Table III. Summary of OS Values (kcal/mol) of Bridged Bicyclic Bridgehead Olefins

<table>
<thead>
<tr>
<th>S no. system</th>
<th>bridge length where double bond is located</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>111</td>
</tr>
<tr>
<td>4</td>
<td>211</td>
</tr>
<tr>
<td>5</td>
<td>221</td>
</tr>
<tr>
<td>6</td>
<td>222</td>
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<tr>
<td>7</td>
<td>222</td>
</tr>
<tr>
<td>8</td>
<td>322</td>
</tr>
<tr>
<td>9</td>
<td>333</td>
</tr>
<tr>
<td>10</td>
<td>422</td>
</tr>
<tr>
<td>11</td>
<td>444</td>
</tr>
</tbody>
</table>

*Order according to the S number of the system and the length of the bridge in a bicyclo[xy,z]alkene in which the double bond is located. S = x + y + z. *b Shorthand notation, xyz, to designate a bicyclo[xy,z]alkene.

and enhanced reactivity. In contrast, the stability of zero-bridged olefins is not related directly to their OS values but depends on the degree of out-of-plane deformation imposed by incorporation into rigid cage structures.

Qualitative rules such as those of Kobrich do not predict bridgehead olefin stabilities accurately. Wiseman is correct, all observable bridgehead olefins do have the trans double-bond moiety in an eight numbered or larger ring. However, some systems which meet this criterion are not observable and the relative stability of isomers are not predictable. Quantitative calculations provide the best guide for the experimentalist who wishes to investigate a new system.

The "hyperstable" olefins, which we have examined calculationally, deserve experimental investigation. Such olefins are stabilized rather than destabilized because of their location at a bridgehead and should be thermodynamically more stable than any of their positional isomers. Hyperstable olefins should be remarkably unreactive.

Highly strained trisubstituted bridgehead olefins offer an as yet unexplored opportunity for stabilization: replacement of the vinyl hydrogen by bulky groups or substituents which provide electronic stabilization might result in observable species. We are examining such systems both experimentally and calculationally. Of course, our OS generalizations for trisubstituted olefins are not directly applicable to such tetrasubstituted analogs.

It is of interest to recalculate the systems reported in this paper by using new and more accurate empirical force fields. This will be facilitated greatly by the results reported here. Since the minimum energy conformations we have located, often with considerable effort, are not expected to be force field dependent, new calculations need to be carried out only on the most stable conformer (or conformers, where more than one form is competitive in energy) of each system. Coordinates of all conformers we have examined are available as supplementary material to this paper.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and by the Deutsche Forschungsgemeinschaft. We thank Dr. J. Chandrasekhar and Professor Maitland Jones for stimulating discussions.

Supplementary Material Available: Tables of the coordinates for all conformers (90 pages). Ordering information is given on any current masthead page.

Tunneling in the Unimolecular Decomposition of Formaldehyde: A More Quantitative Study

Stephen K. Gray, William H. Miller, Yukio Yamaguchi, and Henry F. Schaefer, III

Contribution from the Department of Chemistry and Materials and Molecular Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, and Department of Chemistry and Institute for Theoretical Chemistry, University of Texas, Austin, Texas 78712. Received August 14, 1980

Abstract: Large scale ab initio configuration interaction calculations have been carried out for the reaction path of the unimolecular decomposition of formaldehyde, $H_2CO \rightarrow H_2 + CO$, on its ground-state potential-energy surface. Force constant matrices have also been calculated along the reaction path, making possible a reasonably quantitative treatment of the tunneling dynamics of the reaction within the recently developed reaction path Hamiltonian model. In the energy region of the origin of the $S_0 \rightarrow S_1$ absorption of formaldehyde, the unimolecular decomposition in $S_0$ is entirely by tunneling, with an average rate at this energy of $\sim 6 \times 10^9$ s$^{-1}$.

