potential-energy surface. Such treatments of simpler systems have been carried out,[28] and the goal is to extend these treatments to deal with formaldehyde.

Acknowledgment. We have enjoyed numerous stimulating discussions with Professor C. B. Moore regarding the photochemistry of formaldehyde. This work has been supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract W-7405-Eng-48. Y.Y. and H.F.S. acknowledge support of the National Science Foundation and the Robert A. Welch Foundation. The quantum chemistry calculations were carried out at the University of Texas computing center and the rate constants on the Berkeley minicomputer supported by the National Science Foundation (Grant CHE 79-20181). S.K.G. has been supported in part by a National Sciences and Engineering Research Council of Canada Scholarship.

---

[28] B. A. Waite and W. H. Miller, *J. Chem. Phys.*, **73**, 3713 (1980).

Vinylidene: A Very Shallow Minimum on the C_2H_2 Potential Energy Surface. Static and Dynamical Considerations

Yoshihiro Osamura, Henry F. Schaefer, III,* Stephen K. Gray, and William H. Miller

Contribution from the Department of Chemistry and Institute for Theoretical Chemistry, University of Texas, Austin, Texas 78712, and the Department of Chemistry and Material and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. *Received September 19, 1980*

Abstract: The potential energy surface for the singlet vinylidene → acetylene rearrangement has been investigated by using nonempirical molecular electronic structure theory. A double-ζ plus polarization basis set was used in conjunction with configuration interaction (CI) including single and double excitations, a total of 13 861 configurations.[5] Newly developed analytic CI gradient techniques were used to locate precisely the vinylidene and acetylene minima and the transition state connecting them. Single point calculations were carried out with a larger triple-ζ plus polarization basis. The classical barrier height is calculated to be 6.4 kcal or 5.4 kcal after correction for the effects of higher excitations, and our best estimate of the true classical barrier is 4 kcal. Harmonic vibrational analyses were carried out about each of the three stationary points, and zero-point energy effects lower the effective barrier by 1.8 kcal. Even for energies below this, however, tunneling through the barrier is found to be extremely rapid; for example, with no vibrational excitation energy (above its zero-point energy) the lifetime of vinylidene with respect to rearrangement to acetylene is calculated to be only $\sim 10^{-11}$ s, and with 2 kcal of excitation energy this decreases to $\sim 10^{-12}$ s. These predictions appear to be consistent with the experimental findings of Skell (1972) and Steinfeld (1980).

As the simplest unsaturated carbene,[1,2] vinylidene (the $H_2C{=}C$: molecule) plays a special role in the organic chemistry of reactive intermediates. As such there have been a number of theoretical studies[3-12] of vinylidene. From the experimental perspective, the key question is whether vinylidene in fact exists as a discrete chemical entity. It is certainly established[13-17] that in the circumstances under which the 1,2 hydrogen shift has been observed (eq 1), it is rapid. To be more blunt, reaction 1 is so fast that


(1)

vinylidene has never been identified spectroscopically. Of course, in the limit of zero activation energy for (1), vinylidene is no longer a relative minimum on the C_2H_2 potential energy surface. The singular laboratory evidence for the existence of H_2CC: comes from Skell's trapping experiments,[14] which suggest a lifetime of the order of 10^{-10} s.

The only reliable theoretical study to date of the singlet vinylidene rearrangement (1) yielded a barrier height of 8.6 kcal.[10] From this the true classical barrier was estimated to be 5–8 kcal.[18] However recent experiments by Steinfeld and co-workers[16,17] have challenged this theoretical prediction. Steinfeld demonstrated that multiple infrared photon excitation of chloroethylene by intense CO_2 laser pulses leads to elimination of HCl. Deuterium-labeling studies[16] showed that the reaction proceeds mainly via a three-center elimination, suggesting that $H_2C{=}C$: is the initial product. Since acetylene is the only hydrocarbon product observed, however, the nascent vinylidene must rearrange to acetylene before it has the chance to collide with other species and react to give other hydrocarbon products. Steinfeld et al.[17] then argue that the barrier for this rearrangement should not be more than the internal energy with which the vinylidene intermediate is born. Using an impulsive half-collision model and the data on translational energy release

---

*To whom correspondence should be addressed at The University of California, Berkeley.

