydrogen is parallel to the C=C bond and pointed toward the cationic center,[14b] as shown in Scheme IV.

Scheme III. Charge Distribution and Overlap Populations Calculated for the Most Stable Conformer of the "Bent" 1-Cyclopropylvinyl Cation (**3a**)



Scheme IV. Relative Energies of the "Bisected" 1-Cyclopropylpropenyl Cation with Various Orientations of the Vinyl Methyl Group



	4a	**4b**	**4c**
Δ*E* (kcal/mol)	−1.0	−0.5	0.0

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[13] G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, 4, 49 (1965).

[14] (a) For a theoretical discussion of the effect of methyl substitution on the linear vinyl cation, see R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 91, 5350 (1969); (b) the reasons for this preference may have nothing to do with the empty orbital: see J. P. Lowe, *ibid.*, 92, 3799 (1970).

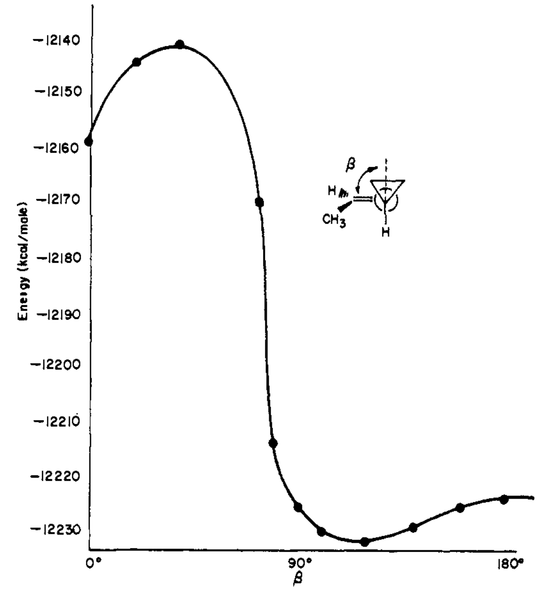
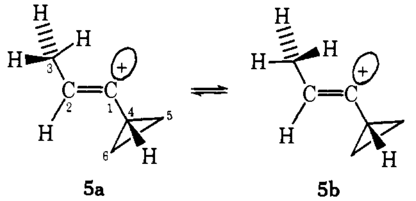
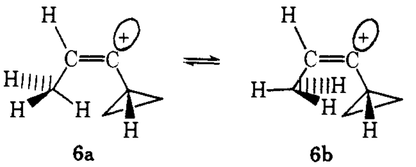


Figure 5. Energies calculated for the "*cis*"-1-cyclopropylpropenyl cation as a function of ring orientation.

We have also calculated the energies of various conformations of "bent" *trans*- and *cis*-1-cyclopropylpropenyl cations ($C_2C_1C_4$ angle = 120°) in which the orientations of the cyclopropyl ring and of the methyl group (analogous to **4a** and **4c**) were varied. *trans*-1-Cyclopropylpropenyl cation shows a similar energy change (Figure 4) when the cyclopropyl ring is rotated as occurs for the "bent" parent ion (Figure 3). With the cyclopropyl ring orientation fixed ($\beta \approx 100°$) the most stable conformation of the methyl group is with one hydrogen directed toward the cationic carbon, **5a**. Structure **5b** is less stable by 0.6 kcal/mol.



5a **5b**

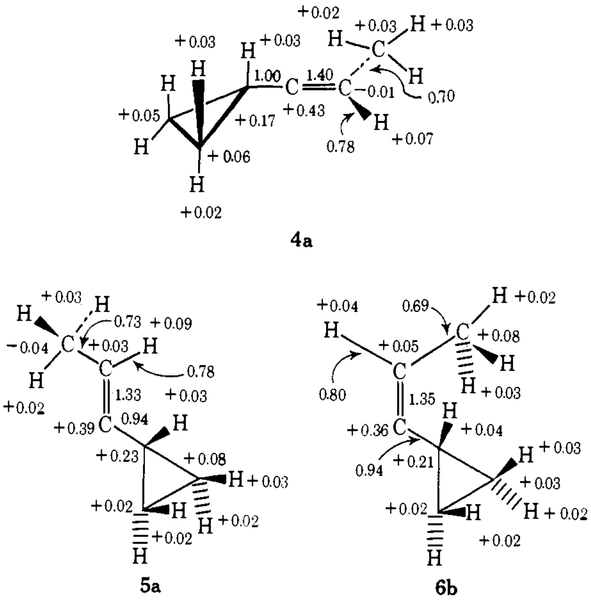


6a **6b**

Similar calculations on the cis isomer show a rather formidable barrier (>90 kcal/mol) to rotation of the cyclopropyl ring past the vinyl methyl group (Figure 5). However, the energy difference between the most stable conformation ($\beta \approx 120°$) and the structure with the cyclopropyl ring directed away from the methyl group ($\beta = 180°$) is still about 7 kcal/mol. It is interesting that at the minimum ($\beta \approx 120°$) conformation **6b** is more stable by 2.34 kcal/mol than **6a**, in contrast to the situation in the trans system.