I. Introduction

The photodissociation of formaldehyde has in recent years assumed the role of a "case study," both experimentally and theoretically, in the reaction dynamics of small polyatomic molecules. Restricting attention to the collisionless limit of the process, a simplified version of the current picture is that after formaldehyde is excited electronically from its ground electronic

(1) For example, the recent U.S.-CECAM discussion meeting "Photodissociation of Polyatomic Molecules", Dec 3-4, Veldhoven, Holland, was restricted to the formaldehyde problem.


Unimolecular Decomposition of Formaldehyde

Unimolecular Decomposition of Formaldehyde

state \( (S_0) \) to a single ro-vibrational state of the first excited singlet state \( (S_1) \) (eq 1), it decays either by reemitting the photon (i.e., \( \text{H}_2\text{CO}(S_0) + h\nu \rightarrow \text{H}_2\text{CO}(S_1) \))

fluorescence)

\[
\text{H}_2\text{CO}(S_1) \rightarrow \text{H}_2\text{CO}(S_0) + h\nu
\]

(2)

or by undergoing a radiationless transition to a highly vibrationally excited state of \( S_0 \)

\[
\text{H}_2\text{CO}(S_1) \rightarrow \text{H}_2\text{CO}^*(S_0)
\]

(3a)

which then decomposes unimolecularly to molecular products.

\[
\text{H}_2\text{CO}^*(S_0) \rightarrow \text{H}_2 + \text{CO}
\]

(3b)

Whether \( S_1 \) decays via eq 2 or 3 depends primarily on the near coincidence of the energy of the particular ro-vibrational state of \( S_1 \) which is excited with that of one of the highly vibrationally excited states of \( S_0 \). (This picture applies for laser energies \( h\nu \) not too much above the origin of the \( S_0 \rightarrow S_1 \) excitation; at higher energies radical products, \( \text{H} + \text{HCO} \), become energetically possible and are seen.)

One of the particularly interesting aspects of this picture is that it appears that unimolecular decomposition in \( S_0 \), reaction 3b, occurs at energies considerably \((\approx 5-10 \text{kcal/mol})\) below the most accurate \( \text{ab initio} \) calculations\(^\text{(11)}\)\(^\text{17}\) of the activation barrier for the reaction; i.e., if one believes the \( \text{ab initio} \) calculations, one must assume that reaction 3b takes place entirely by tunneling. Though this is at first surprising—for tunneling effects are rarely thought to play such a prominent role in kinetics—earlier calculations\(^\text{(11)}\) by one of us, on the basis of the \( \text{ab initio} \) potential surface parameters of Goddard and Schaefer\(^\text{(11)}\) and a simple extension of the RRKM model\(^\text{(10)}\) to incorporate tunneling, suggested that tunneling could indeed provide unimolecular decay rates fast enough to be consistent with the above picture (i.e., rates at least 10 times faster than the radiative decay rate of \( \approx 2 \times 10^{10} \text{ s}^{-1} \)).

The purpose of this paper is to report considerably more quantitative calculations of the unimolecular rate constant for reaction 3b on the basis of (1) the more accurate \( \text{ab initio} \) calculations of Goddard, Yamaguchi, and Schaefer\(^\text{(11)}\) for the ground-state potential-energy surface and (2) a more dynamically rigorous treatment of tunneling that is possible within the reaction path Hamiltonian model developed by Miller, Handy, and Adams.\(^\text{(19)}\) In order to apply this reaction path approach, it is necessary to have the potential energy along the reaction path,\(^\text{(20)}\) the steepest descent path (if mass-weighted Cartesian coordinates are used) down from the transition state of reaction 3b to reactants and products, and also the harmonic force constants along the reaction path. These quantities have been calculated and are also reported herein. It is also of interest to see how sensitive the rate constant is to various levels of accuracy of the potential surface calculations.

