

# Ab Initio Calculation on the Photochemistry of Formaldehyde. The Search for a Hydroxycarbene Intermediate

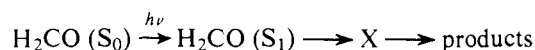
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**Abstract:** Ab initio calculations on the H<sub>2</sub>CO-HCOH rearrangement have been performed. The electronic coupling between the S<sub>1</sub> and S<sub>0</sub> surfaces, which can induce internal conversion, is calculated for this rearrangement and for the reaction coordinates leading directly to radical and molecular products. The coupling is calculated with true adiabatic Born-Oppenheimer functions, i.e., the wave functions and coupling integrals are explicitly calculated as functions of the nuclear geometry. The coupling for the hydroxycarbene rearrangement turns out to be the largest one. This indicates that the hydroxycarbene can serve as an intermediate state in the formaldehyde photochemistry. We also report calculations on the bimolecular H<sub>2</sub>CO-HCOH rearrangement; this interaction gives rise to a decrease of the energy barrier involved.

## I. Introduction

During the last decade there has been a growing interest in the photochemistry of the formaldehyde molecule. The experimental work<sup>2-5</sup> clearly shows the increasing power of the techniques available today. One of the most striking experimental results was obtained by Houston and Moore.<sup>5</sup> They found, under collisionless conditions, a time lag of at least 4 μs between the decay of the formaldehyde S<sub>1</sub> state and the appearance of the CO photoproduct. They could not even exclude that, under collisionless conditions, no photodissociation occurs at all. In view of this point it is interesting to note that Yeung and Moore<sup>4</sup> found that the total rate at which collisions remove molecules from single vibronic levels of H<sub>2</sub>CO is as much as ten times the hard sphere collision rate, thus indicating some long-range interaction between the excited molecule and its neighbors. The conclusion from their work is that some intermediate is involved in the photodissociation of formaldehyde, out of which the molecular and radical products are formed:

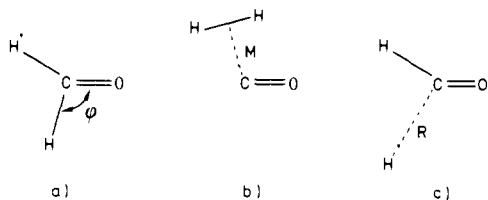


One of the main tasks of formaldehyde photochemistry is now to unravel the nature of this intermediate state X. For this state several possibilities exist: in the first place, internal conversion to an isoenergetic vibrational state, S<sub>0</sub><sup>\*</sup>, of the electronic ground state. This S<sub>0</sub><sup>\*</sup> state should then, under collisionless conditions, have a lifetime of at least 4 μs, after which dissociation to the photoproducts takes place. Recently we showed, however, by means of an accurate ab initio calculation,<sup>6-8</sup> that the coupling in the equilibrium state is too small to induce internal conversion. The second candidate is intersystem crossing to T<sub>1</sub><sup>\*</sup>. Apart from the experimental findings of Tang et al.,<sup>9</sup> which showed that the triplet state plays a negligible mechanistic role in the photochemistry of the 2<sup>2</sup>4<sup>1</sup> (S<sub>1</sub>) level, it is not clear at all, from a theoretical point of view, how the T<sub>1</sub> state, which lies only 3000 cm<sup>-1</sup> below S<sub>1</sub>, can give a level density for this four-atomic molecule that is high enough to give an exponential decay. There exists, however, a third possibility for the intermediate state: the hydroxycarbene HCOH. The first question that arises concerning this candidate involves the energies of the different HCOH configurations (S<sub>0</sub>-trans, S<sub>0</sub>-cis, and T<sub>1</sub>-gauche) relative to the prepared H<sub>2</sub>CO (S<sub>1</sub>) state. Calculations by Pople's group<sup>10</sup> and Altmann et al.<sup>11</sup> place them below the H<sub>2</sub>CO (S<sub>1</sub>) state. These calculations were performed without configuration interaction, leading among others to a H<sub>2</sub>CO S<sub>0</sub>-T<sub>1</sub> energy gap much lower than the experimental one. This result questions of course the reliability

of the obtained values for the HCOH states, but very recently a large-scale CI calculation by Lucchese and Schaefer<sup>12</sup> showed that the results of Pople and Altmann are qualitatively correct and that the hydroxycarbene possibility is quite feasible. We also performed, as a continuation of our study of the decay of the H<sub>2</sub>CO (S<sub>1</sub>) state, ab initio SCF and SCF-CI calculations on the formaldehyde-hydroxycarbene rearrangement. The emphasis in this study, however, does not lie on calculating reliable values for the various HCOH states. Just as important as the knowledge of the energies of the local minima on the potential energy surface is the answer to the question how the molecule can reach these local minima. The most attractive candidate for the intermediate X is the HCOH (S<sub>0</sub>-trans) state, which lies, according to our results, about 20 kcal/mol below H<sub>2</sub>CO (S<sub>1</sub>). To reach this state, the H<sub>2</sub>CO (S<sub>1</sub>) molecule has to leave somewhere the S<sub>1</sub> potential energy surface. Although the coupling in the equilibrium state is too small to induce internal conversion, as stated above, this situation can, in principle, change further away on the reaction coordinate. So in section II we calculate the electronic coupling elements between the S<sub>1</sub> and S<sub>0</sub> surfaces as functions of three reaction coordinates: leading to hydroxycarbene, direct radical dissociation, and direct molecular dissociation, respectively. As we will see in section III, the energy barrier between the S<sub>0</sub><sup>\*</sup> state and the HCOH local minimum will be too high for a single molecule to reach this minimum. That is why we describe in section III calculations of an interaction between a pair of formaldehyde molecules in order to investigate the possibility of lowering this energy barrier. The way the molecules interact in the model described in section III is inspired by the H<sub>2</sub>CO-HCOH reaction pathway; in section IV we will briefly discuss other kinds of interactions.