If one compares the most stable trans cation configuration (**5a**, $\beta \approx 100°$) to the most stable cis cation configuration (**6b**, $\beta \approx 120°$), the latter is found to be more stable by ~2.3 kcal/mol. This at first was surprising, since it was expected that steric interactions in the cis cation would prevent effective stabilization of the cation by the cyclopropyl ring. An examination of the charge distributions and overlap populations for the two isomers (Scheme V) suggests that a methyl group trans to the empty orbital may stabilize the charge at the cationic center more effectively than either a cis methyl group or a trans vinyl hydrogen. (One might call this a carbon–carbon hyperconjugation effect.[15]) In particular, the overlap population of the C_2–C_3 bond decreases from 0.73 to 0.69 when the methyl group is changed from a cis relationship to the empty orbital to a trans relationship. The charge at the methyl carbon changes from −0.04 to +0.08. Similar changes, though of smaller magnitude, occur for the vinyl hydrogen. These shifts indicate, at least qualitatively, a delocalization of electrons out of the bond situated trans to the empty orbital. This effect appears to be more dramatic when the substituent is methyl rather than H. However, one must be cautious in comparing these effects on the charges and overlap populations with the differences in total energy between **5a** and **5b**, since this energy difference is highly dependent on the orientation of the methyl hydrogens.

Scheme V. Charge Distributions and Pertinent Overlap Populations Calculated for the Most Stable Conformations of the *trans*- (**5a**, $\beta \approx 100°$), *cis*- (**6b**, $\beta \approx 120°$), and Linear (**4a**) 1-Cyclopropylpropenyl Cations



4a

5a **6b**

It is instructive, also, to compare the charge distributions and overlap populations of the linear cation **4a** with those of the unsubstituted ion, **1a**. The charges located on the cyclopropyl ring carbons and hydrogens are nearly identical for the two structures. Likewise, the overlap populations for the bonds of the ring and all bonds connected to the ring remain the same. Yet in the methyl-substituted cation, the charges at the cationic center and the adjacent vinylic carbon have decreased in magnitude, +0.54 to +0.43 and −0.13 to −0.01, respectively. The overlap population between these carbons has increased from 1.37 to 1.40. The greater extent of delocalization of charge in **4a** must be entirely due to the methyl substituent.[14a]

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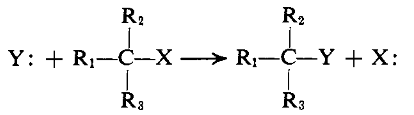
(15) F. R. Jensen and B. E. Smart, *J. Amer. Chem. Soc.*, **91**, 5686 (1969), and references cited there.

If we assume that these calculations are qualitatively correct with regard to the relative stabilities of the *trans*- and *cis*-1-cyclopropylpropenyl cations, rapidly equilibrating isomeric ions should produce a preponderance of product resulting from solvent trapping of the cis cation, **6b**, for the following reasons: (1) the cis cation is calculated to be up to 2.3 kcal/mol more stable than the trans cation. If the rate of interconversion of the cations is 10–10^2 times faster than solvent capture,[2d] the cis cation would predominate throughout the reaction; (2) solvent trapping of the trans cation should be less favorable because of steric hindrance by the methyl group to approach of a solvent molecule (although this effect may in fact be small[16]). In fact, a nearly 1:1 mixture of stereoisomeric *cis*- and *trans*-1-cyclopropylpropenyl acetates is the experimental result.[2d] The slight excess of *cis*-acetate found in most runs[2d] can be rationalized as reflecting a slightly more favorable attack of solvent on the linear molecule, **4a**, opposite from the methyl group.[16]

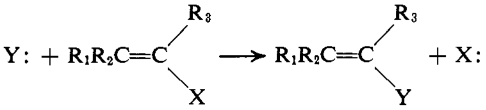
One must keep in mind, however, that, in addition to containing inherent inaccuracies and limitations, EHT calculations reflect energies for unsolvated molecules in the gas phase. Since we are dealing with charged species, extrapolation from the gas-phase calculations to solution chemistry should be even more dangerous than when we are dealing with neutral molecules.

