A theoretical study on the reactivity and spectra of H2CO and HCOH. A dimeric model for nonzero pressure formaldehyde photochemistry

Citation for published version (APA):

DOI:
10.1063/1.440940

Document status and date:
Published: 01/01/1981

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 13. Sep. 2019
A theoretical study on the reactivity and spectra of $H_2CO$ and HCOH. A dimeric model for nonzero pressure formaldehyde photochemistry

M. J. H. Kemper, C. H. Hoeks, and H. M. Buck

Contribution from the Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands

(Received 21 November 1980; accepted 22 January 1981)

The reactivity and spectra of formaldehyde isomers and dimeric complexes between them are studied with ab initio methods. A large number of complexes between $H_2CO$, trans-HCOH, cis-HCOH is calculated. Infrared and Raman spectra of (H$_2$CO)$_2$ are calculated with relatively simple methods using spectroscopic masses and scaled force constants. In this way, the structure of dimers in matrices can be deduced. Hydroxycarbene (HCOH) plays a key role in a model that explains a large number of experimental facts of the nonzero pressure photochemistry. Hydroxycarbene forms complexes with $H_2CO$; the stabilization is due to classical hydrogen bonds. HCOH is a new example of an ambiphilic carbene. Addition products are formed from HCOH-$H_2CO$ complexes. The calculations show that, in agreement with matrix experiments, glycoaldehyde and methanol are easily formed. The formation of trans-HCOH occurs through a dimeric interaction with the shifting hydrogen. This bimolecular process is 9.6 kcal/mol (6-3IG*) in favor of the unimolecular conversion. cis-HCOH might be formed via a nonplanar transition state, where also stabilization at the carbene center is possible. When higher concentrations of HCOH are available, a hydrogen exchange mechanism easily transfers hydroxycarbene back to $H_2CO$. Several experiments are suggested in this paper; notably, molecular beam and isotopic-mixture experiments will give useful information. The involvement of HCOH in the light-induced formose reaction is suggested.

I. INTRODUCTION

During the last decade the study of the formaldehyde molecule has taken a central place in fundamental molecular photochemistry and photophysics. Formaldehyde owes this position to the fact that, on the one hand it can behave as a prototype for the photochemistry and photophysics of larger molecules, and on the other hand it is amenable to detailed and well-defined spectroscopic and theoretical studies. The experimental studies revealed a large number of phenomena. The overall process is seemingly simple: formaldehyde is prepared to the $S_1$ state by light absorption, and the final products are molecular and radical fragments:

$H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \quad \xrightarrow{H+HCO} H_2+CO$

The detailed mechanism, however, is still a tantalizing problem. We will not try to discuss here in an extensive way all the existing literature on this subject. We will only mention in the following section some main results in order to define clearly the problem we are concerned with in this paper: the role of hydroxycarbene in formaldehyde photochemistry.

II. THE PROBLEM

A. Gas-phase and matrix experiments

The experiments on formaldehyde that are of interest here, can be placed in two categories: gas phase and matrix experiments. The most recent experiments indicate, that probably different mechanisms dominate formaldehyde decay at really collisionless pressures and at pressures above ~0.2 Torr. An important result in gas phase experiments is the finding by Houston and Zughul that a time lag is involved in the formation of CO photoproduct. At energies less than 1500 cm$^{-1}$ above the $S_1$ origin, the appearance time of CO light absorption is much longer than the corresponding decay time of $S_1$ formaldehyde fluorescence. The appearance time is hardly dependent on the formaldehyde isotope or the vibrational energy. Extrapolation of the results indicates that the zero pressure intercept of the formation rate $\tau^{-1}$ is at most 0.2 $\mu$sec$^{-1}$. This suggests that photochemistry cannot occur without collisions. As remarked by Weisshaar, it is difficult to reconcile these results with the conclusions that have to be drawn from collisionless ($p < 1$ mTorr) decay experiments. At these low pressures, a rapid collision-free decay channel is observed. This fast decay can be explained, in principle, by a sequential coupling mechanism. The prepared single rotational level in $S_1$ is coupled with the set of high vibrational levels of $S_0$. These $S_0$ levels are broadened to a "lumpy" continuum because of coupling with the continuum of $H_2+CO$ dissociative levels. A level shift technique involving a uniform external electric field enabled Weisshaar to obtain quantitative information about the molecular parameters that determine intramolecular decay rates. It is encouraging to see that the coupling elements obtained by this elegant method are in agreement with calculations of van Dijk and Heller. Weisshaar's conclusion is that the only way to reconcile low and high pressure results is to claim that there are two kinds of mechanisms. At higher pressures, the $S_1$ state can be quenched to a nonfluorescing intermediate state X which requires a subsequent collision to give products:
The quenching (2) must dominate the collision-free channel (1) for pressures above ~0.2 Torr. One of the main tasks of fundamental photochemistry is to unravel the nature of this intermediate state in the nonzero pressure mechanism. Candidates are in short supply: High vibrational levels of the electronic ground state (S₀), the triplet state (T₁), and the hydroxycarbene isomer HCOH. It is difficult to dismiss definitively one of these possibilities; all of them have arguments pro and con. Moreover, the experimentally observed phenomena in formaldehyde photochemistry are so numerous and diverse, that it is unlikely to find just one simple mechanism to explain everything. In this paper, we concentrate on the involvement of the hydroxycarbene isomer, and we will only remark on the other possibilities. More details, including the extensive literature on this topic, can be found in Weisshaar's work.³