## II. The Unimolecular Rearrangement H<sub>2</sub>CO-HCOH

**A. Computational Method.** The computational method is described in detail elsewhere;<sup>7</sup> we will here only repeat the main features. For the calculation of the electronic wave functions of formaldehyde at the different points of the reaction coordinates we used Clementi's IBMOL 5 program<sup>13</sup> with a contracted Gaussian basis set given by Dunning;<sup>14</sup> for carbon and oxygen a (9s5p) [4s3p] set; for hydrogen a (4s) [2s] set. Further, we used Goscinski's transition operator method<sup>15</sup> in order to describe the S<sub>0</sub> and S<sub>1</sub> surfaces with the same accuracy. For the configuration interaction we included 175 configurations selected by the point system of Morokuma and Konishi.<sup>16</sup> The electronic wave functions obtained are true adiabatic Born-Oppenheimer functions: they are explicitly calculated as



**Figure 1.** Reaction coordinates ( $\phi$ ,  $M$ , and  $R$ ) leading to (a) hydroxycarbene formation; (b) direct molecular dissociation; and (c) direct radical dissociation. In (b) the variable  $M$  denotes the distance from the carbon to the midpoint of the H-H bond.

functions of the nuclear geometry, contrary to the conventional "Herzberg-Teller"-like approach, where one tries to include the dependence on the nuclear geometry by means of an expansion around the equilibrium geometry, i.e., an expansion in crude Born-Oppenheimer functions. The geometries which were used as an input in the SCF-CI calculations were obtained from a completely optimized, single-configuration 4-31G calculation.<sup>17</sup> These optimizations were made for different values of the three reaction coordinates depicted in Figure 1: (a) leading to the hydroxycarbene, (b) leading directly to molecular products, and (c) leading directly to radical products. With the SCF-CI program we calculated both the  $S_0$  and  $S_1$  surfaces. With the single determinant Gaussian 70 program, however, no reliable  $S_1$  calculations can be made for formaldehyde: the  $S_1$  wave functions and geometries become unreliable because of spin contamination from functions of different multiplicity. Therefore we used for the  $S_1$  geometries the optimized  $T_1$  structures obtained from the Gaussian 70 program. The results of this procedure will be discussed in section IIB.

The probability for the radiationless transition from  $S_1$  to  $S_0$  is determined by the coupling between the  $S_1$  and  $S_0$  potential energy surfaces. This coupling is caused by the impulse operator  $P$  of the nuclei. The electronic coupling element is given by

$$C_{10}(Q) = \langle \phi_1(q, Q) | P/M | \phi_0(q, Q) \rangle_q P$$

Here,  $q$  and  $Q$  denote the complete sets of electron and nuclear coordinates, respectively;  $\phi_1$  and  $\phi_0$  are the electronic wave functions of excited and ground state;  $M$  denotes the set of nuclear masses, while the subscript  $q$  denotes integration over the electron coordinates. This integral can be rewritten<sup>7</sup> as a linear combination of integrals of the electric field operator:

$$C_{10}(Q) \sim \frac{\sum_n \sum_{j'} D_{jk}^n Z_n \langle \phi_1(q, Q) | \sum_e - (q_j^e - s_j^n) / r_{en}^3 | \phi_0(q, Q) \rangle_q}{\Phi_0(Q) - \Phi_1(Q)} P \quad (II.1)$$

Here,  $s_j^n$  and  $q_j^e$  are the  $j$ 'th Cartesian coordinate of nucleus  $n$  and electron  $e$ , respectively;  $Z_n$  stands for the charge of nucleus  $n$ ;  $D_{jk}^n$  is an element of the Jacobian matrix, which transforms the Cartesian coordinates to the normal coordinates  $k$ , while  $\Phi_0(Q)$  and  $\Phi_1(Q)$  represent the adiabatic potential energy surfaces. At this point the methods used here and the one used for the calculation of the "static"  $S_1$ - $S_0$  internal conversion<sup>7</sup> start to diverge. In the latter calculation the starting point was a formaldehyde molecule "resting" in some vibrational state,  $\chi_{1i}(Q)$ , of the local minimum corresponding to  $H_2CO$  ( $S_1$ ). In order to obtain the total coupling,  $v_{1i,0j}$ , between the prepared state and an element of the coupling  $S_0^*$  manifold, the electronic coupling element  $C_{10}(Q)$  has to be integrated over  $Q$ :

