

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

S no.	bicyclic system ^b	bridge length where double bond is located				
		1	2	3	4	5
3	111	21.0				
4	211	33.2	25.0			
5	221	38.5	34.9			
	311	39.1		28.9		
6	222		40.4			
	321	36.7	27.2	28.6		
	411	37.8			35.0	
7	322		20.6	19.5		
	331	48.2		15.2		
	421	21.6	9.1		14.1	
	511	14.5				17.5
8	332		18.9	4.7		
	422		7.9		8.2	
	431	22.0		3.0	2.5	
9	333			3.9		
	432		1.4	-7.2	-5.4	
	441	22.3			-1.5	
10	442		5.0		-13.0	
11	444				-14.1	

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

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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

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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 $\sim 6 \times 10^6 s^{-1}$.

I. Introduction

The photodissociation of formaldehyde has in recent years assumed the role of a "case study",¹ both experimentally²⁻⁸ and theoretically,⁹⁻¹⁷ 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

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(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.

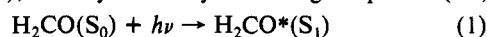
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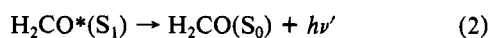
(4) J. R. Sodeau and E. K. C. Lee, *Chem. Phys. Lett.*, **57**, 71 (1978).

(5) H. L. Selzle and E. W. Schlag, *Chem. Phys.*, **43**, 111 (1979).

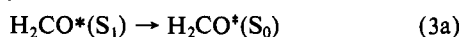
state (S_0) to a single ro-vibrational state of the first excited singlet state (S_1) (eq 1), it decays either by reemitting the photon (i.e.,



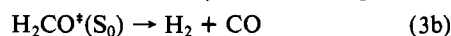
fluorescence)



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



which then decomposes unimolecularly to molecular products.



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 vibrational 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.^{6b})

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 (~ 5 – 10 kcal/mol) below the most accurate ab initio calculation^{12,17} of the activation barrier for the reaction; i.e., if one believes the 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 calculations¹³ by one of us, on the basis of ab initio potential surface parameters of Goddard and Schaefer¹² and a simple extension of the RRKM model¹⁸ 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 $\sim 2 \times 10^5 \text{ s}^{-1}$).

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 ab initio calculations of Goddard, Yamaguchi, and Schaefer¹⁷ 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.¹⁹ In order to apply this reaction path approach, it is necessary to have the potential energy along the reaction path,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

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Table I. Harmonic Vibrational Frequencies^a of H_2CO

	DZ-SCF ^b	DZP-SCF	DZ-CI	DZP-CI	exptl
$\omega_1(a_1)$	3223	3149	3028	3074	2944
$\omega_2(a_1)$	1878	2006	1703	1869	1764
$\omega_3(a_1)$	1651	1656	1544	1596	1563
$\omega_4(b_1)$	1324	1335	1194	1243	1191
$\omega_5(b_2)$	3315	3226	3112	3155	3009
$\omega_6(b_2)$	1349	1367	1263	1306	1287

^a Units for frequencies are cm^{-1} . ^b Various column headings refer to the various ab initio basis sets and extent of configuration interaction included in the calculations. ^c The experimental harmonic frequencies given in ref 21.

Table II. Transition-State Parameters^{a, b} for $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$

	DZ-SCF	DZP-SCF	DZ-CI	DZP-CI	scaled ^c
$\omega_1(a')$	3156	3243	3159	3263	3125
$\omega_2(a')$	1948	2092	1764	1939	1830
$\omega_3(a')$	1371	1526	1310	1555	1523
$\omega_4(a')$	800	829	803	876	839
$\omega_5(a')$	2320i	2305i	1997i	2124i	2026i
$\omega_6(a')$	1015	1024	889	~ 950	936
V_0 , kcal mol ^{-1 d}	113.7	105.9	100.3	98.1	92 ^e

^a Same as footnote a, Table I. ^b Same as footnote b, Table I.

^c Scaled frequencies, as defined by eq 4. ^d Barrier height relative to vibrationless H_2CO . ^e The best estimates of Goodard et al. (ref 17) of the classical barrier, with a probable error of ± 1 kcal/mol.

ground-state potential-energy surface of formaldehyde from the ab initio calculations, including the reaction path information. The rate constants obtained at various levels of accuracy for the potential surface are given in section III, along with our best estimates of the "true" rate constant for reaction 3b.

Finally, one should bear in mind that the rate constants which are calculated and reported in this paper are the *microcanonical* rate constants for reaction 3b, i.e., the average rate constant for a given total energy E . This does not in any way preclude the possibility that some vibrationally excited states of S_0 with this energy may react faster than this average rate and others with essentially the same energy react slower. To address this question of mode specificity, however, requires a more detailed dynamical treatment of the intramolecular vibrational dynamics of formaldehyde on its ground-state potential-energy surface.