The other type of experiment which is of interest here is the photolysis of formaldehyde in low temperature matrices. These matrix experiments are complementary to gas-phase work. It is for instance possible to study in a direct way in an inert-gas matrix the differences between monomeric and dimeric formaldehyde. Particularly, the work of Lee's group has to be mentioned here.⁴ Diem⁵ photolyzed H₂CO in an Ar matrix. Infrared absorption before and after the photolysis showed that the dissociation of formaldehyde is effected by the cage dimer. The amount of photoproducts, CH₃OH plus CO, paralleled the amount of dimer present before photolysis; the monomer peaks did not decrease at all after photolysis. So, matrix isolated H₂CO is not photochemically dissociated. (Recall, that it is not yet clear at this moment, whether or not photoproducts are formed in gas-phase experiments for ρ = 0. Extrapolation to zero pressure has only given an upper limit for ρ.) In more highly concentrated matrices, Sodeau⁶ observed the formation of glycoaldehyde, methanol, and carbon monoxide. Also some evidence for hydroxycetene (CH(OH)CO) was reported. The intermediacy of hydroxycarbene in the formation of these addition products was suggested. In the next section we will put together all these experimental facts and offer a model to explain them.

B. Hydroxycarbene

Houston and Moore¹ mentioned for the first time trans-hydroxycarbene as a possible intermediate in formaldehyde photochemistry. Extensive calculations by Goddard² and Pople¹⁰ place HCOH (S₀) at energies of 52.8 and 56.6 kcal/mol, relative to the formaldehyde ground state. So, the local S₀ minimum which corresponds to HCOH is, in principle, accessible from the first excited singlet of H₂CO (E S₁ = 80.6 kcal/mol). In an earlier paper,¹¹ we reported calculations on the electronic coupling elements between the S₁ and S₀ surfaces. These elements, which induce S₁ ~ S₀ internal conversion, increase as the molecule is distorted towards a HCOH-like geometry. The increase of the coupling elements for the reaction coordinates leading directly to molecular and radical products is much less dramatic. This suggests, that the H₂CO = HCOH reaction path is important, because it gives the molecule a maximal opportunity to leave the S₁ potential energy surface. We also showed¹¹ that bimolecular interaction between two H₂CO molecules lowers the energy barrier to HCOH rearrangement.

In order to be acceptable as in intermediate in formaldehyde photochemistry, HCOH must give reasonable explanations for the main findings mentioned in Sec. II A:

- Cage dimers of H₂CO must lead, via HCOH, to the addition products glycoaldehyde and methanol.

- Mainly the matrix experiments show that the unimolecular formation of HCOH either must be very difficult or it must be a very rapid reversible one.

- In gas-phase experiments molecular and radical products are formed. This process can be induced by collisions; zero-pressure dissociation is uncertain.

The explanation for the time lag is, of course, obvious. Just as T₁ would do, HCOH gives the formaldehyde molecule a place to wait a while. After relaxation of (a part) of the internal energy the route to products is blocked and subsequent collisions are needed to produce gas-phase products.

Our model for the nonzero pressure mechanism of formaldehyde photochemistry can be put together in Scheme I. Here, M is a second formaldehyde molecule in its electronic ground state. We will also pay some attention to CO, H₂O, and H₂ as quenchers. In the next three sections we give the results of a large number of ab initio calculations on this model. In Sec. III, we give calculated bimolecular complexes between molecules of H₂CO and HCOH. These complexes are used in Sec. IV as a starting point for step (2) of the model: the formation of addition products. In Sec. V, we discuss steps (1) and (3): the formation of hydroxycarbene.

Finally, we note that the reverse reaction (4) involves a larger energetic problem than transition (3). This is illustrated very schematically in Fig. 1. The barrier to HCOH lies slightly above the S₁ origin.¹² As will be discussed in Sec. V tunneling and/or bimolecular interactions give an effective lowering of this barrier beneath the S₁ origin. If we start, however, with a Fischer-type transition metal–carbene complex like

[Scheme I diagram]

the carbene ligand can split off from the metal. Then immediately a hydrogen shift occurs,13 yielding an aldehyde; there is no trace of $\text{RCOH}$ at all. As remarked by Lucchese,14 this indicates that $\text{HCOH} \rightarrow \text{HzCO}$ must be very easy. The carbene ligand might have some internal energy after the split off, but part of the $\text{HCOH}$ molecules will relax to the vibrationless level at 52.8 kcal/mol. From there no unimolecular escape to $\text{HzCO}$ is possible because the energy barrier of $\sim 31$ kcal/mol is too high. However, no $\text{HCOH}$ is detected at all in transition metal chemistry. The way to escape from the $\text{HCOH}$ configuration is a bimolecular hydrogen exchange and will be discussed in Sec. VB.

All $ab$ initio calculations with STO-3 G and 4-31 G basis sets were done with the GAUSSIAN 70 program; for the 6-31 G* calculations the GAUSSIAN 76 program was used.

### III. COMPLEXES OF $\text{H}_2\text{CO}$ ISOMERS AND THEIR SPECTRA

#### A. The complexes

In Table I, we give the stable, dimeric complexes between formaldehyde isomers. All calculations were done with the STO-3 G basis set; all intra- and intermolecular geometrical parameters were optimized with respect to the total energy of the system. The effect of optimizing intramolecular parameters instead of holding them at their monomeric values is relatively small in the case of weakly bonded complexes. If there is however, a strong interaction or even a complete reaction between two molecules (as in Sec. IV) reoptimization is, of course, necessary. In order to treat all systems in an equivalent way, we decided to optimize all geometrical parameters throughout this work. The intermolecular parameters are elucidated in Fig. 2. The first