$$v_{1i,0j} = \langle \chi_{1i}(Q) | C_{10}(Q) | \chi_{0j}(Q) \rangle_Q \quad (II.2)$$

where  $\chi_{1i}(Q)$  and  $\chi_{0j}(Q)$  denote the (anharmonic) vibrational wave functions involved. For the static situation, these vibrational wave functions, corresponding to the normal vibrations, can be calculated from the potential energy surfaces  $\Phi_0(Q)$  and  $\Phi_1(Q)$ . For the dynamic situation, however, where the molecule does not just fluctuate around the equilibrium configuration, but instead wanders about on the potential energy surface, the vibrational part of the coupling cannot be easily calculated. Therefore we only calculated at each point of the reaction coordinates the 12 integrals of the electric field operator:

$$E_{jn}(Q) = \langle \phi_1(q, Q) | \sum_e - (q_j^e - s_j^n) / r_{en}^3 | \phi_0(q, Q) \rangle_q \quad (II.3)$$

As a measure of the electronic coupling we can choose for instance the length of the vector  $\mathbf{E}$ , defined by

$$E^2(Q) = \sum_{n=1}^4 \sum_{j'=1}^3 Z_n \{ E_{jn}(Q) \}^2 \quad (II.4)$$

We will return to this choice in the discussion in section IIC.

Apart from an increasing  $\mathbf{E}$  vector, the probability for the radiationless transition can also be enhanced because of the decreasing distance,  $|\Phi_0(Q) - \Phi_1(Q)|$ , between the potential energy surfaces. The total coupling due to electronic factors is then given by

$$v^E(Q) = \mathbf{E}(Q) / \{ |\Phi_0(Q) - \Phi_1(Q)| \} \quad (II.5)$$

**B. Results.** In Tables I and II we show the geometries and energies of the various formaldehyde states. For the sake of clarity we note once more that we optimized the geometries with a single configuration 4-31G program (method I) and that these geometries were used as input in the large basis set + CI calculation (method II). No further geometry search was attempted in the CI study performed here, in contradistinction to what we did in a previous paper<sup>7</sup> for the  $H_2CO$  ( $S_0$ ) and  $H_2CO$  ( $S_1$ ) states. The results from ref 7 are also shown in Table I for comparison. The table shows that the  $H_2CO$  ( $T_1$ ) geometry from method I agrees reasonably well with the CI optimization for  $H_2CO$  ( $S_1$ ) from ref 7 and with the experimental data for  $H_2CO$  ( $S_1$ ). The same holds for the  $H_2CO$  ( $S_0$ ) geometries. This indicates that the procedure for choosing the geometry input for method II works satisfactorily, at least in the starting points for the potential energy surface scan. Further we see from Table I that the unimolecular rearrangement occurs in one plane for the  $S_0$  case, leading to the hydroxycarbene trans configuration. For the rearrangement in the  $T_1$  state we find an increasing out of plane angle  $\theta$ , leading to the HCOH ( $T_1$ )-gauche configuration. Table II shows the energies of the various states, relative to the  $H_2CO$  ( $S_0$ ) values obtained by the same method. Concerning the value for  $H_2CO$  ( $S_1$ ) we have to distinguish between the 71.9 kcal/mol for the optimized  $S_1$  structure (bent) and the value of 91.7 kcal/mol for the  $S_1$  geometry which is reached by a vertical (Franck-Condon) transition from the  $S_0$  equilibrium geometry. Using a complete optimization in the CI calculation, van Dijk<sup>8</sup> found for these energies 74.2 and 91.7 kcal/mol, respectively. This similarity gives another positive affirmation for the procedure used. The potential energy surfaces for the  $H_2CO$ -HCOH rearrangement, obtained by method II, are given in Figure 2. In this figure the full lines represent the optimized  $S_0$  and  $S_1$  surfaces, while the dotted lines,  $S_0^b$  and  $S_1^p$ , represent the  $S_0$  surface with bent and the  $S_1$  surface with planar geometry, respectively. The energy barrier for the unimolecular rearrangement on the  $S_0$  surface is 102 kcal/mol. We see from Table II that the extension of method I to method II decreases this barrier only by 8 kcal/mol. We do not expect that a further geometry optimization in the CI calculation will have a sub-

**Table I.** Optimized Bond Lengths (Å) and Angles (deg) for H<sub>2</sub>CO, HCOH, and the Transition States (TS) for the Unimolecular Rearrangement