Section II first summarizes the pertinent properties of the

Table I. Harmonic Vibrational Frequencies\(^a\) of \( \text{H}_2\text{CO} \)

<table>
<thead>
<tr>
<th>( \omega_i )</th>
<th>( \omega_i )</th>
<th>( \omega_i )</th>
<th>( \omega_i )</th>
<th>( \omega_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{DZP-CI} )</td>
<td>( \text{DZP-CI} )</td>
<td>( \text{DZP-CI} )</td>
<td>( \text{DZP-CI} )</td>
<td>( \text{DZP-CI} )</td>
</tr>
<tr>
<td>( \omega_i(\text{expt}) )</td>
<td>( \omega_i(\text{expt}) )</td>
<td>( \omega_i(\text{expt}) )</td>
<td>( \omega_i(\text{expt}) )</td>
<td>( \omega_i(\text{expt}) )</td>
</tr>
<tr>
<td>3223</td>
<td>3149</td>
<td>3028</td>
<td>3074</td>
<td>2944</td>
</tr>
<tr>
<td>1878</td>
<td>2006</td>
<td>1703</td>
<td>1869</td>
<td>1764</td>
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<td>1651</td>
<td>1656</td>
<td>1544</td>
<td>1596</td>
<td>1563</td>
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<td>1194</td>
<td>1243</td>
<td>1191</td>
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<td>3315</td>
<td>3226</td>
<td>3112</td>
<td>3155</td>
<td>3009</td>
</tr>
<tr>
<td>1349</td>
<td>1367</td>
<td>1263</td>
<td>1306</td>
<td>1287</td>
</tr>
</tbody>
</table>
Table I. Frequency Variation along Reaction Path

<table>
<thead>
<tr>
<th>s, amu$^{-1/2}$ Å</th>
<th>ω1</th>
<th>ω2</th>
<th>ω3</th>
<th>ω4</th>
<th>ω5</th>
<th>ω6</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.21</td>
<td>3517</td>
<td>1932</td>
<td>1594</td>
<td>955</td>
<td>-950</td>
<td>-950</td>
</tr>
<tr>
<td>0</td>
<td>3263</td>
<td>1939</td>
<td>1555</td>
<td>876</td>
<td>-950</td>
<td>-950</td>
</tr>
<tr>
<td>+0.21</td>
<td>2642</td>
<td>1981</td>
<td>1648</td>
<td>738</td>
<td>-950</td>
<td>-950</td>
</tr>
</tbody>
</table>

*The out-of-plane bending frequency.*

The scaled barrier height $V_0$ in Table II is the best estimate of Goddard et al. The new ab initio potential surface information reported in this paper has to do with the reaction path and its properties. Calculations were carried out at the most accurate (DZP-CI) ab initio level on the potential surface, i.e., the transition state, and following the scaled barrier height as the ab initio values. The Eckart potential, which was used, is seen to provide an excellent fit to the shape of the ab initio potential along the reaction path.

The reaction path is determined by starting at the saddle point on the potential surface, i.e., the transition state, and following the steepest descent path (if mass-weighted Cartesian coordinates were used) down to reactants and to products. Calculations of this type have recently been carried out by us for the unimolecular isomerization of hydrogen isocyanide, HNC → HCN, and related calculations have been reported by Morokuma and co-workers, although not at the level of accuracy of the present results. The specific calculations are the essentially the same as before. Because the barrier is so high in this case and the steepest descent path thus so steep, there is need to use the methods of Ishida, Morokuma, and Komornicki to stabilize the reaction path calculation.

Figure 1 shows the potential-energy profile along the reaction path in the vicinity of the saddle point, as given by the DZP-CI gradient calculation; it has been determined beforehand that for the tunneling calculations one only needs to consider the region on either side of the saddle point to where the potential has fallen to ~8 kcal/mol below its value at the saddle point. The points in Figure 1 are the ab initio values, and the solid curve is an Eckart potential function chosen to have the same curvature and barrier height as the ab initio values. The Eckart potential, which was used in the earlier tunneling calculations, is seen to provide an excellent fit to the shape of the ab initio potential along the reaction path.