<table>
<thead>
<tr>
<th>H atoms</th>
<th>$R$ ($\text{Å}$)</th>
<th>$\psi_1$</th>
<th>$\psi_2$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>Energy* (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{CO} + \text{HzCO}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1234</td>
<td>3.72</td>
<td>70</td>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1234</td>
<td>3.59</td>
<td>53</td>
<td>71</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>1234</td>
<td>3.44</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1234</td>
<td>4.07</td>
<td>101</td>
<td>48</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1234</td>
<td>4.19</td>
<td>107</td>
<td>43</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1234</td>
<td>3.92</td>
<td>54</td>
<td>54</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO} + \text{trans-HCOH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1238</td>
<td>4.06</td>
<td>74</td>
<td>56</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1238</td>
<td>3.91</td>
<td>65</td>
<td>46</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>1247</td>
<td>5.93</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>1238</td>
<td>5.94</td>
<td>0</td>
<td>0</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>1247</td>
<td>4.51</td>
<td>191</td>
<td>322</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>1238</td>
<td>3.89</td>
<td>44</td>
<td>282</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>1247</td>
<td>4.14</td>
<td>54</td>
<td>18</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO} + \text{cis-HCOH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1248</td>
<td>3.47</td>
<td>66</td>
<td>282</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>1237</td>
<td>4.48</td>
<td>9</td>
<td>51</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>1237</td>
<td>4.59</td>
<td>8</td>
<td>50</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>1248</td>
<td>4.53</td>
<td>32</td>
<td>304</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>1248</td>
<td>3.67</td>
<td>125</td>
<td>128</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>1248</td>
<td>3.55</td>
<td>176</td>
<td>116</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>1237</td>
<td>3.54</td>
<td>120</td>
<td>304</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>$\text{trans-HCOH} + \text{trans-HCOH}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1674</td>
<td>2.77</td>
<td>68</td>
<td>68</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>2754</td>
<td>3.31</td>
<td>70</td>
<td>70</td>
<td>90</td>
<td>90</td>
</tr>
</tbody>
</table>

*Relative to the sum of energies of the noninteracting molecules.

*Related complexes and energies as given in Ref. 17.
column in Table I gives the hydrogen atoms which are actually present in each complex. The intramolecular distances and angles differ only slightly from the values in the single molecules (except for 21).

\[ \text{H}_2\text{CO} + \text{H}_2\text{CO} \]. Our results on \text{H}_2\text{CO} dimers parallel qualitatively the results of Del Bene. The differences with her results are probably caused by the fact, that we also optimized the intramolecular parameters.

\[ \text{H}_2\text{CO} + \text{HCOH} \]. There are seven complexes between \text{H}_2\text{CO} and HCOH with interaction energies larger than 1 kcal/mol. We will discuss only these complexes. The stabilization energy is caused by the formation of a hydrogen bond. In the complexes 12–17 we have a HCOH–H⋯OCH$_2$ bond. In complex 18 formaldehyde is the hydrogen donor; this is the only complex where the carbon atom of hydroxycarbene serves as a hydrogen acceptor. We did not find complexes with the carbene oxygen as an acceptor. That hydrogen bonding is important is suggested by several findings. In the first place, the equilibrium geometries of 12–17 show that the directed lone pair of the formaldehyde oxygen forms a nearly linear O⋯H–O bond. This is consistent with the general hybridization model of Del Bene, who studied ROH⋯OH$_2$ dimers, where R is H or one of the isoelectronic substituents CH$_3$, NH$_2$, OH, or F. Also 18 fits in this model; in this complex the formaldehyde C–H bond is nearly colinear with the nonbonding orbital on the hydroxycarbene carbon. The hydrogen bond character of the interaction is also shown by a small but significant interatomic electron density (IED) for the O–H⋯O and C–H⋯C bonds. There is also a small charge transfer associated with the hydrogen bond formation.

\[ \text{HCOH} + \text{HCOH} \]. There is a very large number of starting geometries if one looks for complexes between two HCOH (cis/trans) molecules. We did not make very extensive calculations in this region of the potential energy surface. Most calculations involved the energetically favored trans-isomer. Nearly all starting geometries we tried were either repulsive or they converged to the highly stabilized complex 21. This complex plays a central role in the rearrangement HCOH \( \rightarrow \) H$_2$CO (reaction (4) in Scheme I), and will be discussed in Sec. VB. The weakly stabilized complex 22 can rearrange easily to 21. The geometry of weak complexes can be predicted rather well by minimal basis set calculations. This is also the case for the stabilization energy\(^{51}\) for the most extensively studied dimers (H$_2$O)$_2$ and (HF)$_2$, the STO-3G stabilization is about the same as the result from near Hartree–Fock limit + configuration interaction. We realize, however, that it might be dangerous to extrapolate this to the complexes studied in this paper. Therefore, we investigate in the next section a much more refined consequence of dimer formation.

### B. Infrared and Raman spectra

Differentiation of the potential energy surface with respect to the geometrical parameters gives the force field of a molecule. From these force constants the infrared and Raman frequencies can be obtained. As stated by Pulay, the calculation of diagonal force constants to experimental accuracy is not easily possible from single determinant Hartree–Fock wave functions. There are, however, near-systematic errors which allow for empirical corrections to improve significantly the agreement with experiment. Theoretical prediction of interaction constants is more successful. The predicting possibilities of a semiempirical calibration of force constants were recently shown by Bock et al., in studies on glyoxal and acrolein. He used a scale factor method for the adjustment of diagonal force constants; he also used the so-called spectroscopic masses in (HF)$_2$ to allow for anharmonicity. The agreement between calculated and experimental frequencies is to within 2%. First, we investigated on the basis of H$_2$CO as to how such a procedure must be done for STO-3 G calculated force constants; then we calculated the spectra of (H$_2$CO)$_2$ and HCOH. The required force constants are obtained by quadratic fitting to points near the equilibrium structures. The force constants are transformed to frequencies using the conventional FG method.

\[ \text{H}_2\text{CO} \text{ and HCOH} \]. The results for \text{H}_2\text{CO} and HCOH are shown in Table II. We scaled down the diagonal constants; the interaction constants are left unchanged. We only use two scale factors: for the stretchings we use 0.65, and for the bendings we take 0.9. In their study on ethane, Blom and Altona also found a ratio of 0.65 between the STO-3 G and the optimized C–C-stretch force constant. In the last column of Table II, we give the frequencies for the most important HCOH structure: the trans-isomer.