H <sub>2</sub> CO (S <sub>0</sub> )	method I <sup>a</sup>	ref 7 <sup>b</sup>	exp <sup>c</sup>	H <sub>2</sub> CO (S <sub>0</sub> )-TS	method I	HCOH (S <sub>0</sub> )-trans method I
CO	1.204	1.23	1.208	CO	1.305	1.328
CH = CH'	1.081	1.10	1.116	CH'	1.087	1.098
∠HCH'	116.2	116	116.5	CH	1.266	1.936
θ <sup>d</sup>	0	0	0	φ <sup>e</sup> (= ∠HCO)	55	26.5
				∠H'CO	116.5	103.5
				θ	0	0
H <sub>2</sub> CO (T <sub>1</sub> )	method I		exp	H <sub>2</sub> CO (T <sub>1</sub> )-TS	method I	HCOH (T <sub>1</sub> )-gauche method I
CO	1.367		1.307	CO	1.354	1.354
CH = CH'	1.070		1.096	CH'	1.072	1.072
∠HCH'	121.0		118	CH	1.448	1.782
θ	32.3		37.9	φ (= ∠HCO)	50	34.3
				∠H'CO	126.7	126.0
				θ	52.3	67.8
H <sub>2</sub> CO (S <sub>1</sub> )		ref 7	exp			
CO		1.36	1.325			
CH = CH'		1.06	1.095			
∠HCH'		112.5	118			
θ		30	33.1			

<sup>a</sup> Method I: single configuration 4-31G. <sup>b</sup> As calculated in ref 7 with the (9s5p) [4s3p] basis set + CI with geometry optimization. <sup>c</sup> Experimental data taken from ref 18. <sup>d</sup> θ denotes the out of plane angle. <sup>e</sup> φ denotes the reaction coordinate for H<sub>2</sub>CO-HCOH. See Figure 1.

**Table II.** Energies (kcal/mol) for the Various Formaldehyde States, Relative to the H<sub>2</sub>CO (S<sub>0</sub>) Value Obtained by the Same Method

	method I <sup>a</sup>	method II <sup>b</sup>	other work
H <sub>2</sub> CO (S <sub>0</sub> )	0 (= -113.692 61) <sup>d</sup>	0 (= -113.862 07)	0 (= -113.863 54) <sup>8</sup>
H <sub>2</sub> CO (S <sub>0</sub> )-TS <sup>c</sup>	110.2	102.0	
HCOH (S <sub>0</sub> )-trans	51.2	52.5	51.7 <sup>12</sup>
H <sub>2</sub> CO (T <sub>1</sub> )	35.5		68.9 <sup>12</sup>
H <sub>2</sub> CO (T <sub>1</sub> )-TS	100.9		
HCOH (T <sub>1</sub> )-gauche	58.7		73.0 <sup>12</sup>
H <sub>2</sub> CO (S <sub>1</sub> )		71.9 (91.7) <sup>e</sup>	74.2 <sup>8</sup> (91.7) <sup>8</sup>
H <sub>2</sub> CO (S <sub>1</sub> )-TS		153.4	
HCOH (S <sub>1</sub> )		123.7	

<sup>a</sup> Method I: single configuration 4-31G. <sup>b</sup> Method II: (9s5p) [4s3p] + CI, with the geometries from method I. <sup>c</sup> TS = transition state. <sup>d</sup> The absolute energies are given in atomic units. <sup>e</sup> The value in parentheses is the vertical (Franck-Condon) energy difference. See text.

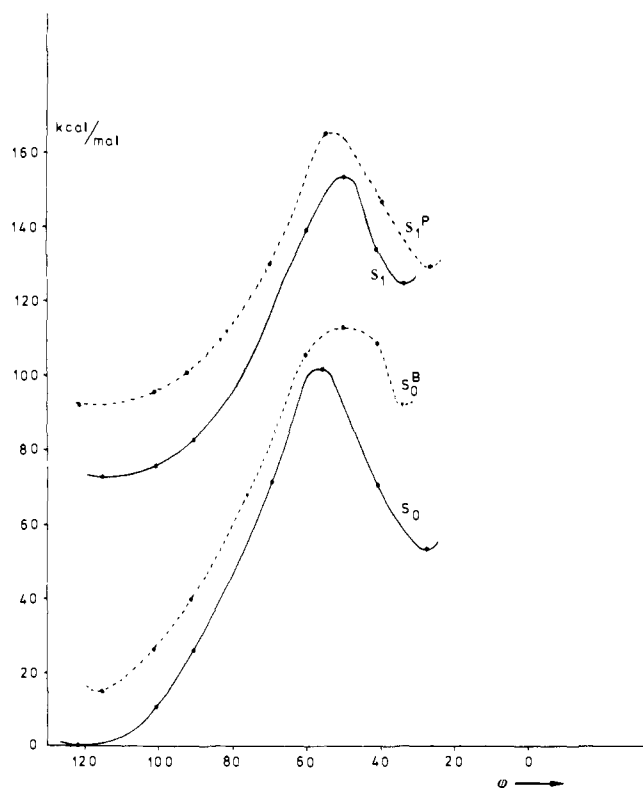
stantial effect. This can be seen, for instance, from the absolute energies for H<sub>2</sub>CO (S<sub>0</sub>) given in Table II (second and third column): they are the same within 1 kcal/mol. The barrier on the S<sub>1</sub> surface is a little lower: 81.5 kcal/mol.

The calculated electronic couplings,  $v^E(Q)$  (see eq II.5), for this rearrangement are given in Figure 3. The most important result for the unimolecular rearrangement is given in Figure 4. Here we compare the electronic coupling,  $v^E(Q)$ , for the first part of the three reaction coordinates, starting from the S<sub>1</sub> equilibrium geometry. The calculation for the two direct dissociations was done in the same way as for the H<sub>2</sub>CO-HCOH rearrangement: calculate for several values of the reaction coordinates  $M$  and  $R$  (see Figure 1) the optimized triplet geometry and use this geometry in the S<sub>1</sub> calculation with the large basis set + CI program.