The Nucleophilic Displacement Reaction

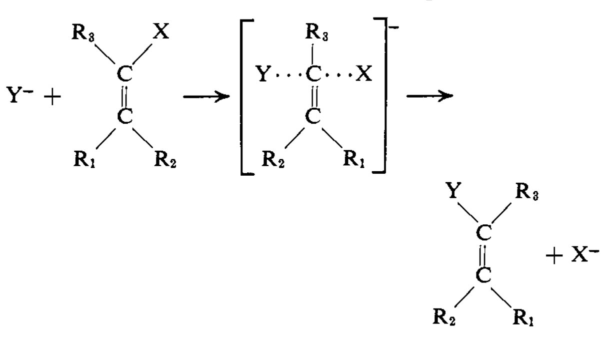
The displacement reaction at a saturated carbon center, eq 1, has been extensively studied for several years.[17] Only recently has it been shown[2] that the displacement at a vinylic center, eq 2, can occur *via* vinyl cations. There are, of course, several other possible pathways for substitution at vinyl carbon, such as elimination–addition or addition–elimination.[2d] However, only two mechanisms preserve the carbon-carbon double bond throughout the reaction: the SN1 reaction and the SN2 reaction (eq 3).



$$Y: + R_1-\overset{R_2}{\underset{R_3}{C}}-X \longrightarrow R_1-\overset{R_2}{\underset{R_3}{C}}-Y + X: \qquad (1)$$



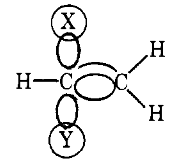
$$Y: + R_1R_2C{=}\overset{R_3}{\underset{X}{C}} \longrightarrow R_1R_2C{=}\overset{R_3}{\underset{Y}{C}} + X: \qquad (2)$$



$$Y^- + \begin{array}{c}R_3\quad X\\ C\\ \|\\ C\\ R_1\quad R_2\end{array} \longrightarrow \left[\begin{array}{c}R_3\\ Y\cdots C\cdots X\\ \|\\ C\\ R_2\quad R_1\end{array}\right]^- \longrightarrow \begin{array}{c}Y\quad R_3\\ C\\ \|\\ C\\ R_2\quad R_1\end{array} + X^- \qquad (3)$$

To our knowledge the direct displacement reaction has not been observed for vinylic systems, although the possibility of such a reaction path was considered some time ago,[18] and this mechanism has been assumed to occur in at least one instance.[19] It may be that displacement at a vinylic center is energetically unfavorable, but there is no clear evidence against such a reaction taking place under the appropriate conditions.[20] The atomic orbital configuration for the vinyl SN2 transition state should look very much like a "specifically solvated" vinyl cation, as shown in Scheme VI.

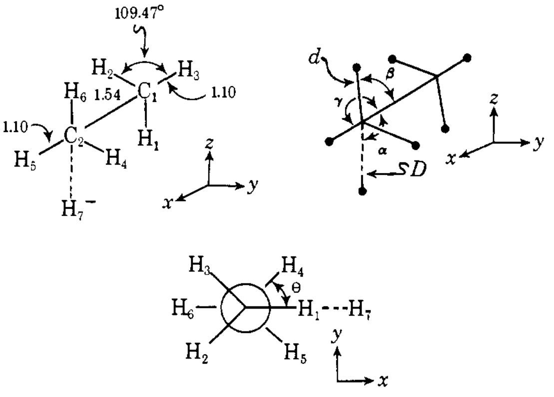
Scheme VI. Possible Atomic Orbital Configuration for the Transition State Involved in Displacement at a Vinylic Center



In view of the paucity of experimental or theoretical data concerning SN2 displacement at an sp^2-hybridized carbon, we chose to "look" at the SN2 attack of a hydride ion on ethane and on ethylene using the extended Hückel (EHT) method.[3] A comparison of the two calculations should allow one to estimate if, indeed, direct displacement at the vinylic center is an energetically unfavorable reaction pathway.

Ethane. Even for such a small molecule as ethane, it is extremely difficult to minimize energy with respect to all possible degrees of freedom along the reaction coordinate. At least 11 bond lengths, bond angles, and twist angles could be varied, and the cost of such an extensive calculation would be prohibitive, even though a single EHT calculation is relatively inexpensive. We therefore allowed only five degrees of freedom to vary. The fixed bond lengths and angles, the variable bond lengths and angles, and the orientation of the molecule and the hydride ion are shown in Scheme VII.

Scheme VII. The Fixed and Variable Bond Lengths and Angles for Hydride Attack on Ethane



The nonreacting bond lengths were fixed at 1.10 Å (C–H) and 1.54 Å (C–C). The molecule is shown in the staggered conformation with $H_6C_2C_1H_1$ and H_7 in the *xz* plane. H_4 and H_3 extend in the $+y$ direction; H_2 and H_5 in the $-y$ direction. The hydride ion, H_7, approaches C_2 at the backside relative to H_6, which will

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(16) From the data in Table I in ref 2d one can calculate that solvent attack on the linear cation "trans" to the vinyl methyl group is favored by as much as 0.10 kcal/mol or disfavored by as much as 0.04 kcal/mol relative to "cis" attack. The "average" value is 0.035 kcal/mol in favor of "trans" attack (at 25°).