<table>
<thead>
<tr>
<th>\text{H}_2\text{CO}</th>
<th>\text{D}_2\text{CO}</th>
<th>\text{HDCO}</th>
<th>\text{HCOH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>2701.7</td>
<td>2005.2</td>
<td>2778.6</td>
<td>3275.4</td>
</tr>
<tr>
<td>1754.2</td>
<td>1614.0</td>
<td>1665.2</td>
<td>2615.0</td>
</tr>
<tr>
<td>1562.4</td>
<td>1209.0</td>
<td>1478.5</td>
<td>1626.1</td>
</tr>
<tr>
<td>1043.6</td>
<td>845.9</td>
<td>949.9</td>
<td>1321.5</td>
</tr>
<tr>
<td>2841.0</td>
<td>2138.1</td>
<td>2063.5</td>
<td>1166.9</td>
</tr>
<tr>
<td>1240.5</td>
<td>990.6</td>
<td>1047.2</td>
<td>1082.8</td>
</tr>
</tbody>
</table>

Average deviation from experiment: 3.2%, 4.6%, 4.4%.

| \text{Experimental frequencies from H}_2\text{CO Ref. 29; D}_2\text{CO and HDCO, Ref. 30.} |
(H₂CO)₂. From Sec. II A it will be clear that cage dimers of formaldehyde are very interesting: It was shown by Diem and Lee⁵⁰ that product formation is affected by the dimer; matrix isolated monomeric formaldehyde is not photochemically dissociated. Infra-red and Raman spectra of formaldehyde in argon and nitrogen matrices were studied by Khoshkhoo and Nixon.¹¹ They concluded from the fact that only single infrared and Raman lines occur for the dimer in each of the fundamental vibrational regions, that a plausible dimer structure would be one with a center of symmetry. These facts indicate that the complexes 1 and 6 are plausible candidates.

The structures 1 and 6 belong to the point group C₂₅; this results in sets of mutually exclusive infrared and Raman bands. We calculated the force fields for 1 and 6; only stretchings and bendings were taken into account, while the intermolecular internal coordinates are the same as in Fig. 2 (R, ψ₁, and ψ₂). From such a force field we obtain 13 frequencies; three of them are low-frequency intermolecular vibrations (<75 cm⁻¹). The symmetry of the normal mode movement shows whether a vibration is infrared or Raman active. Of course, these calculated dimer frequencies cannot be compared directly with the experimental values. The experimental dimer frequencies are shifted from the monomer gas phase values not only because of dimer formation (effect A), but also because of the influence of the matrix (effect B). These two effects can be separated in argon and nitrogen matrices; they cannot be separated in solid formaldehyde, which can be considered as an association of molecular dimers.¹² In a calculation only effect A, the difference between monomer and dimer frequencies, can be considered. Table III gives the results for the infrared shifts. There is a good qualitative agreement between the A shifts of the planar complex 1 and the experimental data for argon and nitrogen, with the exception of the mode 6 frequency. We note, however, that for modes 1 to 5 the results of A and B on the frequencies are similar; both shifts have the same sign. For mode 6, A and B have an opposite effect. This might indicate that for this asymmetric bending mode, A and B influence each other; a separation of the total shift into two components and the comparison of one of these components to a calculated value is not permitted then. The solid phase results of Schneider and Bernstein agree for all modes with our calculation on complex 1. We performed a number of numerical tests to investigate the uncertainty in the calculated shifts. It is well known,² for instance, that force constants are very sensitive to the choice of reference geometry. Our tests indicate that the signs of the calculated A shifts are probably correct; the absolute values can have uncertainties as large as 50%. So, qualitative agreement with experiment is the best that can be expected. Fortunately, we found that the differences between infrared and Raman frequencies in the complexes 1 and 6 are almost insensitive to small changes in reference geometry. So, the numerical accuracy in ν₃₅₄₅ (infrared) - ν₃₅₄₅ (Raman) is much better than for the A shifts. Our results are compared with experiment in Table IV. Unfortunately, in this case the experimental data have a large uncertainty.¹¹ The measurement of adequate Raman spectra required a relatively wide spectrometer slit; the significantly poorer resolution than in the infrared caused differences of up to 2 cm⁻¹ between the measured Raman and infrared frequencies for the monomer fundamentals. This might also explain the strange qualitative difference between H₂CO and D₂CO.

Several conclusions can be drawn from this calculation. First of all it is seen that a simple minimal basis set calculation can reproduce rather subtle spectroscopic changes which are due to complex formation. This fact is quite surprising, because the interaction energies in (H₂CO)₂ are low (<1 kcal/mol). The agreement between theory and experiment is at least as good as obtained with larger basis sets for stronger complexes.⁹,¹⁴ A

TABLE III. Experimental and calculated shifts (cm⁻¹) in infrared frequencies, due to A, dimer formation (ν₃₅₄₅ - ν₃₅₄₅), and B, influence of matrix environment [ν₃₅₄₅ (matrix) - ν₃₅₄₅ (gas)].