The direct dissociation paths have already been calculated on a CI level by Hayes, Jaffe, and Morokuma.<sup>19-21</sup> Our 4-31G results for the radical dissociation are the same as theirs: for the dissociation on the T<sub>1</sub> potential energy surface the out of plane angle increases remarkably; the leaving H atom is swung away from the rest of the molecule. For the direct molecular dissociation on the T<sub>1</sub> potential energy surface we also found an increasing out of plane angle (the angle between the CO

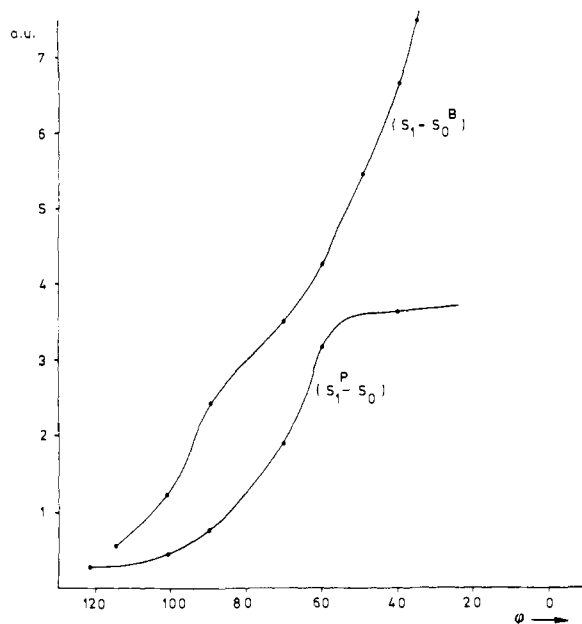
bond and the HCH plane in the coordinate system we used in this case), while the two H atoms depart in a slightly asymmetric way from the carbon atom. This asymmetry is much less dramatic, however, as found by Hayes, Jaffe, and Morokuma<sup>20,21</sup> for the S<sub>0</sub> dissociation.

**C. Analysis and Discussion.** We start our discussion with the results given in Figure 4. We see there that the total coupling,  $v^E(Q)$ , given by eq II.5 is unequal to zero in the starting point. This is because of the following reasons. In the first place, the starting point is the S<sub>1</sub> equilibrium geometry, which differs from the S<sub>0</sub> equilibrium structure. For this latter geometry the vibrational and translational components of the electronic coupling are zero because of symmetry reasons.<sup>7,8</sup> The most important contribution to the starting point coupling, however, comes from the rotational components. We conclude this from the following argumentation: as stated in section IIA, the electric field integrals (II.3) are transformed in the static calculation from Cartesian to normal coordinates by means of the Jacobian matrix elements  $D_j^n_k$ . If the normal coordinate transformation is exactly known, it is possible<sup>7,8</sup> to distinguish completely between the vibrational, rotational, and translational components of the electronic coupling. In the calculation reported here, the movement of the molecules is too far away



**Figure 2.** Calculated potential energy surfaces (method II) for the  $\text{H}_2\text{CO-HCOH}$  rearrangement:  $\phi$  denotes the reaction coordinate.  $S_0^B = S_0$  with bent  $S_1$  geometry;  $S_1^P = S_1$  with planar  $S_0$  geometry. The zero point on the energy scale corresponds with  $-113.86207$  au (see Table II).

from the starting  $S_1$  equilibrium geometry to transform with one single, constant Jacobian: we end up at a completely different (hydroxycarbene) configuration. Although, because of this reason, it is not possible here to exactly distinguish between the various kinds of couplings, we can perform the transformation of the integrals (II.3) for the first part of the three reaction coordinates in order to get an approximate insight into the relative importance of the components. The result of this transformation is given in Figure 5. We only give five of the obtained nine curves because the translational vectors for the reaction coordinates (b) and (c) are almost the same as the one shown in the figure, while the rotational vectors become only slightly ( $\approx 10^{-4}$  au) larger for (b) and (c) at energies higher than 110 kcal/mol. So we see that the main difference between the couplings shown in Figure 4 is caused by the differences between the *vibrational* components for the three reaction coordinates. And only these components can be responsible for inducing an internal conversion. This is so because the translational components have no physical relevance, being the consequence of keeping the electron coordinates fixed while differentiating with respect to the translational coordinates.<sup>7</sup> Concerning the rotational components we note that, although they are dominant in the neighborhood of the  $S_1$  equilibrium geometry, they do not contribute much to the rate of internal conversion. This is so because the electronic components have to be integrated between the vibrational and rotational eigenfunctions involved; see eq II.2. This leads to a negligible contribution to the final coupling elements of the rotational components.<sup>7</sup> The result from these considerations is the conclusion that those electronic coupling components, which can effectively induce internal conversion, are larger for the  $\text{H}_2\text{CO-HCOH}$  rearrangement than for the direct dissociations. It is hard to say exactly how much larger the possibility for internal conversion is for this rearrangement because of the