(1) H. D. Hartzler, "Carbenes", Vol. II, R. A. Moss and M. Jones, Eds., Wiley, New York, 1975, pp 44–100.

(2) P. J. Stang, *Acc. Chem. Res.*, **11**, 107 (1978); *Chem. Rev.*, **78**, 383 (1978).

(3) R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968).

(4) A. C. Hopkinson, K. Yates, and I. G. Csizmadia, *J. Chem. Phys.*, **55**, 3835 (1971).

(5) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Am. Chem. Soc.*, **94**, 9095 (1972).

(6) O. P. Strausz, A. C. Hopkinson, M. Schoenborn, and I. G. Csizmadia, *Theor. Chim. Acta*, **29**, 183 (1973).

(7) W. A. Lathan, L. A. Curtis, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).

(8) D. Poppinger, *Chem. Phys. Lett.*, **35**, 550 (1975).

(9) J. H. Davis, W. A. Goddard, and L. B. Harding, *J. Am. Chem. Soc.*, **99**, 2919 (1977).

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

(11) J. W. Kenney, J. Simons, G. D. Purvis, and R. J. Bartlett, *J. Am. Chem. Soc.*, **100**, 6930 (1978).

(12) M. P. Conrad and H. F. Schaefer, *J. Am. Chem. Soc.*, **100**, 7820 (1978).

(13) P. S. Skell and J. H. Plonka, *J. Am. Chem. Soc.*, **92**, 5620 (1970).

(14) P. S. Skell, F. A. Fagone, and K. J. Klabunde, *J. Am. Chem. Soc.*, **94**, 7862 (1972).

(15) P. S. Skell, J. J. Havel, and M. J. McGlinchey, *Acc. Chem. Res.*, **6**, 97 (1973).

(16) C. Reiser, F. M. Lussier, C. C. Jensen, and J. I. Steinfeld, *J. Am. Chem. Soc.*, **101**, 350 (1979).

(17) C. Reiser and J. I. Steinfeld, *J. Phys. Chem.*, **84**, 680 (1980).

(18) H. F. Schaefer, *Acc. Chem. Res.*, **12**, 288 (1979).

0002-7863/81/1503-1904$01.25/0

following multiphoton excitation of $H_2C{=}CHCl$, Reiser and Steinfeld[17] estimate a vibrational excitation energy of 2–5 kcal in the vinylidene fragment. Accordingly they conclude that the barrier should not be greater than 2 kcal, significantly below the lower limit of the theoretical estimate,[18] 5–8 kcal.

From the perspective of $3^1/_2$-year hindsight, one must therefore ask whether there is reason to question the reliability of the previous study[10] of the barrier height for (1). Dykstra and Schaefer's study of the vinylidene isomerization used a reasonable basis set and description of electron correlation. However several obvious weaknesses do come to mind. First, the transition state was located in an approximate matter, assuming a particular reaction coordinate. The recent development of analytic CI gradient techniques[19,20] makes feasible the precise determination of the saddle-point geometry. Second, no account was taken of the effect of higher than double excitations, i.e., configurations differing by more than two orbitals from the Hartree–Fock reference configuration.[21] Third, the effects of zero-point vibrational energy (ZPVE) were ignored by Dykstra and Schaefer,[10] and such effects can be significant, as noted in a recent study[22] of the formaldehyde isomerization (see eq 2). For reaction 2, the

$$H_2CO \longrightarrow HCOH \qquad (2)$$

transition state has 4 kcal less ZPVE than does formaldehyde, effectively lowering the classical threshold for the reaction by this amount, and a similar effect might be operative for the vinylidene rearrangement. Finally, since the vinylidene rearrangement primarily involves the motion of only a single hydrogen atom, there is the possibility that tunneling through the barrier may be fast enough to lower the effective barrier height even further. Tunneling has, in fact, been predicted[23,24] to be an important feature in the formaldehyde unimolecular reactions (2) and (3) at energies as much as ~6–8 kcal below the zero-point energy-corrected barrier heights.