<table>
<thead>
<tr>
<th></th>
<th>H₂CO</th>
<th></th>
<th></th>
<th>D₂CO</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiments</td>
<td>Calculated</td>
<td></td>
<td></td>
<td>Experiments</td>
<td>Calculated</td>
</tr>
<tr>
<td>Solid a</td>
<td>A+B</td>
<td>A</td>
<td>B</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>Mode a</td>
<td>Solid a</td>
<td>in N₂</td>
<td>in Ar ²</td>
<td></td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>1</td>
<td>54</td>
<td>17.3</td>
<td>8.8</td>
<td>14.7</td>
<td>12.5</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>-32</td>
<td>-6.2</td>
<td>-3.3</td>
<td>-4.0</td>
<td>-3.7</td>
<td>-10.7</td>
</tr>
<tr>
<td>3</td>
<td>-12</td>
<td>0.6</td>
<td>-5.2</td>
<td>-1.3</td>
<td>-16.5</td>
<td>-6.8</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>0.2</td>
<td>6.6</td>
<td>0.9</td>
<td>10.0</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>21.4</td>
<td>6.2</td>
<td>19.6</td>
<td>10.0</td>
<td>2.9</td>
</tr>
<tr>
<td>6</td>
<td>-33</td>
<td>-4.9</td>
<td>3.6</td>
<td>-4.5</td>
<td>3.6</td>
<td>-11.4</td>
</tr>
</tbody>
</table>

aThe modes are derived from free H₂CO; the vibrations of (H₂CO)₂ differ only slightly from these.
Reference 32.
Reference 31.
Reexamination of the experimental data is desirable. Such experiments should be done preferably with molecular beams to avoid the large (see Table III, effect B) matrix-complex interactions. Such a molecular beam determination of a dimer structure has already been done for water. Our calculations show that for a reliable determination of the complex structure, Raman frequencies are just as important as infrared frequencies; infrared Raman differences are calculated more accurately than monomer–dimer shifts. The available data show that the planar complex 1 clearly is the best candidate for the \((\text{H}_2\text{CO})_2\) structure; this will be used in Sec. V, where we study the formation of HCOH.

IV. FORMATION OF ADDITION PRODUCTS

The thermal formation of addition products from \(\text{H}_2\text{CO} + \text{H}_2\text{CO}\) is difficult. Calvert and Steacie report that methanol and carbon monoxide are the major products of a very slow reaction in the temperature range 150–350 °C. So, there are high activation barriers to products on the \(S_0\) potential energy surface. In Sec. II, we mentioned that \(S_1\) excitation in matrices induces the formation of glycoaldehyde and methanol. We suggested in Scheme I, that HCOH is formed after such an excitation. Hydroxycarbene has an energy of about 55 kcal/mol, relative to the formaldehyde ground state. So, the product formation can be easier if one starts with a complex between HCOH and \(\text{H}_2\text{CO}\). In this section, we investigate this possibility. A number of test calculations showed that, in general, it is unwise to start with an intuitively estimated starting geometry for \(\text{H}_2\text{CO} \cdots \text{HCOH}\). The most important reason for this is the difficulty to define a good reaction coordinate. We have to search for a low energy path on an 18-dimensional energy surface; this reaction path has to be chosen as a function of one or, at most, two parameters. It turned out that the easiest way to do this, is to start from one of the complexes reported in Sec. III; actually, this was the main reason for calculating these complexes. The selection of a particular complex is made by considering two aspects. First, the geometry of the complex must be product-like; otherwise the reaction coordinate will be too long and uncontrollable. Second, the interatomic electron densities (IED) in the complex can be taken as indication where bond formation can occur. So, the IED helps to define the reaction coordinate. Then, the energy is calculated as a function of this coordinate; at every point of the reaction the geometry is completely optimized.

**Glycoaldehyde.** Complex 12 is an attractive candidate for the formation of glycoaldehyde. As indicated in Scheme II, we calculated several reactions for 12:
TABLE IV. Experimental\(^a\) and calculated values (cm\(^{-1}\)) for \(\nu_{\text{amide}}\) (infrared) – \(\nu_{\text{amide}}\) (Raman).

<table>
<thead>
<tr>
<th>Mode (^a)</th>
<th>H(_2)CO</th>
<th>D(_2)CO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiments</td>
<td>Calculated</td>
</tr>
<tr>
<td></td>
<td>(\text{in N}_2)</td>
<td>(\text{in Ar})</td>
</tr>
<tr>
<td>1</td>
<td>-3.5</td>
<td>-0.4</td>
</tr>
<tr>
<td>2</td>
<td>4.6</td>
<td>6.3</td>
</tr>
<tr>
<td>3</td>
<td>-1.1</td>
<td>-8.9</td>
</tr>
<tr>
<td>4</td>
<td>-1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>5</td>
<td>-1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>-1.7</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(^a\)The modes are derived from free \(\text{H}_2\text{CO}\); the vibrations of \((\text{H}_2\text{CO})_2\) differ only slightly from these.

Reference 31.

The first main path (1) is the one which can be expected in carbene chemistry.\(^{37}\) The reaction leads to the insertion into a C–H bond. We took two reaction parameters: the C\(_2\)C\(_3\) and C\(_1\)H\(_7\) distances. A rather extensive scan of the two-dimensional potential energy surface as a function of these parameters was performed; we note once more that all the other parameters were completely optimized. If we start from 12 and decrease both parameters, we will obtain a four-electron three-center, cyclic transition state (1a). Such a transition state was originally presumed for this type of reaction.\(^{35,39}\) A second mechanism (1b) was suggested by Benson.\(^{40,41}\) He proposed an abstraction-like insertion: the carbene initially attacks the hydrogen atom. Then, the two alkyl radicals give C–C bond formation. This mechanism was theoretically supported by Dobson\(^{42}\) in his study on singlet methylene. We scanned the energy surface for reaction (1). However, we did not find low barriers for path (1): If we move into this direction, the energy increases steeply. We did not determine the transition state energies exactly; they are however, definitely larger than 60 kcal/mol. So, neither the three-center transition state (1a) nor the abstraction-like way (1b) is possible. Instead, we found that decreasing the C\(_2\)C\(_3\) distance leads to an increasing IED for O\(_2\)H\(_s\). This leads to reaction (2), where we have six-electron five-center, cyclic transition state. H\(_s\) is transferred from the hydroxycarbene to the formaldehyde. The energy barrier is small: starting from 12 we need 6.37 kcal/mol.