Ab initio force constant matrices are calculated at the DZP-CI level at values of mass-weighted cartesian coordinate $s = \pm 0.21$ amu$^{-1/2}$ Å; these are points at which $V_0(s)$ has fallen to ~8 kcal/mol below its value at the saddle point. Frequencies for vibration normal to the reaction path were obtained by diagonalizing the projected force constant matrix, and these values are given in Table III, along with the values at the saddle point $s = 0$. Due to the additional computational effort involved, out-of-plane calculations were not carried out at these two points along the reaction path, so that the out-of-plane bending frequency $\omega_5$ was not determined at these points away from the saddle point. Since it is one of the lower frequencies, however, one does not expect its variation with $s$ to have a significant effect on the rate constant.

The reaction path Hamiltonian involves coupling elements $B_{k,k'}(s)$ which cause energy transfer between motion along the reaction coordinate and the various transverse vibrational modes and between one vibrational mode and another. These coupling elements are defined by eq 5, where $L_{ik}(s)$ is the $i$th Cartesian component of the $k$th eigenvector of the projected force constant matrix, as a function of $s$. In practice the force constant matrix (and thus its eigenvectors) is determined at discrete values of the reaction coordinate $s_i$, and the coupling elements are obtained via a finite difference approximation

\[ B_{k,k'}(s) \approx \frac{1}{2}(s_j + s_{j+1}) - \frac{1}{2}(s_j - s_{j+1}) \]

or in the explicitly antisymmetric form

\[ B_{k,k'}(s) \approx \frac{1}{2}(s_j + s_{j+1}) - \frac{1}{2}(s_j - s_{j+1}) \]

Because initial estimates of the coupling elements indicated their effect on the tunneling rate constant to be small (cf. the results in Section III B), a highly accurate determination of them was not necessary for present purposes. The finite difference approximation (eq 6) was thus used with the three values of $s$ = -0.21, 0, +0.21 amu$^{-1/2}$ Å, and estimates are that this gives an accuracy of \( \pm 0.003m_{1/2}^{-1} \) in the coupling elements. Within this uncertainty the largest coupling elements were found to be $B_{1,3} = 0.010$, $B_{5,4} = 0.015$, $B_{1,4} = 0.005$, and $B_{1,5} = -0.009 m_{1/2}^{-1}$, where the mode $k = F$ denotes the reaction coordinate. Modes 1 and 3 are both C–H stretches, so it is not unexpected that they are coupled relatively strongly with each other and to the reaction coordinate (which is itself mostly C–H motion).

III. Unimolecular Rate Constants

A. Simple RRKM Plus Tunneling Model. We first present, in Table IV, the results of the simple "RRKM plus tunneling" model used earlier, but with the ab initio potential surface parameters in Tables I and II. For a given total energy $E$ the...
Table V. Effect on Rate of More Rigorous Dynamical Model

<table>
<thead>
<tr>
<th>$E - V_o$, kcal/mol</th>
<th>$\log k$, s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>$-2$</td>
<td>2.99</td>
</tr>
<tr>
<td>$0$</td>
<td>3.92</td>
</tr>
<tr>
<td>$2$</td>
<td>4.83</td>
</tr>
<tr>
<td>$4$</td>
<td>5.74</td>
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<td>$6$</td>
<td>6.63</td>
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<tr>
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<td>8.36</td>
</tr>
<tr>
<td>$12$</td>
<td>9.05</td>
</tr>
</tbody>
</table>

See text for a description of the theoretical models corresponding to columns A–E.

rate of reaction 3b is extremely sensitive to the barrier height $V_o$, especially for the lower energies that are below the classical threshold. To remove this sensitivity in comparing the rate constants given by the various ab initio models, the results in Table IV are compared as a function of $E - V_o$, although $V_o$ is itself different (cf. Table II) for the five different columns in Table IV. The rate constants under the DZ-SCF column in Table IV, for example, result from using the DZ–SCF frequencies for H$_2$CO and the transition state as given in Tables I and II, respectively; the fifth column in Table IV (scaled), which uses the experimental H$_2$CO frequencies and the scaled transition state frequencies, is thus the best estimate of the rate given by this model.