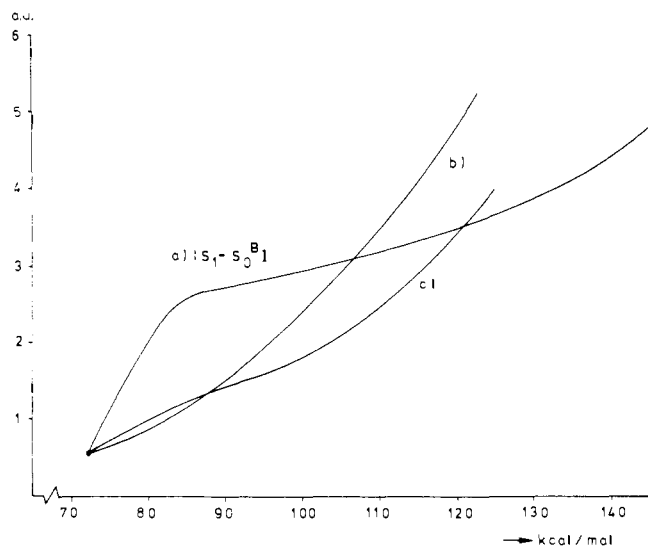


**Figure 3.** Calculated electronic couplings,  $v^E(Q)$ , for the  $\text{H}_2\text{CO-HCOH}$  rearrangement:  $\phi$  denotes the reaction coordinate.

uncertainties inherent in the method used; the obtained differences between the rearrangement and the direct dissociations are so systematic, however, that we have no doubt about the qualitative conclusion made above. Unfortunately, this does not mean that the hydroxycarbene is the solution for the intermediate state problem; we showed earlier<sup>7</sup> that the magnitude of the total  $S_0-S_1$  coupling elements is so low that in the static situation there is not internal conversion at all. What we have shown here is that the  $\text{H}_2\text{CO-HCOH}$  rearrangement leads to such a combination of normal mode movements that we have a favorable combination of coupling components. The increase of the coupling, relative to the static calculation, is not large enough, however, to explain the  $\text{H}_2\text{CO}$  ( $S_1$ ) decay. So we conclude that formaldehyde needs another molecule to induce the internal conversion, a conclusion in agreement with the experimental findings mentioned before.<sup>5</sup> Such a second molecule is needed for another purpose too: as can be seen from Figure 2, the formaldehyde molecule will end up at the wrong side of the  $\text{H}_2\text{CO-HCOH}$  energy barrier; it cannot reach the  $\text{HCOH}$  ( $S_0$ ) local minimum on the potential energy surface. In principle there are two ways to lower this barrier (the possibility that the hydrogen tunnels through the barrier is mentioned briefly in the next section). The first way is an extension of the calculational method: it is well known that equilibrium structures can be described satisfactorily at a lower level of calculational sophistication than transition states. So an extension of the method might lower the barrier.<sup>34</sup> The second way to achieve this is introducing a second molecule; this possibility is treated in the next section.

### III. The Bimolecular Rearrangement $\text{H}_2\text{CO-HCOH}$

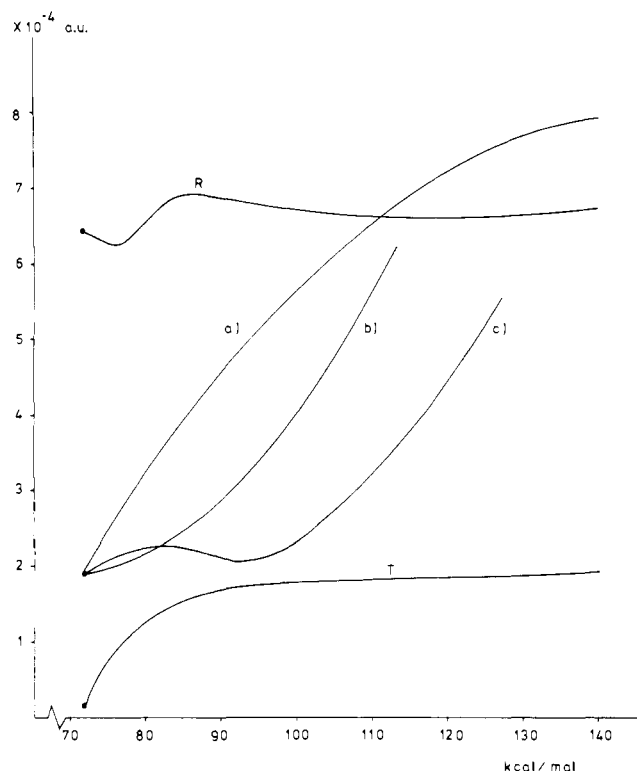
**A. Introduction.** As described above, the potential energy surfaces for both the  $S_0$  and  $S_1$  states show a large barrier for the unimolecular rearrangement  $\text{H}_2\text{CO-HCOH}$ . A second molecule is needed to lower the  $S_0$  barrier, in order to give the  $\text{H}_2\text{CO}$  ( $S_0^*$ ) molecule the opportunity to reach the  $\text{HCOH}$  ( $S_0$ ) minimum. Moreover, a second molecule is needed already for inducing the  $S_1-S_0$  internal conversion. It cannot even be excluded that there will be a much larger medium effect. Remember, for instance, the well-known  $\text{HCN-CN}$  rearrangement. Calculations<sup>22</sup> show that there is a large barrier for this reaction, and yet it takes place almost immediately in the laboratory. The hydrogen isocyanide was observed for the