This barrier is 1.96 kcal/mol higher than the dissociation energy for 12. The final products of reactions (1) and (2) are the same; experiments with mixtures of, for instance, D\(_2\)CO + HCOH might give, in principle, an experimental verification of the distinction between these two reaction paths. It is easily seen that, starting from D\(_2\)CO + HCOH, reaction (1) leads to a racemic mixture with C\(_3\) as the asymmetric carbon, whereas in reaction (2) chirality is absent.

There is one other interesting starting complex to form glycoaldehyde: 20. We found that, in this case, a C–H insertion is possible according to the abstraction-like path (1b): The hydrogen atom shifts towards the carbene before the C–C bond is formed. However, the energy barrier is still high; starting from 20 it demands 42.2 kcal/mol.

\[ E = -0.82 \text{ kcal/mol} \quad \text{and} \quad E = 41.4 \text{ kcal/mol} \]

\textbf{Methanol + carbon monoxide.} The complexes 14 and 16 are interesting possibilities for the formation of methanol and carbon monoxide. Starting from the \textit{cis}-complex 14, we scanned the energy surface as a function of the O\(_2\)H\(_s\) and C\(_2\)H\(_7\) distances; all the other parameters were optimized. We found a transition state just 10.4 kcal/mol above the starting complex. The transfer of hydrogen atoms H\(_7\) and H\(_8\) occurs in a nearly simultaneous way; the increase
in \( \text{O}_2\text{H}_4 \) IED is slightly ahead of the formation of the \( \text{C}_1\text{H}_7 \) bond. The transition state is of the same type as for reaction (2): a six-electron cyclic state. In complex 16 the CO bonds of formaldehyde and hydroxycarbene are anti-parallel. For reaction (5) we could not find a low-lying transition state to products.

**Methylformate.** Methylformate is a third possible product from two formaldehydes. Among the complexes from Sec. III, there is no clear candidate as a starting geometry. In this case we put \( \text{H}_2\text{CO} \) and \( \text{trans-HCOH} \) as indicated below, and calculated

**reaction (6).** It was necessary again to take a combination of two reaction parameters, \( \text{C}_1\text{H}_7 \) and \( \text{O}_2\text{C}_3 \). If one only takes, for instance, the \( \text{C}_1\text{H}_7 \) distance as a reaction coordinate, the \( \text{O}_2\text{C}_3 \) distance will increase upon optimization, and no product formation occurs. The calculation showed that the addition reaction is abstraction-like [compare with (1b) and (3)]. In the transition state electron density has shifted from \( \text{O}_4\text{H}_7 \) to \( \text{C}_1\text{H}_7 \), while the nature of the two CO bonds is intermediate between single and double bond. Most of the changes in IED occur after passage of the high energy barrier (35.1 kcal/mol, relative to \( \text{H}_2\text{CO} + \text{trans-HCOH} \)).

The results are summarized in Table V. In our model, \( \text{S}_1 \) excitation of formaldehyde produces a \( \text{H}_2\text{CO} \cdots \text{HCOH} \) complex. The energy of this complex, relative to \( 2\text{H}_2\text{CO} \), is given in the first column. The second column gives \( \Delta E \): the calculated STO-3 G barrier to the addition product. For reactions (2) and (4) we recalculated the reaction using a 4-31 G basis set. The table shows that the results are virtually unchanged. We also calculated whether or not the basis set superposition effect \(^43\) has an influence on the energy barrier. This could be the case because the error introduced by this effect might be different in the starting complex and near the transition
A discussion on the applicability in formaldehyde photochemistry will be given in Sec. VI.

V. THE REARRANGEMENT $\text{H}_2\text{CO} \leftrightarrow \text{HCOH}$

In this section, we describe two types of bimolecular interactions which can be involved in the $\text{H}_2\text{CO} \leftrightarrow \text{HCOH}$ rearrangement: barrier lowering and hydrogen exchange. A discussion on the applicability in formaldehyde photochemistry will be given in Sec. VI.

A. Barrier lowering: $\text{H}_2\text{CO} + \text{M} \rightarrow \text{HCOH} + \text{M}$

Very accurate calculations on the unimolecular rearrangement $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ were recently published by Goddard and Schaefer.\textsuperscript{9,12} The energy relative to the formaldehyde ground state required for this reaction was calculated to be 84 kcal/mol at the double zeta + polarization + CI level with the inclusion of zero-point corrections. This seems to be a rather ultimate value for the barrier. Unfortunately, this is still slightly above the $S_1$ origin (80.6 kcal/mol), where photochemical dissociation definitely occurs. Recently, Miller showed in an elegant paper how to include tunneling corrections in unimolecular rate constants. He suggests, that tunneling is quite significant in formaldehyde photochemistry, both for the direct molecular dissociation ($\text{H}_2\text{CO} \rightarrow \text{H}_3 + \text{CO}$) and for the hydroxycarbene rearrangement. As we wrote in an earlier paper,\textsuperscript{11} however, tunneling has the inherent difficulty of being extremely sensitive to the parameters involved (potential energy curves, etc.). So, it is difficult to judge how realistic a quantitative treatment is. Of course, tunneling cannot be dismissed on these grounds, but for the nonzero pressure mechanism we offered in an earlier paper\textsuperscript{11} an alternative (or additional) explanation for the barrier problem. We suggested that unimolecularly there might be no rearrangement to HCOH, but that a second formaldehyde molecule lowers the barrier. We took the flat transition state (HCOH) of the $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ rearrangement and placed the second (catalyzing) molecule in such a way that the migrating hydrogen interacts with the oxygen lone pair of the catalyst [see also Fig. 3(b)]. The lowering effect from a partially optimized 4-31 G calculation was reported to be 7.7 kcal/mol. This seemed to be much too small to form an attractive alternative, because our unimolecular barrier was as high as 102 kcal/mol. However, in view of Goddard's much lower barrier, a bimolecular effect of several kcal/mol is very substantial. Therefore we reinvestigated the barrier lowering.