(17) See A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

(18) V. Gold, *J. Chem. Soc.*, 1430 (1951).

(19) S. D. Ross, W. A. Leach, and I. Kuntz, *J. Amer. Chem. Soc.*, **74**, 2908 (1952).

(20) For a discussion on the unfavorability of an SN2 reaction at a vinylic carbon, see S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 265 (1968), and S. I. Miller and P. K. Yonan, *J. Amer. Chem. Soc.*, **79**, 5931 (1957).

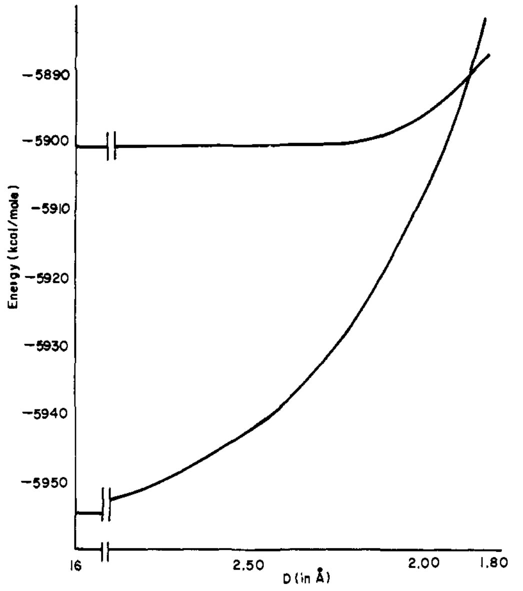


Figure 6. Calculated energies for energy-minimized configurations (lower curve) and symmetrical configurations (upper curve) for H^- attack on ethane.

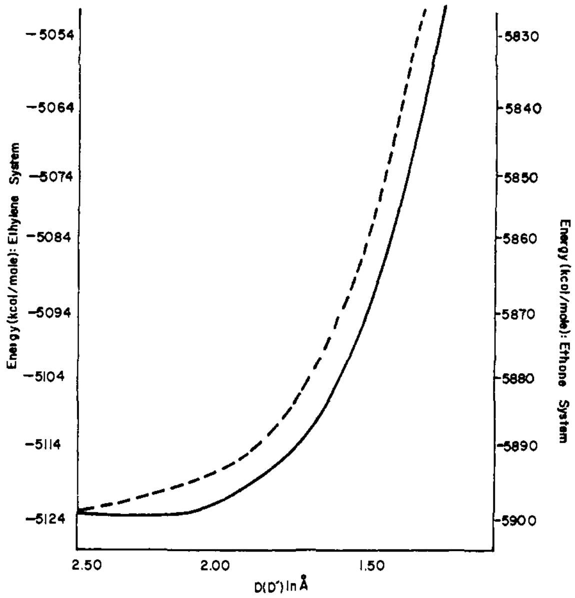


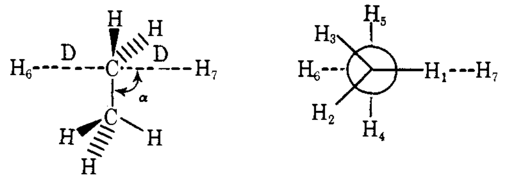
Figure 7. Energies calculated for the "transition state" geometries for ethane (———) and ethylene (------).

eventually leave as a hydride ion. The variable parameters are as follows: *D*, the "forming" bond length; α, the approach angle of H_7^- in the *xz* plane; *d*, the "breaking" bond length; β, the orientation of H_6 in the *xz* plane; θ, the twist angle orientation of the nonreacting hydrogens, H_4 and H_5, relative to the *xz* plane. The $C_1C_2H_4{=}C_1C_2H_5$ angles, γ, were made into pseudovariables and arbitrarily varied from 109.47 to 120° as θ varied from 60 to 90°.

First, however, we decided to establish a "calibration" for our SN2 surface by carrying out calculations on a set of symmetrical states in which $D = d$ and only the angle α and forming and breaking C–H bonds are varied (Scheme VIII). It was expected that the subsequently calculated SN2 energy curve would intersect this "symmetrical" curve at an energy close to that corresponding to the SN2 transition state.

The energies for this geometry were calculated for $D = 4.0$ Å to $D = 1.0$ Å and with the angle α varied from 82 to 100°. At large values of *D* (>2.25 Å), the calculated charge distribution shows the system to be an ethyl cation flanked by two hydride ions. As the hydrogens H_6 and H_7 are brought closer ($D \leq 2.25$ Å), the energy begins to rise (upper curve of Figure 6) but nowhere is a minimum in this curve found (see also Figure 7). The absolute values of the charges at C_2, H_6, and H_7 begin to decrease at $D \leqslant 2.50$ Å.