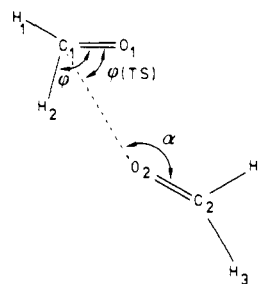
**Figure 4.** Calculated electronic couplings,  $v^E(Q)$ , for (a)  $\text{H}_2\text{CO}$ - $\text{HCOH}$  rearrangement; (b) direct molecular dissociation; and (c) direct radical dissociation. The energy scale is taken relative to the  $\text{H}_2\text{CO}$  ( $S_0$ ) energy.

first time in interstellar space<sup>23</sup> where we have almost collisionless conditions; as soon as there is the possibility for collisions one obtains the "normal" HCN. The same holds for vinyl alcohol. Although a 4-31G calculation predicts a barrier of 85 kcal/mol for its unimolecular rearrangement to acetaldehyde,<sup>24</sup> it was only recently possible to detect vinyl alcohol in the gas phase.<sup>25</sup> So for both the hydrogen isocyanide and the vinyl alcohol case we can expect a medium interaction which gives a large decrease of the barrier on the potential energy surface. The same may hold for formaldehyde.

**B. Method and Results.** We treat the two formaldehydes as one super molecule using the Gaussian 70 program. We place the second formaldehyde as follows (see Figure 6 for the case where we try to lower the barrier on the  $S_0$  surface): the oxygen  $\text{O}_2$  of the second molecule is placed on the line formed, in the unimolecular transition state, by  $\text{C}_1$  and the migrating hydrogen  $\text{H}_2$ . We then optimize on the STO-3G level for several positions ( $\phi$ ) of  $\text{H}_2$  at, and in the neighborhood of, the unimolecular transition state ( $\phi(\text{TS})$ ) the bond lengths  $\text{C}_1\text{H}_2$  and  $\text{C}_1\text{O}_2$ , and the angle  $\alpha$  describing the position of the second (catalyzing) molecule relative to the first (migrating) one. Some tests showed that the total energy was minimized upon keeping  $\text{C}_1$ ,  $\text{H}_2$ ,  $\text{O}_2$ , and  $\text{C}_2$  in one plane. The remaining geometrical parameters were kept fixed at the 4-31G optimized values of the noninteracting molecules. With the optimized STO-3G structures a 4-31G calculation was performed; a further 4-31G optimization did not change anything considerably. We calculated at several positions  $\phi$  in order to see if the angle corresponding to the energy maximum shifts to another value, compared to the unimolecular case. This turned out not to be the case. We found the interaction between  $\text{H}_2\text{CO}$  (TS) and  $\text{H}_2\text{CO}$  to be attractive: there is a shallow minimum in the potential energy curve as a function of the  $\text{C}_1\text{O}_2$  distance. This attractive character is in contradistinction to the (STO-3G) curves for the  $\text{H}_2\text{CO}$ - $\text{NH}_3$  interaction;<sup>26</sup> the situation reported here resembles more the hydrogen bond between  $\text{H}_2\text{CO}$  and  $\text{H}_2\text{O}$ <sup>27</sup> and the  $\text{H}_2\text{CO}$ - $\text{H}$  system.<sup>28</sup> From the optimized position of the catalyzing molecule, the obtained MOs, and Mulliken population analysis we found that the interaction of the two molecules is mainly due to the interaction between the migrating hydrogen  $\text{H}_2$  and the  $n$  orbital of the oxygen  $\text{O}_2$ . In Table III we show the main results of the calculation and compare them to the unimolecular rearrangement. We note



**Figure 5.** Lengths of vectors formed by the vibrational components for (a)  $\text{H}_2\text{CO}$ - $\text{HCOH}$  rearrangement; (b) direct molecular dissociation; and (c) direct radical dissociation. The rotational, **R**, and translational, **T**, vectors for (a) are given for comparison. The energy scale is taken relative to the  $\text{H}_2\text{CO}$  ( $S_0$ ) energy.