$$H_2CO \longrightarrow H_2 + CO \qquad (3)$$

The first goal of the present study is then to reexamine the vinylidene potential energy surface with an eye to the above-mentioned shortcomings of the previous theoretical study. Second, the rate constant for unimolecular isomerization of vinylidene to acetylene needs to be determined including the effects of tunneling through the barrier. We then wish to relate these considerably more reliable, state-of-the-art theoretical results to the Reiser–Steinfeld experiments[16] to see if theory and experiment are consistent. Finally, the calculated lifetime (the reciprocal of the unimolecular rate constant) of vinylidene can also answer the question[25] of whether or not it is possible for it to exist in interstellar gas clouds (it cannot) and can also suggest the nature of the experiments that might be able to observe it.

The C_2H_2 Potential Energy Surface

A. Theoretical Details. The basis set used here is essentially the same as that of Dykstra and Schaefer and is of double-ζ plus polarization (DZ+P) quality. Specifically the Huzinaga–Dunning contracted Gaussian basis[26] C(9s5p/4s2p), H(4s/2s) was augmented by a set of p functions on hydrogen and a set of d functions on carbon. All six d-like functions (x^2, y^2, z^2, xy, xz, yz) were included in the basis and polarization function exponents were 0.75 (d on carbon) and 1.0 (p on hydrogen). Thus the basis set included 42 contracted Gaussian functions.

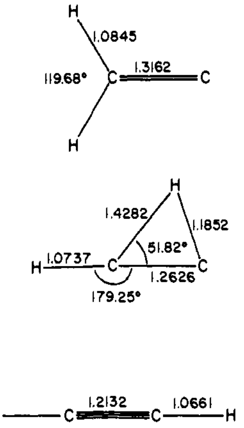

Figure 1. Stationary point geometries predicted at the DZ+P CI level of theory for vinylidene, acetylene, and the transition state connecting them.

Table I. Predicted DZ+P CI Harmonic Vibrational Frequencies for Vinylidene, Acetylene, and the Transition State State Connecting Them

species	freq, cm^{-1}	normal-mode description
vinylidene	3344	CH asym stretch
	3239	CH sym stretch
	1710	CC stretch
	1288	CCH bend
	787	out-of-plane
	444	CH_2 rock
transition state	3454	CH_a stretch
	2699	CH_b stretch
	1874	CC stretch
	937	HCC bend
	573	out-of-plane
	1029i	reaction coord
acetylene	3583	CH asym stretch
	3488	CH sym stretch
	2073	CC stretch
	764	CCH bend
	610	CCH bend

The effects of electron correlation were variationally considered by using the loop-driven graphical unitary group approach.[27,28] The configurations included were all single and double excitations relative to the Hartree–Fock reference configuration. Restrictions on the above were that the two lowest occupied self-consistent field (SCF) molecular orbitals were held doubly occupied in all configurations and the two highest lying virtual orbitals were deleted from the CI. These four orbitals are all localized in the core or carbon 1s region and are not expected to play a significant role in describing the valence electrons. For point groups C_s and C_1 (no elements of symmetry other than the identity) the CI's thus described included 7501 and 13 861 configurations, respectively.

With use of the analytic CI gradient methods[19] mentioned above, the vinylidene and acetylene minima were located precisely, as was the transition state connecting them. For each of these three stationary points, all quadratic force constants in terms of cartesian coordinates were subsequently computed. The appropriate 12 × 12 matrices were then diagonalized to yield the harmonic vibrational frequencies.

B. Geometrical Structures. The three stationary point geometries predicted at the DZ+P CI level of theory are illustrated in Figure 1. The experimental structure for acetylene has $r_e(C{\equiv}C) = 1.203$ and $r_e(C{-}H) = 1.060$,[29] both somewhat smaller

---

(19) B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **72**, 4652 (1980).