II. Transition State and Reaction Path Properties

Tables I and II give the harmonic vibrational frequencies of stable formaldehyde and the harmonic vibrational frequencies and barrier height of the transition state of reaction 3b, respectively, obtained from ab initio calculations¹⁷ at various levels of sophistication. DZ and DZP refer to the size of the basis set used, "double zeta" and "double zeta plus polarization", respectively, and SCF and CI refer to the one-configuration self-consistent-field approximation and a large-scale configuration interaction (all single and double excitations), respectively. The "experimental" frequencies in Table I are the harmonic frequencies inferred from experiment²¹ (not the experimental transition frequencies used in ref 13), and the "scaled" frequencies of the transition state in Table II are the following empirical modification of the best ab initio values (DZP-CI)

$$(\omega_i^{\text{scaled}})_{\text{TS}} = (\omega_i^{\text{DZP-CI}})_{\text{TS}} \left(\frac{\omega_i^{\text{exptl}}}{\omega_i^{\text{DZP-CI}}} \right)_{\text{H}_2\text{CO}} \quad (4)$$

TS = transition state, H_2CO = stable formaldehyde

to provide a "best guess" at the true transition-state frequencies. The idea is that residual errors in the DZP-CI results should be similar in H_2CO and the transition state on a mode-for-mode basis.

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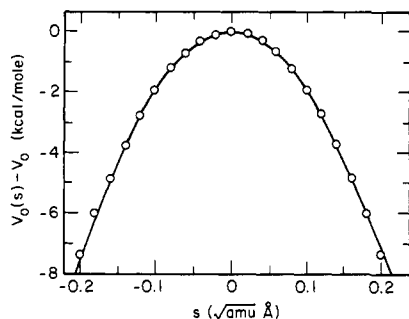


Figure 1. Potential energy along the reaction path, as a function of mass-weighted reaction coordinate. Points are the ab initio (DZP-CI) results and the solid curve an Eckart potential function fit to the ab initio curvature at $s = 0$.

Table III. Frequency Variation along Reaction Path

	$s, \text{amu}^{1/2} \text{Å}$		
	-0.21	0	+0.21
ω_1	3517	3263	2642
ω_2	1932	1939	1981
ω_3	1594	1555	1648
ω_4	953	876	738
ω_6^a	(~950)	~950	(~950)

^a The out-of-plane bending frequency.

The scaled barrier height V_0 in Table II is the best estimate of Goddard et al.¹⁷

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 by using recently developed analytic CI gradient methods.²² Second derivatives of the electronic energy, necessary to determine the force constants along the reaction path, were evaluated by finite difference of the first derivatives (i.e., gradients).

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 out²³ by us for the unimolecular isomerization of hydrogen isocyanide, $\text{HNC} \rightarrow \text{HCN}$, and related calculations have been reported by Morokuma²⁴ and co-workers, although not at the level of accuracy of the present results. The specifics of the calculations are essentially the same as before.²³ Because the barrier is so high in this case and the steepest descent path thus so steep, there is no need to use the methods of Ishida, Morokuma, and Komornicki²⁵ 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 function²⁶ 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,¹³ is seen to provide an excellent fit to the shape of the ab initio potential along the reaction path.

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Table IV. Rate Constants via Simple RRKM + Tunneling Model

$E - V_0$, kcal/mol	$\log k, \text{s}^{-1}$				
	DZ- SCF	DZP- SCF	DZ-CI	DZP-CI	scaled
-2	3.57	3.41	2.91	2.99	2.95
0	4.41	4.26	3.90	3.92	3.92
2	5.24	5.10	4.87	4.83	4.88
4	6.06	5.93	5.83	5.74	5.81
6	6.88	6.76	6.77	6.63	6.75
8	7.68	7.57	7.71	7.51	7.67
10	8.43	8.34	8.57	8.36	8.55
12	9.02	9.00	9.17	9.05	9.21

Ab initio force constant matrices are calculated at the DZP-CI level at values of mass-weighted cartesian coordinate $s = \pm 0.21 \text{amu}^{1/2} \text{Å}$; 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,¹⁹ 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 ω_6 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 Hamiltonian¹⁹ 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 $L_{i,k}(s)$ is the i th Cartesian

$$B_{k,k'}(s) = \sum_{i=1}^{3N} \frac{\partial L_{i,k}(s)}{\partial s} L_{i,k'}(s) \quad (5)$$