The main conclusion that can be drawn from the comparisons in Table IV is the unimolecular rate constant is relatively insensitive to the uncertainty in frequencies given by the various levels of ab initio calculation; e.g., for the energy region for which the rate constant is $\sim 10^5$ s$^{-1}$ or larger, there is less than a factor 3 difference between the rate constant given by the various sets of frequencies. For a given set of frequencies the rate constant changes by about the same amount with a change of only 1 kcal/mol in $V_o$ (for fixed $E$), and one sees in Table II that the variation in $V_o$ given by the various ab initio calculations is much greater than this.

Within this microcanonical transition state (i.e., RRKM) model, the most important single parameter needed to determine the unimolecular rate constant for a given total energy $E$ is the barrier height. Unfortunately, this is also the most difficult quantity to calculate accurately.

B. More Rigorous Dynamical Treatment of Tunneling. With the information about the reaction path, the variation of the frequencies along it, and the coupling elements of the reaction path Hamiltonian, it is possible to treat the tunneling dynamics more rigorously than via the simple model in Section IIIA. These dynamical models have been developed and applied before in our treatment$^{25}$ of the HNC → HCN isomerization, and the appropriate formulas are given there.

Table V compares the rate constants given by various levels of approximation to the tunneling dynamics, all with the DZP–CI ab initio potential surface. Column A is the simple RRKM plus tunneling model of the previous section (Eckart barrier, constant transition-state frequencies, and no coupling), i.e., the DZP–CI column of Table IV; column B is the same as A with the Eckart potential replaced by the ab initio potential $V_0(x)$ and with the WKBJ approximation for the tunneling probability; column C is the same as B but allowing for variation of the frequencies along the reaction path (this is the "vibrationally adiabatic zero-curvature" approximation);$^{27,14}$ column D includes the effect of coupling between the vibrational modes, with the coupling elements obtained from the ab initio reaction path calculation as described in Section II; column E is the same model as D but with the coupling elements multiplied by 2, to see the effect of this larger amount of coupling on the rate constant. (For columns C, D, and E the frequency variation was treated by quadratic interpolation from the values in Table III, and the coupling constants were taken as constant over the region.)

One sees in Table V how relatively insensitive the rate constant is to the level of rigor used to describe the tunneling dynamics, i.e., the simplest model, column A, differs from the most rigorous and presumably most accurate one, column D, by less than 20% at energies for which the rate is larger than $10^5$ s$^{-1}$. We recall that a similar insensitivity to nonseparable coupling effects was seen$^{22}$ for the rate of HNC → HCN isomerization, but one must be cautious in concluding that this will always be the case. For the well studied H + H$_2$ → H$_2$ + H reaction, for example, these coupling effects change the rate by 1–2 orders of magnitude in the tunneling region.$^{15,27}$ For the present system, however, it appears that the very simplest treatment of tunneling is reasonably accurate.

C. Best Estimates. We summarize here our best estimates of the microcanonical rate of reaction 3b at the energy of the origin of the $S_0 = S_1$ excitation, $h\nu = 80.6$ kcal/mol. The zero-point energy of ground-state H$_2$CO is 16.8 kcal/mol (using the experimental harmonic frequencies rather than the transition frequencies), so that the total energy $E = 97.4$ kcal/mol. The best theoretical estimate for $V_o$ is that in the last column of Table II, 92 kcal/mol, so that $E - V_o = 5.4$ kcal/mol; interpolation from the last column of Table IV then gives

$$k = 5.9 \times 10^5 \text{s}^{-1}$$

which includes a factor of 2 due to the 2-fold rotational symmetry of H$_2$CO that has heretofore been omitted. (Note that since the zero-point energy of the "scaled" transition state is 11.8 kcal/mol, this energy $E$ is $\sim 6.4$ kcal/mol below the classical threshold of the reaction.)