(20) R. Krishnan, H. B. Schlegel, and J. A. Pople, *J. Chem. Phys.*, **72**, 4654 (1980).

(21) E. R. Davidson, "The World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., D. Reidel, Dordrecht, Holland, 1974, pp 17–30.

(22) J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, to be submitted for publication.

(23) W. H. Miller, *J. Am. Chem. Soc.*, **101**, 6810 (1979).

(24) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Am. Chem. Soc.*, in press.

(25) S. Green and E. Herbst, *Astrophys. J.*, **229**, 121 (1979).

(26) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); T. H. Dunning, *ibid.* **53**, 2823 (1970).

(27) I. Shavitt, *Int. J. Quantum Chem., Quantum Chem. Symp.*, **11**, 131 (1977); **12**, 5 (1978).

(28) B. R. Brooks and H. F. Schaefer, *J. Chem. Phys.*, **70**, 5092 (1979); B. R. Brooks, W. D. Laidig, P. Saxe, N. C. Handy, and H. F. Schaefer, *Phys. Scr.*, **21**, 312 (1980).

than the theoretical predictions. Specifically the predicted C≡C distance in Figure 1 is 0.010 Å greater than experiment and the predicted C—H distance of 0.006 Å too long. Vinylidene has a much longer predicted carbon–carbon distance, 1.316 Å, consistent with its formal double bond. Perhaps not too surprisingly, the transition-state C—C distance is intermediate between the two, namely, 1.263 Å.

Further examination of the transition-state structure shows that it is "closer" to that of the product acetylene than the reactant vinylidene. This may be seen first by noting that the nonmigrating H-C-C angle is 179.3°, very close to 180° value in acetylene. Second, the migrating hydrogen atom is much closer (1.185 Å) to the C atom to which it is migrating than to the one from whence it came (1.428 Å). This result is particularly intriguing since it runs counter to Hammond's postulate[30] that for an exothermic reaction (such as vinylidene → acetylene) the transition state should resemble the reactant.

C. Vibrational Frequencies. The predicted harmonic vibrational analyses are summarized in Table I. These DZ+P CI frequencies are expected to be ~3.5% greater than the exact *harmonic* frequencies, based on comparisons[31] for a range of experimentally characterized molecules. Comparison with the known *anharmonic* (i.e., $v = 0 \rightarrow v = 1$ energy differences) frequencies[32] is possible for acetylene, in which case $\nu_1 = 3373$, $\nu_2 = 1974$, $\nu_3 = 3295$, $\nu_4 = 612$, and $\nu_5 = 729$ cm^{-1}. The differences between theory and experiment are 210 (6.2%), 99 (5.0%), 193 (5.9%), -2 (-0.3%), and 35 cm^{-1} (4.8%). Note of course that these disparities are due both to differences between the theoretical and exact potential hypersurface and to the neglect of anharmonicity in the theoretical predictions.

The above comparisons suggest that the predicted vibrational spectrum of the experimentally unknown vinylidene should be quite reliable. For example, the observation of C–H stretching frequencies about 240 cm^{-1} below those of acetylene might be due to vinylidene. Similarly there is no danger of any of the other vinylidene frequencies (except the out-of-plane mode predicted at 787 cm^{-1}) being mistaken for those of acetylene. The biggest drawback to the experimental detection of the $H_2C{=}C$: infrared spectrum, as we shall see later, is its very short lifetime with respect to unimolecular decay.

It is of interest to compare the transition state vibrational frequencies with those for the closely related[22] formaldehyde → hydroxycarbene rearrangement (2). The main difference, of course, between these two potential surfaces is that the formaldehyde barrier is more than 10 times the vinylidene barrier. Thus it is not surprising that the imaginary vibrational frequency or reaction coordinate is 2356i for the formaldehyde case, but only 1029i for the vinylidene rearrangement. In both cases the imaginary mode "borrows" to a considerable degree from the two hydrogen stretching frequencies of the reactant.