![FIG. 3. Geometries for uni- and bimolecular rearrangements.](http://jcp.aip.org/about/rights_and_permissions)
We improved two aspects of our older study. All possible orientations of H₂CO, relative to HCHO, were studied and, if necessary, a larger basis set and complete optimization were implied. First, we calculated the energy surface for the unimolecular rearrangement H₂CO → HCHO as a function of the angles θ and ϕ [see Fig. 3(a)]. The other parameters were optimized. The 4-31 G result is shown in Fig. 4. Optimizations in critical regions with θ–31 G* showed that the characteristics of the surface are unchanged if one uses this larger basis set. Modes with an inversion of H₄ towards the other side of the molecule resulted in high energy barriers, as already found by Allmann et al. Contrary to her results, however, Fig. 4 shows that a concerted rearrangement to cis-hydroxycarbene does not have a barrier much higher than the one leading to trans-HCHO.

What is of special interest here is the fact that, although the energy of the transition state changes little upon increasing the out-of-plane angle, the character of the molecule changes remarkably. This is reflected in the ways on which a barrier lowering is possible. There are two ways to stabilize the carbenic-like transition states: (a) at the carbenic center (–C═) and (b) directly at the shifting hydrogen. (a) Moss et al. recently introduced the concept of ambiphilicity in the carbenic selectivity spectrum. According to his criteria, hydroxycarbene is a second example of an ambiphilic carbene. We took three structures on the “mountain ridge” between formaldehyde and HCHO: at out-of-plane angles θ = 0, 30, and 70 deg (see Fig. 4). It can be shown that the planar transition state (TS-pl) has a nucleophilic interaction with H₂CO, while the interaction between H₂CO and the nonplanar transition states (TS-np) will be ambiphilic. An ambiphilic interaction leads to a larger number of stabilizing orientations.

(b) For the direct interaction with the shifting hydrogen charge effects will be important. The shifting atom H₄ has a positive net charge in the transition state; with all basis sets this charge in the flat structure TS-pl is considerably higher than in TS-np. So, for TS-pl, we expect a stronger interaction with an electron-rich side of H₂CO, especially with the oxygen lone pairs. The relative strength of the two interactions is difficult to predict. Recall from Sec. IIIA, however, that of the seven most stable complexes between H₂CO and HCHO there is only one (18) where in the interaction the HCHO–carbon is involved. So, we expect that the direct interaction with H₄ gives rise to higher stabilization. These predictions are completely confirmed by our calculations. In the neighborhood of the transition states we placed at a large number of stabilizing orientations a second molecule and optimized the structure while θ and ϕ were kept fixed. A stabilizing interaction between the transition state and the quencher gives an effective lowering of the barrier. To check if the ridge shifts to another value of ϕ, we also calculated at several neighboring points of the transition states. We concentrated on formaldehyde itself as a quencher, but also did some calculations with H₂O, CO₃, and H₄ as a quenching molecule. We found a fairly large number of "complexes", most of them are stabilized by 0.5 to 3.5 kcal/mol. We discuss these structures only briefly. For the bent transition states (θ = 30, and θ = 70), there are indeed more orientations with a stabilizing interaction with the carbenic carbon than for TS-pl. With molecular hydrogen we did not find interactions; with water or formaldehyde as a quencher the stabilization is slightly larger than with carbon monoxide.

When stabilization is due to the interaction with the shifting hydrogen, the barrier lowering indeed increases for lower θ values. Complexes stabilized by 1–4 kcal/mol were obtained with H₂O, CO₃, and H₂CO. For this type of interaction we found one orientation which gives by far the largest energy lowering: it occurs when the planar transition state TS-pl interacts with the oxygen lone pair of a second formaldehyde. We discuss this structure, which was partially 4–31 G optimized already in an earlier study, in more detail. The structure is sketched in Fig. 3(b); the main features are given in Table VI. The table shows that there is a substantial barrier lowering. The C₃H₄ distance is lengthened considerably by the interaction; we note, however, that the energy surface as a function of this parameter is flat near the transition state. The table also shows that the transition state angle O₁C₃H₄ shifts to a slightly larger value. The IED values for C₃H₄, O₂H₄, and O₃H₄ show that in the transition state H₄ is shared by C₁, O₂, and O₃; all three IED's are about the same. There is a significant charge transfer from the catalyzing formaldehyde to HCHO (6–31 G*: 0.18 electrons). The analogous stabilization in the out-of-plane transition states is, as expected, considerably lower.

We conclude here that this bimolecular interaction is strong enough to bring the barrier to trans-HCHO below the formaldehyde S₄ level. The formation of the cis-isomer costs a few kcal/mol more. Excitation with shorter wavelengths than corresponding to the lowest vibrational levels of H₂CO (S₄) will be able however, to produce cis-HCHO; the larger number of stabilizing orientations can manifest itself then. In Sec. IV we showed that trans-HCHO is a suitable precursor to...
TABLE VI. Uni- and bimolecular transition state $\text{H}_2\text{CO} \rightarrow \text{HCOH}$. See Fig. 3(b) for the atom numbering.