Scheme VIII. Symmetrical Geometries for the SN2 Displacement on Ethane ($D = d$, $\alpha = \beta$, $\theta = 90°$, $\gamma = 120°$)



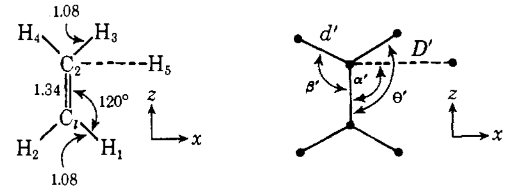
The full SN2 calculations were next carried out by fixing *D* and minimizing the energy with respect to the other variables[21] discussed above (Scheme I). The values of the variables were not allowed to "exceed" the initial ideal geometry, *i.e.*, we allowed only $d \geq 1.10$ Å, $\theta \geq 60°$, $\beta \leq 109.47°$, and $\gamma \geqslant 109.47°$. All calculations reported here used Slater exponents of 1.625 for carbon and 1.2 for hydrogen; the Coulomb integral parameters were −13.06 (H1s), −19.44 (C2s), and −10.67 eV (C2p).[12] The configurations calculated for various values of *D*, the "forming" bond, are shown in Table II, and the energies are plotted as a function of *D* in Figure 6 (lower curve).

Table II. Energy-Minimized Configurations for Hydride Attack on Ethane

D, Å	α	*d*, Å	θ	β	*E*, kcal/mol
16	90	1.10	60	109.5	−5953.91
2.50	90	1.10	60	109.5	−5942.36
2.25	90	1.10	65	107	−5930.44
2.00	90	1.10	70	104	−5907.37
1.96	90	1.10	70	103	−5902.30
1.90	90	1.10	70	103	−5893.62
1.88	90	1.10	70	102	−5890.39

Ethylene. As in the calculations for ethane, a portion of the ethylene molecule was held invariant throughout the "reaction." The fixed bond lengths and angles and the variable lengths and angles are shown in Scheme IX. The nonreacting bond lengths

Scheme IX. Fixed and Variable Bond Lengths and Angles for Hydride Attack on Ethylene



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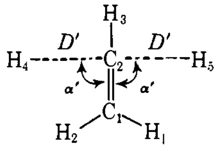
[21] The increments for the variables were 0.05–0.2 Å for *d* and *d'*, 1–2° for β and β', 3–5° for θ and θ', and 2° for α and α'. The values of *D* and *D'* were 16, 2.50, 2.25, 2.00, 1.96, 1.90, and 1.88 Å and several values below 1.88 Å.

were held at 1.08 Å (CH) and 1.34 Å (C=C). All of the atoms lie in the xz plane, and the atomic p orbitals of the π bond lie in the yz plane. The hydride ion, H_5, approaches the reaction center C_2 from the backside relative to H_4, which will eventually leave as a hydride ion. The variable parameters are analogous to those used for the ethane system, and all angles are measured in the xz plane.

Once again, the calculations were begun by investigating a set of possible symmetrical ($D' = d'$) structures (Scheme X). At large values of D', the calculated charge distribution for the symmetrical species shows a vinyl cation flanked by two hydride ions. As H_5 and H_4 are moved toward C_2, the energy rises more steeply than for comparable values of D for the ethane "transition state" (Figure 7), and the absolute values of the charges on C_2, H_4, and H_5 decrease. Again, no energy minimum is found along this curve.

Scheme X. Symmetrical Geometries for SN2 Displacement on Ethylene ($D' = d'$, $\alpha' = \beta'$, $\theta' = 180°$)



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Calculations on the vinyl SN2 pathway were then carried out by fixing D and searching for the energy minimum with respect to the other variables[21] indicated in Scheme IX. The values of the variables were not allowed to "exceed" the initial ideal geometry, *i.e.*, we allowed only $d' \geqslant 1.08$ Å, $\theta' \geqslant 120°$, and $\beta' \leqslant 120°$. The calculated configurations of the molecule at various values of D' are shown in Table III, and these energies are plotted as a function of D' in the lower curve in Figure 8.

Table III. Energy-Minimized Configurations for Hydride Attack on Ethylene

D', Å	α'	d', Å	θ'	β'	E, kcal/mol
16	(90°)	1.08	120	120	−5185.00
2.50	84	1.08	130	119	−5169.78
2.25	84	1.08	135	116	−5153.98
2.00	86	1.08	150	110	−5125.70
1.96	86	1.08	150	109	−5120.06
1.90	86	1.08	155	106	−5109.76
1.88	86	1.08	155	106	−5106.43

Discussion

At $D = 16$ Å, the ethane molecule is unperturbed by the approaching hydride ion and remains so until D reaches a value of about 3 Å. At this point the energy of the system begins to rise (Figure 6, lower curve) but remains lower in energy than the symmetrical states (Figure 6, upper curve). This relationship holds until the hydride ion is 1.88 Å away from C_2. We then cannot find a configuration of the system that is more stable than the symmetrical species. We therefore assume that the symmetrical configuration of the molecule at 1.88 Å is close to the "transition state" of the reaction.