The zero-point vibrational energies of the three stationary points within the harmonic approximation are 15.46 (vinylidene), 13.63 (transition state), and 17.00 kcal (acetylene). This means that the zero-point corrected barrier (or activation energy in the sense of transition-state theory) is 1.83 kcal less than the classical barrier. Similarly the zero-point corrected exothermicity is predicted to be 1.54 kcal less than the classical exothermicity.

D. Relative Energies. The DZ+P CI energies at the three stationary points are -77.019 235 (vinylidene), -77.006 299 (transition state), and -77.082351 hartrees (acetylene). The classical barrier at this level of theory is therefore predicted to be 8.1 kcal, only slightly less than the 8.6 kcal obtained by Dykstra and Schaefer.[10] Similarly the classical exothermicity is 39.6 kcal, compared to the Dykstra prediction of 40.0 kcal.

At the DZ+P CI geometries for vinylidene and the transition state, single calculations were carried out with a more flexible C(9s 5p 1d/5s 3p 1d), H(4s 1p/3s 1p) basis set. These final calculations were done after J. A. Pople (private communication) reported that a larger basis of this general type reduces the predicted barrier height. Consistent with Pople's prediction, the larger basis set reduced the barrier from 8.1 to 6.4 kcal.

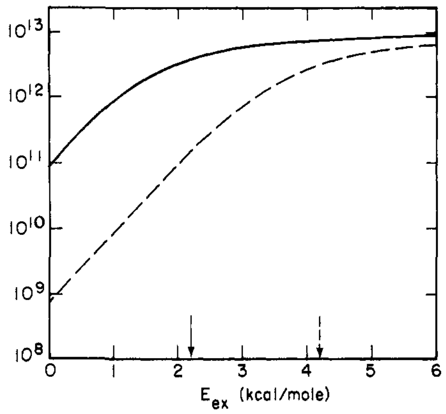

Figure 2. Rate of the vinylidene → acetylene rearrangement as a function of excess vibrational energy in vinylidene, i.e., vibrational energy in addition to its zero-point energy. The solid curve is for a classical barrier of 4 kcal/mol and the broken line for a classical barrier of 6 kcal/mol. The arrows on the energy axis indicate the classical thresholds for the reaction (the zero-point energy-corrected barrier height) for the two cases.

The Davidson correction[21] for unlinked clusters suggests that their contribution is 15.4 kcal for vinylidene and 16.4 kcal for the transition state, so that this correction lowers the classical barrier to 5.4 kcal. Further basis set expansion and electron correlation might be expected to lower the barrier another kilocalorie or so, leading to a "best estimate" for the true classical barrier of 4 kcal. Similarly, the best estimate for the zero-point energy corrected barrier is 4 − 1.8 = 2.2 kcal.

Dynamics of the Unimolecular Vinylidene Rearrangement

A. The Model. The most rigorous methodology currently available for describing tunneling in polyatomic reaction dynamics is based on the reaction path Hamiltonian recently derived by Miller, Handy, and Adams.[33] This has been applied, for example, to the unimolecular decomposition of formaldehyde[24] (reaction 3) and to the unimolecular isomerization of hydrogen isocyanide[34] (HNC → HCN). The rigorous application of this approach requires knowledge of the potential energy surface along the reaction path which connects the saddle point of the potential surface (i.e., the transition state) to reactants and to products and also of the matrix of force constants along the reaction path. For these earlier applications,[24,34] however, it has been found that the much simpler microcanonical transition state model[23] ("RRKM plus tunneling") gives rate constants which are essentially the same (i.e. within ~20%) as those given by the more rigorous model. This simpler approach only requires knowledge of the usual transition-state information (i.e., the barrier height and vibrational frequencies) and is the method used to determine the rates reported below. The appropriate formulas have been given before[23] and need not be repeated here. Based on the earlier results for HNC and H_2CO, we expect that these rate constants should be reliable to ~20–30% for a given set of transition-state parameters.