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 $\{s_j\}$, and the coupling elements are obtained via a finite difference approximation

$$B_{k,k'}\left(\frac{s_j + s_{j-1}}{2}\right) \approx \frac{\sum_{i=1}^{3N} L_{i,k}(s_j)L_{i,k'}(s_{j-1}) - \delta_{k,k'}}{s_j - s_{j-1}} \quad (6a)$$

or in the explicitly antisymmetric form

$$B_{k,k'}\left(\frac{s_j + s_{j-1}}{2}\right) \approx \frac{\sum_{i=1}^{3N} [L_{i,k}(s_j)L_{i,k'}(s_{j-1}) - L_{i,k}(s_{j-1})L_{i,k'}(s_j)]}{2(s_j - s_{j-1})} \quad (6b)$$

Because initial estimates of the coupling elements indicated their effect on the tunneling rate constant to be small (cf. the results in Section IIIB), 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 $s = -0.21, 0, +0.21 \text{amu}^{1/2} \text{Å}$, and estimates are that this gives an accuracy of $\sim \pm 0.003 m_e^{-1/2} a_0^{-1}$ in the coupling elements. Within this uncertainty the largest coupling elements were found to be $B_{1,3} = 0.010$, $B_{3,4} = 0.015$, $B_{1,F} = 0.005$, and $B_{3,F} = -0.009 m_e^{-1/2} a_0^{-1}$, 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,¹³ 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

$E - V_0$, kcal/mol	$\log k, \text{s}^{-1}{}^a$				
	A	B	C	D	E
-2	2.99	3.14	3.17	3.14	2.98
0	3.92	4.00	4.03	4.00	3.86
2	4.83	4.86	4.89	4.86	4.74
4	5.74	5.72	5.75	5.72	5.62
6	6.63	6.58	6.61	6.58	6.50
8	7.51	7.50	7.52	7.49	7.41
10	8.36	8.34	8.35	8.33	8.25
12	9.05	9.04	9.04	9.02	8.97

^a 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_0 , 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 $E - V_0$, although V_0 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_2CO and the transition state as given in Tables I and II, respectively; the fifth column in Table IV (scaled), which uses the experimental H_2CO frequencies and the scaled transition state frequencies, is thus the best estimate of the rate given by this model.

The main conclusion to 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 $\sim 10^5 \text{ s}^{-1}$ 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_0 (for fixed E), and one sees in Table II that the variation in V_0 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 thus 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 treatment²³ of the $\text{HNC} \rightarrow \text{HCN}$ 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 $V_0(s)$ and with the WKB 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);^{27,19} 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 seen²³ for the rate of $\text{HNC} \rightarrow \text{HCN}$ isomerization, but one must be cautious in concluding that this will always be the case. For the well studied $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ reaction, for example, these coupling effects change the rate by 1-2 orders of magnitude in the tunneling region.^{19,27} 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 $S_0 \rightarrow S_1$ excitation, $h\nu = 80.6 \text{ kcal/mol}$. The zero-point energy of ground-state H_2CO is 16.8 kcal/mol (using the experimental harmonic frequencies rather than the transition frequencies), so that the total energy $E = 97.4 \text{ kcal/mol}$. The best theoretical estimate for V_0 is that in the last column of Table II, 92 kcal/mol, so that $E - V_0 = 5.4 \text{ kcal/mol}$; interpolation from the last column of Table IV then gives

$$k = 5.9 \times 10^6 \text{ s}^{-1} \quad (7)$$

which includes a factor of 2 due to the 2-fold rotational symmetry of H_2CO 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 $\sim 6.4 \text{ kcal/mol}$ 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 $\sim 20\%$, but a change of 1 kcal/mol in V_0 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 earlier¹³ estimate of the tunneling rate, the value given above is in fortuitously good agreement with the value $5.8 \times 10^6 \text{ s}^{-1}$ 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 $\sim 20\%$ 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 $\sim 2-3$ —so that an accurate calculation of the rate at a given energy E requires its precise determination. The recent ab initio calculations¹⁷ 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 $\sim 20-30\%$, 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_2CO (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_2CO (S_0) randomizes before unimolecular reaction occurs, and to answer it requires a more detailed theoretical model of the intramolecular vibrational dynamics of H_2CO on its ground-state

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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.

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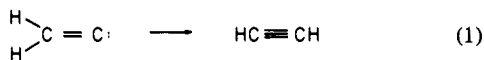
Vinylidene: A Very Shallow Minimum on the C₂H₂ Potential Energy Surface. Static and Dynamical Considerations

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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 H₂C=C: molecule) plays a special role in the organic chemistry of reactive intermediates. As such there have been a number of theoretical studies³⁻¹² of vinylidene. From the experimental perspective, the key question is whether vinylidene in fact exists as a discrete chemical entity. It is certainly established¹³⁻¹⁷ 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



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 C₂H₂ potential energy surface. The singular laboratory evidence for the existence of H₂CC: 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 CO₂ laser pulses leads to elimination of HCl. Deuterium-labeling studies¹⁶ showed that the reaction proceeds mainly via a three-center elimination, suggesting that H₂C=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

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