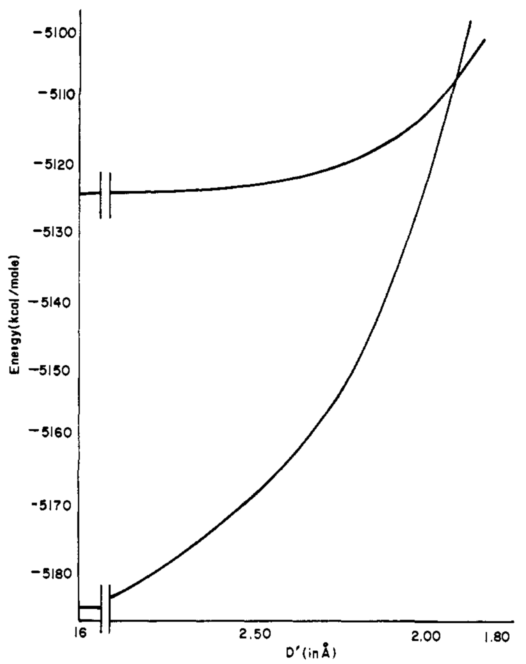

Figure 8. Calculated energies for the energy-minimized configurations (lower curve) and symmetrical configurations (upper curve) for H^- attack on ethylene.

The energy difference between this state and the reactants gives an activation energy[22] of 63.5 kcal/mol.

The same procedure is used in the ethylene system (Figure 8). The unsymmetrical, energy-minimized structure remains lower in energy than the corresponding symmetrical structure until $D' = 1.88$ Å. At this point the symmetrical "transition state" is lower in energy. The activation energy calculated for this reaction is about 78 kcal/mol.

The electron–electron and nuclear–nuclear repulsion terms missing from EHT calculations make these two barrier heights somewhat ambiguous, especially in view of the large geometrical changes involved in going from ground to transition states in these reactions. If such error contributions are similar for ethane and ethylene, however, the $\Delta\Delta E^{\ddagger}$ of 14.5 kcal/mol should be more reliable than the absolute $\Delta E^{\ddagger}$ values.

We should emphasize that the pairs of curves in Figures 6 and 8 do not cross at $D(D') = 1.88$ Å. On the multidimensional reaction surface they represent two structurally distinct species. When $D(D') = 1.90$ Å, the unsymmetrical system lies below the symmetrical. But when $D(D') = 1.88$ Å, the system has presumably shifted to some point above the threshold. We may then take a path leading from the unsymmetrical structure to the symmetrical one. This involves stretching the H_6–C_2 bond in ethane (H_4–C_2 for ethylene) and changing its orientation, moving the nonreacting hydrogens, and shifting the angle (α or α') of the hydride ion. When these intermediate points are calculated, there appears to be an additional barrier of ~5 kcal/mol.[23] With the molecule in the unsymmetrical configuration at $D(D') = 1.88$ Å, our location on the en-

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[22] (a) See M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, 8, 438 (1969); (b) since our calculated energy barriers are high, the activation energy should be close to the threshold energy.[22a]

[23] We have not carried out detailed calculations to determine the minimum barrier for this pathway due to the large geometric changes involved.

ergy surface with respect to the "transition state" is uncertain, and the path we calculate in getting to the symmetrical species is also vague. We cannot therefore determine whether or not all approaches to the transition state must go over this additional ~5-kcal barrier, *i.e.*, we cannot tell if our transition state may in fact be an intermediate. Of course, we might be able to establish the nature of the calculated transition state by doing detailed calculations in the region of $D(D') = 1.90$–1.86 Å, but these calculations are likely to be expensive and—in view of the approximate nature of the calculations themselves—perhaps worthless.

Even if the additional barrier is real, its magnitude is judged to be close to the same value in both systems. This does not affect the main conclusion of our investigation. *The energy barrier for the SN2 reaction of a hydride ion with ethylene is predicted to be 14.5 kcal/mol higher than the barrier for the SN2 attack on ethane.*

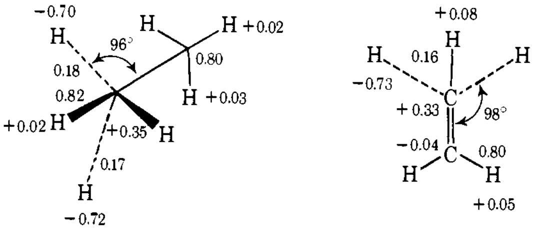
Ritchie and Chappell have recently reported MO-SCF calculations using linear combinations of Gaussian functions on the SN2 hydride attack on methane.[24] Their calculations show a threshold energy of 48.7 kcal/mol and a reacting bond distance, D, in the transition state of ~1.76 Å. Our results, *i.e.*, 63.5 kcal/mol and $D = 1.88$ Å, for the ethane system are similar and differ in the direction one might expect.[24a]