B. Results and Discussion. Figure 2 shows the microcanonical rate for the vinylidene rearrangement as a function of vibrational excitation energy in the reactant vinylidene, i.e., the vibrational energy in excess of its zero-point vibrational energy. These rates are for zero total angular momentum, and they include a factor of 2 due to the symmetry of vinylidene. The frequencies used for the calculation are those in Table I. The solid curve in Figure 2 is for the classical barrier $V_0 = 4$ kcal/mol, our best estimate

---

(29) W. J. Lafferty and R. J. Thibault, *J. Mol. Spectrosc.*, **14**, 79 (1964).

(30) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(31) Y. Yamaguchi and H. F. Schaefer, *J. Chem. Phys.*, **73**, 0000 (1980).

(32) G. Herzberg, "Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1967, p 611.

(33) W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, **72**, 99 (1980).

(34) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2733 (1980).

(35) W. H. Miller, unpublished results.

of the true value, and the broken curve is the rate for $V_0 = 6$ kcal/mol, which should certainly be an upper limit to the correct value. The arrows on the energy axis indicate for each case the zero-point energy-adjusted barrier height, i.e., the threshold for the reaction if tunneling is ignored. One thus sees that tunneling is extremely important in this reaction.

The tunneling rates in Figure 2 are in good agreement with Skell's earlier work,[14] which indicated a rearrangement rate greater than 10^{10} s^{-1}, and also with the more recent Steinfeld experiments[16,17] which observed no reaction products from vinylidene. Thus with the ~2–5-kcal excitation energy estimated by Steinfeld and Reiser[17] the solid curve in Figure 2 shows a lifetime of less than 10^{-12} s for vinylidene, and since the time between collisions in the experiment is $\sim 10^{-7}$ s, vinylidene rearranges to acetylene before it has the chance to collide and react. This would also be true if vinylidene were born with no excitation energy, since the lifetime is only $\sim 10^{-11}$ s for $E_{ex} = 0$. Even with a barrier of $V_0 = 8$ kcal/mol and with an excitation energy $E_{ex} > 2$ kcal/mol, our calculations give the lifetime of vinylidene to be less than 10^{-8} s, so that the results of the Steinfeld–Reiser[17] experiments are actually consistent with a classical barrier as large as this.

The lifetime of vinylidene is so short, in fact, that it is probably of little significance under most chemical conditions. With a lifetime of $\sim 10^{-11}$ s in its ground vibrational state, though, it does live long enough to have some semblance of a vibrational spectrum, but to observe it would require experiments on a picosecond time scale.

Another conclusion from these results is that vinylidene does not live long enough to be present in interstellar gas clouds;[25] it will tunnel to the acetylene conformation and be stabilized there. This is in contrast to the species *trans*-hydroxymethylene, HCOH, which has a classical barrier of ~36 kcal/mol with respect to rearrangement to the more stable formaldehyde, H_2CO. With use of the latest results[22] for the energies and vibrational fequencies of HCOH and the transition state of HCOH $\rightleftarrows$ H_2CO, the rate of the HCOH → H_2CO rearrangement is calculated[35] to be $\sim 10^3$ s^{-1} at an energy ~20 kcal below the zero-point energy-adjusted barrier height, which corresponds to an excitation energy of ~12 kcal in HCOH. Since the rate of spontaneous IR emission is $\sim 10^3$ s^{-1}, this means that if HCOH is formed with less than ~12 kcal of excess vibrational energy, it will decay via spontaneous emission rather than by tunneling to H_2CO and thus will be stabilized as HCOH; HCOH that is formed with more than this amount of energy will tunnel to H_2CO and will be stabilized via spontaneous emission in this conformation.

C. Tunneling Rates at Low Excitation Energy. In concluding this section on the tunneling dynamics of vinylidene we note that one may legitimately question the reasonableness of using the microcanonical transtion-state model at very low excitation energies, even $E_{ex} \to 0$. In this energy region, for example, the reactant molecule is certainly not expected to behave microcanonically. We discuss this point here.