Were the barrier height $V_0$ exactly correct, we would expect the above value to be correct to ~20%, but a change of 1 kcal/mol in $V_o$ will change the rate by a factor of ~2.75 in this energy region. It is thus probably not realistic to claim the above value to be closer than a factor of 2 to the "true" microcanonical rate. It is amusing to note that although the various potential parameters used in this paper differ in some significant ways from those used in the earlier$^{13}$ estimate of the tunneling rate, the value given above is in fortuitously good agreement with the value $5.8 \times 10^5$ s$^{-1}$ estimated before.

The above rate is for total angular momentum $J = 0$. Unimolecular decay rates for nonzero values of $J$ can be computed as before.$^{13}$

IV. Conclusion

Unimolecular decomposition of formaldehyde thus appears to be one of the fortunate reactions for which the simplest treatment of the tunneling dynamics is accurate to ~20% or so, which is probably less than the error caused by uncertainty of the precise values of the transition-state frequencies. In the tunneling region, however, the rate is extremely sensitive to the barrier height—e.g., a change in it of 1 kcal/mol changes the rate by a factor of ~2–3—so that an accurate calculation of the rate at a given energy $E$ requires its precise determination. The recent ab initio calculations$^{27,14}$ are of sufficient accuracy that the rate given by eq 7 is believed to be accurate to a factor of 2. Since the rates in Tables IV and V are given as a function of energy relative to the barrier height, however, and should be accurate as such to ~20–30%, they can be used to determine more accurate values of the rate when more precise values of the barrier height become available.

These calculations give considerably more confidence to the earlier suggestion that tunneling can yield rates for reaction 3b that are fast enough to be consistent with the picture of formaldehyde photodissociation described in the introduction. Perhaps the most interesting question now is that of mode specificity; i.e., do all vibrational states of H$_2$CO ($S_0$) with essentially the same total energy $E$ dissociate unimolecularly at the average rate $k(E)$ or do some react faster and some slower. This is a question of whether or not the intramolecular vibrational energy of H$_2$CO ($S_0$) randomizes before unimolecular reaction occurs, and to answer it requires a more detailed theoretical model of the intramolecular vibrational dynamics of H$_2$CO on its ground-state.
potential-energy surface. Such treatments of simpler systems have been carried out, 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.

Vinylidene: A Very Shallow Minimum on the C2H2 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-$
+ \text{p}$ plus polarization basis set was used in conjunction with configuration interaction (CI) including single and double excitations, a total of 13 661 configurations. 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-$
+ \text{p}$ 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 $\sim 10^{-15}$ s, and with 2 kcal of excitation energy this decreases to $\sim 10^{-17}$ s. These predictions appear to be consistent with the experimental findings of Skell (1972) and Steinfeld (1980).

As the simplest unsaturated carbene, vinylidene (the $\text{H}_2\text{C}≡\text{C}$ molecule) plays a special role in the organic chemistry of reactive intermediates. As such there have been a number of theoretical studies of vinylidene. From the experimental perspective, the key question is whether vinylidene in fact exists as a discrete chemical entity. It is certainly established that in the circumstances under which the $\text{H}_2\text{C}≡\text{C}$ hydrogen shift has been observed (eq 1), it is rapid. To be more blunt, reaction 1 is so fast that

$$
\text{H}_2\text{C}≡\text{C} \rightarrow \text{HC}≡\text{CH}
$$

(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 $\text{C}_2\text{H}_2$ potential energy surface. The singular laboratory evidence for the existence of $\text{H}_2\text{CC}$ comes from Skell’s trapping experiments, which suggest a lifetime of $\sim 10^{-10}$ s.

The only reliable theoretical study to date of the singlet vinylidene rearrangement (1) yielded a barrier height of 8.6 kcal. However recent experiments by Steinfeld and co-workers 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 showed that the reaction proceeds mainly via a three-center elimination, suggesting that $\text{H}_2\text{C}≡\text{C}$ 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. 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

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