**Figure 6.** Configuration used for calculating barrier lowering. See text.

that the interaction does not lead to a hydrogen abstraction from the migrating to the catalyzing molecule: the  $\text{C}_1\text{H}_2$  distance is increased relative to the unimolecular case, but the hydrogen  $\text{H}_2$  stays with its original molecule. In Figure 7 we give as an illustration the obtained net atomic charges for the  $\text{T}_1$  (migrating) +  $\text{S}_0$  (catalyzing) case; the other situations reported in Table III give the same picture. As can be seen from Figure 7, the amount of charge transfer between the molecules is negligible ( $\approx 0.02$  electrons). Table III shows that there is indeed a barrier lowering effect; this effect, however, is relatively small, 6.5–10 kcal/mol. So we see that we still have an energy barrier in the rearrangement: the unimolecular single-determinant barrier is 110.2 kcal/mol; configuration interaction (see Table II) results in 102.0 kcal/mol, while the bimolecular interaction reported in this section gives a further lowering, resulting in a barrier of approximately 95 kcal/mol. This is still about 25 kcal/mol above the vibrationless  $S_1$  level. The qualitative key to the solution of this kind of problem is of course tunneling. The problem with this mechanism, however, is the fact that the calculated tunneling probabilities are

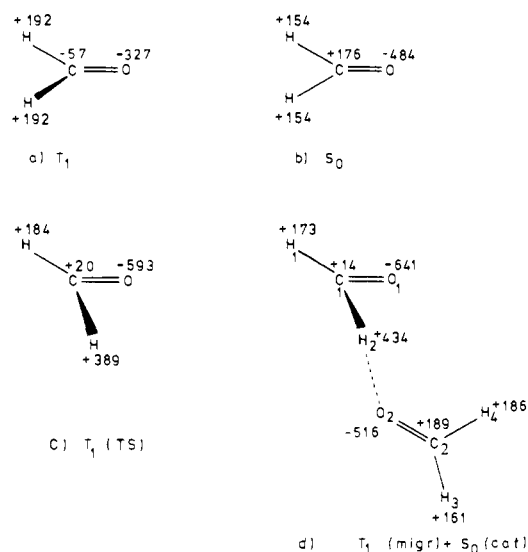
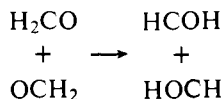


Figure 7. Calculated (4-31G) net atomic charges ( $10^{-3}$  electrons).

extremely sensitive to the parameters involved (potential energy curves, energy of the state involved, etc.).<sup>29,30</sup> So in principle it is probably possible to adjust or parameterize the (calculated) parameters in such a way that the observed  $\text{H}_2\text{CO}$  decay and also the differences between  $\text{H}_2\text{CO}$  and  $\text{D}_2\text{CO}$  are explained, but one never knows how realistic such a treatment will be. These argumentations concerning tunneling hold, of course, for the unimolecular rearrangement too.

#### IV. Summary and Conclusion

The  $\text{H}_2\text{CO}$ - $\text{HCOH}$  rearrangement shows a large barrier on both the  $S_0$  and  $S_1$  potential energy surfaces. For the single determinant calculation with modest basis set this result was obtained already by Altmann et al.;<sup>11</sup> we showed that extension to a larger basis set + CI only slightly decreases this barrier. One of the main results of this work is the finding that internal conversion to  $S_0^*$  is more probable for the hydroxycarbene rearrangement than for the direct dissociation mechanisms. This is due to the fact that those coupling components which can effectively induce the radiationless transition are larger for the rearrangement than for the direct mechanisms. This indicates that the hydroxycarbene can serve as an intermediate state in the formaldehyde photochemistry. Interactions with other molecules will be needed, however, to effect this transition and probably also to reach the intermediate state. The inclusion of a second molecule in the process complicates the description because of the numerous ways the molecules can interact. Apart from the possibility reported in section III, which only leads to a relatively small decrease of the barrier, we can mention, for instance, hydrogen abstraction leading to  $\text{HCO} + \text{H}_2\text{COH}$ . Another interesting possibility is a hydrogen exchange between two (excited)  $\text{H}_2\text{CO}$  molecules leading to two hydroxycarbenes as indicated in a schematic way below:



The energy barrier for this process might be lower than for the single hydrogen abstraction, in analogy with the bifunctional catalyzed [1,3] hydrogen shift in propene<sup>32</sup> and the simultaneously moved hydrogen atoms leading to double well poten-

Table III. Calculated 4-31G Results for the Interaction between a "Migrating" and a "Catalyzing"  $\text{H}_2\text{CO}$  Molecule

migrating	catalyzing	barrier <sup>a</sup>	$\text{C}_1\text{H}_2$ , Å <sup>b</sup>	$\text{C}_1\text{O}_2$ , Å	$\alpha$ , deg
$S_0$		110.2	1.266		
$S_0$	$T_1$	99.9	1.391	4.002	116
$S_0$	$S_0$	102.5	1.319	3.361	118
$T_1$		65.4	1.448		
$T_1$	$S_0$	59.0	1.472	3.754	112

<sup>a</sup> In kcal/mol relative to two noninteracting molecules in their equilibrium configuration. <sup>b</sup> Parameters from Figure 6.

tials in the guanine-cytosine pair and the formic acid dimer.<sup>33</sup>

Our final conclusion is that there are a number of indications that the hydroxycarbene structure can play a key role in the  $\text{H}_2\text{CO}$  ( $S_1$ ) decay, but that a lot of experimental and theoretical work has still to be done to come to a satisfactory understanding of the photochemistry of this seemingly simple molecule. This future work might focus on the direct experimental confirmation of the hydroxycarbene structure and both experimental and theoretical work on interactions between formaldehyde and other quenching molecules.

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