For energies sufficiently below the classical reaction threshold that only the ground state of the transition state contributes to the tunneling, the microcanonical transition-state expression[23] for the unimolecular rate constant is

$$k(E) = \frac{P(E - \epsilon_0^{\ddagger})}{2\pi\hbar\rho(E)} \tag{4}$$

where P is the tunneling probability for one-dimensional motion along the reaction coordinate, E is the total energy, $\epsilon_0^{\ddagger}$ is the zero-point energy of the transition state, and $\rho(E)$ is the density of states of the reactant. If, on the other hand, one uses a *separable* approximation for the unimolecular reaction dynamics, the expression for the rate constant is[36]

$$k(E) = \frac{\omega_r}{2\pi}P(E - \epsilon_0^{\ddagger}) \tag{5}$$

where ω_r is the frequency of the reactant molecule that correlates with the reaction coordinate; i.e., $\omega_r/2\pi$ is the number of times per second that the particle hits the barrier as it vibrates classically in the reactant potential well. This latter model is essentially Slater's[37] picture of the unimolecular reaction, modified here to include tunneling.

The difference between the transition state expression (eq 4) and the separable expression (eq 5) is in the frequency factors, $[2\pi\hbar\rho(E)]^{-1}$ and $\omega_r/2\pi$, respectively. The frequency ω_r which correlates adiabatically with the reaction coordinate is the lowest frequency of the reactant molecule, which for vinylidene is the 444-cm^{-1} CH_2 rock in Table I. At zero excitation energy the total energy E is the zero-point energy of the reactant

$$E = \frac{1}{2}\sum_{i=1}^{F}\hbar\omega_i \tag{6}$$

and with the usual[38] semiempirical density of states the frequency factor of the transition state model is

$$[2\pi\hbar\rho(E)]^{-1} = \frac{(F-1)!}{2\pi}\frac{\prod_{i=1}^{F}\omega_i}{\left(\frac{a}{2}\sum_{i=1}^{F}\omega_i\right)^{F-1}} \tag{7a}$$

$$\equiv \bar{\omega}/2\pi \tag{7b}$$

where "a" is the usual empirical parameter introduced by Rabinowitch et al.[38]

For the present system the effective frequency $\bar{\omega}$ defined by eq 7 for the transition-state model differs by less than 10% from the frequency $\omega_r = 444$ cm^{-1} of the separable model, so that one has some confidence that the results shown in Figure 2 are reasonable even in the limit of zero excitation energy. This close agreement of the two models need not always be the case, and for the limit of zero excitation energy the separable model is probably the more justifiable one. One operational way to reconcile the two is to equate the frequency $\bar{\omega}$ defined by eq 7 to ω_r and let this define the value of the empirical parameter "a" in the limit $E_{ex} \to 0$. The value of "a" so determined no longer relates to the density of states[38] but is simply a parameter which converts the transition-state rate expression into the separable one in the limit of zero excitation energy.

Concluding Remarks

From a broad perspective, the significance of the research reported here is the demonstration that a reactive intermediate may lie in a well-defined potential minimum and nevertheless be unobservable by existing experimental techniques. Vinylidene, although facing a classical barrier to isomerization of ~4 kcal, tunnels through this barrier in 10 ps. The pertinence of this finding to the future detection of similar organic free radicals should be apparent.

Future theoretical research might profitably be directed toward the question of the much longer lifetimes of substituted vinylidenes such as the difluoro and dimethyl species. In the former case, the potential surface has a higher barrier, but the added (relative to $H_2C{=}C{:}$) stability of dimethylvinylidene could be due to the absence of tunneling by the heavier CH_3 group.

Acknowledgment. Yoshihiro Osamura and Henry F. Schaefer were supported by the U.S. National Science Foundation and the Robert A. Welch Foundation. Stephen K. Gray and William H. Miller were supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-Eng-48. S.K.G. also acknowledges a Natural Sciences and Engineering Research Council of Canada Scholarship.

---

(36) See, for example, B. A. Waite and W. H. Miller, *J. Chem. Phys.*, **73**, 3713 (1980).

(37) N. B. Slater, "Theory of Unimolecular Reactions", Cornell University Press, Ithaca, N.Y., 1959.

(38) See, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, 1972, pp 131–134.