Since a symmetrical transition state is not implicitly required by the principle of microscopic reversibility,[25] Ritchie and Chappell looked for structures of C_{3v} symmetry as well as those of D_{3h} symmetry. The lowest energy state was of the latter symmetry class (triangular bipyramid).[24] For ethane one might expect the "transition state" to have a pseudo-D_{3h} symmetry, that is with $\alpha = 90°$, $\gamma = 120°$, and $\theta = 90°$ (see Scheme VII). However, the methyl group is evidently not a small perturbation, and we find $\alpha = 96°$ (with θ and γ assumed to be 90 and 120°, respectively). The incoming and leaving hydrogen atoms are directed "away" from the methyl substituent in the transition state. In the case of ethylene, this orientation in the transition state, α', is 98°. The reasons for the low energy of these conformations are not completely clear, but evidently have to do with a careful balance between favorable orbital overlap and unfavorable steric interactions. The indications that $\alpha(\alpha')$ need not be 90° and that $D(D')$ may be as large as 1.88 Å suggest that steric crowding in the SN2 transition state of ethylene may not be so overwhelming as has been assumed.[20,26]

In Figure 7, which shows the energies for symmetrical SN2 geometries, the curves are drawn so that we may compare relative energy differences between ground and energized systems at a given value of $D(D')$. At 16 Å (not shown in Figure 7), $\Delta\Delta E^{\ddagger} \sim 7$ kcal/mol;[22b] at 1.88 Å, $\Delta\Delta E^{\ddagger} \sim 7 + 7.5 \sim 14.5$ kcal/mol. As $D(D')$ becomes even shorter, $\Delta\Delta E^{\ddagger}$ increases, since the curve for ethylene is steeper than the curve for ethane. It is interesting that while the transition state for the ethylene reaction lies relatively higher in energy than the ethane reaction, the partial bond lengths, D and D', are predicted to be nearly identical.

The calculated charge distributions and overlap populations for the transition states for ethane and ethylene, as shown in Scheme XI, are very similar. Examination of the relative energy changes that occur for the occupied molecular orbitals as a hydride ion approaches ethane and ethylene shows that in both cases, most of the MO energies remain nearly constant or change by <0.2 eV, but one orbital undergoes a dramatic increase in energy (decrease in absolute value). This orbital consists entirely of the 1s atomic orbital on the hydride ion when $D(D') = 16$ Å. As $D(D')$ decreases, this MO shows increasing contributions from atomic orbitals on the nonreacting hydrogens at C_2, from the 1s orbital on the leaving hydrogen, and a contribution from the $2p_x$ and 2s orbitals at C_2. (In the case of ethylene, there is also a contribution from the 2s and $2p_z$ orbitals at C_1.)

Scheme XI. Calculated Charge Distributions and Overlap Populations for SN2 Transition States ($D = d = D' = d' = 1.88$ Å)



We must emphasize some rather perplexing aspects of the conformational details of these reactions. Table II shows that hydride approaches the ethane molecule at 90° (α), β begins to decrease as D decreases, and θ begins to increase. But the configuration appears to become "stuck" by the time the hydride distance, D, has reached 2.00 Å. And by the time the energy has come very close to that of the assumed "transition state," *i.e.*, at $D \approx 1.90$ Å, the nonreacting hydrogens (H_4 and H_5, Scheme VII) have moved only about one-third of the distance toward the transition geometry, the leaving hydrogen has changed its orientation by about three-fourths of the total change, and the "breaking" bond has not begun to stretch at all.

The configurations shown in Table III for hydride attack on ethylene show similar trends. In this case it is more favorable by ~1 kcal/mol for the hydride ion to approach at an angle of 84–86°, evidently because the nonreacting hydrogen (H_3, Scheme IX) interferes more. By the time the hydride ion is 1.90 Å away, the nonreacting hydrogen has moved one-half to two-thirds of the way toward the symmetrical geometry and the leaving hydrogen has moved about two-thirds through its angle, but the length of the breaking bond remains 1.08 Å. It is also interesting that the hydride ion tends to approach at an angle <90° but that the orientation at the transition state has $\alpha = 96$–$98°$.

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(24) C. D. Ritchie and G. A. Chappell, *J. Amer. Chem. Soc.*, **92**, 1819 (1970).

(24a) Note Added in Proof. A modified PNDO-SCF calculation by N. L. Allinger, J. C. Tai, and F. T. Wu (*ibid.*, **92**, 579 (1970)), of the D_{3h} "transition state" for CH_5^- gives reacting partial bond lengths of 1.210 Å. This distance is inconsistent with the longer (~1.76 Å) value calculated by Ritchie and Chappell[24] and with 1.74 and 1.63 Å calculated by W. Th. A. M. Van der Lugt and P. Ros (*Chem. Phys. Lett.*, **4**, 389 (1969)) and J. J. C. Mulder and J. S. Wright (*ibid.*, **5**, 445 (1970)), respectively. We feel the larger values are intuitively more reasonable, although the reasons for the differences are not readily apparent.

(25) R. L. Burwell, Jr. and R. G. Pearson, *J. Phys. Chem.*, **70**, 300 (1966).

(26) The calculated overlap populations indicate that the total Slater interaction may be nearly the same for the ethane and ethylene transition states.

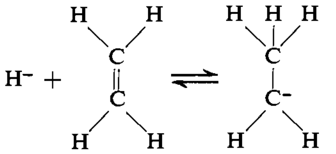
These large structural differences between the isoenergetic points on the two curves in Figure 6 (and Figure 8) may be a result of either the approximations inherent in extended Hückel theory, a significant energy minimum at the symmetrical activated complex, or significant asymmetry in the true SN2 transition state. While we have no way of ruling out these possibilities, it is important to at least consider a further alternative—that the calculations are qualitatively correct in suggesting the substrate molecule retains a configuration close to that of its ground state for as long as possible during the reaction, and then undergoes a major structural reorganization in the energy region close to the transition state.

Comparison of the SN2 Pathway to Other Mechanisms. As we have discussed above, our calculations show that with a hydride ion nucleophile and leaving group the SN2 attack on ethylene is less favorable energetically than the SN2 attack on ethane. It would be tempting to try to compare the calculations for the SN2 attack to ones for SN1 dissociation to form vinyl cations, *e.g.*, eq 4. This is not possible using EHT calculations.

$$CH_2{=}CH_2 \longrightarrow CH_2{=}C^{+}H + H^{-} \qquad (4)$$

The SN2 reaction is a negatively charged system and the SN1 reaction is (overall) neutral. The missing electron repulsions will not be approximately cancelled when the energy values for the two systems are compared.

We can, however, make a reasonable comparison of the SN2 reaction of H^- and ethylene to the addition–elimination reaction, eq 5. We calculate a $\Delta E = 18$ kcal/mol for this reaction. Presumably the reaction coordinate would involve hydride attack on the π system. Although we have not carried out any detailed calculations to arrive at an energy barrier for the reaction, it is reasonable to assume that the energy barrier would be of the same order as ΔE, *i.e.*, a threshold energy of 20–40 kcal/mol for the addition. Since this system and the SN2 reaction on ethylene are both negatively charged and the transition states of intermediates are of comparable overall geometry, we should expect a comparison of the reactions to be reasonable. The threshold energy of 78 kcal/mol calculated for the SN2 reaction suggests that an addition-elimination pathway is energetically more favorable by 40–60 kcal/mol.



(5)

Conclusions

Our extended Hückel calculations predict the energy barrier for an SN2 hydride displacement on ethylene to be 14.5 kcal/mol higher than that for similar hydride attack on ethane. Qualitatively this energy difference indicates that the SN2 attack at an sp^2 carbon is energetically more difficult than SN2 attack at an sp^3 center, as might have been intuitively expected. It does not, by any means, rule out the possibility that SN2 attack at a vinylic center is energetically feasible, particularly in other reaction systems.

The comparison of the SN2 attack on ethylene with the addition–elimination pathway does suggest, however, that if an SN2 pathway is not particularly unfavorable in an *absolute* sense, the reason this mechanism has not been observed for vinylic systems is due to the *relative* energetic favorability of other reaction pathways, such as addition–elimination, elimination–addition, or SN1 reactions. It remains to be seen if reactants and reaction conditions can be devised in which the lowest energy path will involve a direct displacement at a vinylic center.

Finally, an examination of atomic motions in the region of the transition states for these reactions suggests that the leaving C–H bond may not undergo very much cleavage until the new C–H bond is nearly formed, thus necessitating a large degree of atomic motion in the region of the transition state energy. This sort of behavior may be an artifact of the approximations involved in the EHT method, or of our assumption that the transition state is symmetrical. It may reflect the behavior of the real system, however, and although this conflicts to some extent with our intuitive feeling that one-step chemical reactions ought to occur "smoothly," the destabilization due to molecular compression in such a situation may be compensated by significant stabilization due to increased bonding interactions. In our opinion, this sort of inference is an example of one of the main justifications for carrying out highly approximate theoretical studies: even if the quantitative results are suspect, one often generates new ways of thinking about chemical reactions which can provide general insight or influence the direction of future experimental studies.

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