<table>
<thead>
<tr>
<th></th>
<th>STO-3G</th>
<th>4–31G/STO-3G</th>
<th>4–31G</th>
<th>6–31G*/4–31G</th>
<th>6–31G*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimolecular</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$ (kcal/mol)</td>
<td>128.4</td>
<td>109.4</td>
<td>110.2</td>
<td>105.1</td>
<td>104.6</td>
</tr>
<tr>
<td>$O_2C_2H_4$</td>
<td>57.3</td>
<td>57.3</td>
<td>55.0</td>
<td>55.0</td>
<td>56.3</td>
</tr>
<tr>
<td>$C_1H_4$ (Å)</td>
<td>1.208</td>
<td>1.208</td>
<td>1.266</td>
<td>1.266</td>
<td>1.219</td>
</tr>
<tr>
<td>Bimolecular</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E$ (kcal/mol)</td>
<td>117.4</td>
<td>98.7</td>
<td>94.0</td>
<td>95.3</td>
<td>95.0</td>
</tr>
<tr>
<td>$O_2C_2H_4$</td>
<td>60.4</td>
<td>60.4</td>
<td>55.0</td>
<td>55.0</td>
<td>59.0</td>
</tr>
<tr>
<td>$C_1H_4$ (Å)</td>
<td>1.272</td>
<td>1.272</td>
<td>1.645</td>
<td>1.645</td>
<td>1.638</td>
</tr>
<tr>
<td>Stabilization</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in kcal/mol</td>
<td>11.0</td>
<td>10.7</td>
<td>16.2</td>
<td>9.8</td>
<td>9.6</td>
</tr>
</tbody>
</table>

*STO-3G = geometry optimized with STO-3G basis set; 4–31G/STO-3G = 4–31G calculation in STO-3G optimized structure, etc.

Energies relative to $\text{H}_2\text{CO}$.

Partially optimized results from Ref. 11: $E = 102.5$; $O_2C_2H_4 = 55$; $C_1H_4 = 1.319$; stabilization = 7.7.

glycoaldehyde, while methanol is easily formed from the cis-isomer. So, product formation studies as a function of excitation energy might give valuable information. Also the vibrational mode of the formaldehyde molecule will be important: if the accepting mode which is reached after the radiationless transition is an in-plane mode, trans-CH$_2$O will be formed via the planar transition state. If, on the other hand, the out-of-plane vibration is highly excited, more cis-CH$_2$O will be produced via a nonplanar transition state. Finally, if we recall the HCO–HCO complexes from Sec. III A, it is seen that the centrosymmetric complex 1 is the most natural precursor to the transition state given in Fig. 3(b). In Sec. III B, we showed that 1 is the best candidate for the (HCO)$_2$ structure in matrices. The fact that precisely this matrix structure leads to the highest barrier lowering is another indication for the involvement of dimeric interactions.

B. Hydrogen exchange: $2\text{HCOH} \rightarrow 2\text{H}_2\text{CO}$

As described in Sec. II B, the dissociation of a transition metal–carbene complex will result in the formation of HCOH. Part of these molecules will reach the vibrationless level at 52.8 kcal/mol. From there, unimolecular rearrangement to H$_2$CO is practically impossible. Experimentally, however, no hydroxycarbene is detected. A bimolecular way to transform trans-HCOH into H$_2$CO is a hydrogen exchange mechanism:
two HCOH molecules form (HCOH)$_2$, the released stabilization energy will cause the system to overcome easily the barrier to formaldehyde.

We note that the hydrogen exchange is nearly symmetric ($C_6H_4 \approx C_6H_2$ during the reaction). The STO-3 G barrier for the completely symmetric ($C_3v$) exchange is only slightly larger than the asymmetric one. For the larger basis sets we limited our calculations to $C_3v$ symmetry. We also determined the infrared and Raman frequencies of 21 according to the method described in Sec. II B. This confirmed that 21 is a true stationary state (no imaginary frequencies). We merely remark, that the frequencies and modes are intermediate between the ones for H$_2$CO and HCOH; this agrees with the highly stabilized character of 21.

VI. CONCLUSIONS AND DISCUSSION

We will now return to the model offered in Scheme I. Our calculations show that unimolecular formation of HCOH is difficult; only tunneling might give a possible way to reach HCOH from the vibrationless S$_1$ level. In the nonzero pressure mechanism an alternative (or additional) lowering occurs: the bimolecular interactions described in Sec. II A lower the barrier to hydroxy carbon considerably [reactions (1) and (3) in Scheme I]. Once HCOH is formed, the formation of addition products is easy [reaction (2)]. Glycoaldehyde is formed via a five-center cyclic transition state and not via the expected CH insertion; methanol and carbon monoxide are other possible products. In dissociation experiments with transition metal-carbene complexes the HCOH concentration can be relatively high. In that case, a hydrogen exchange between two hydroxycarbene complexes occurs [reaction (4)]. This offers a low energy path for HCOH → H$_2$CO. If one irradiates H$_2$CO, the concentration of HCOH will be too low to make such an exchange likely. In that case the HCOH + H$_2$CO complexes can dissociate in gas-phase experiments. The liberated HCOH then gives molecular and radical photoproducts. The precise nature of these final reactions ([5] and [6] in Scheme I) needs further study: the product formation might go through the H$_2$CO configuration again; it is also possible that subsequent collisions are involved. In a rigid matrix dissociation of HCOH + H$_2$CO is not possible; here the lowest barriers are the ones leading to the addition products.

The easiest way to form HCOH is the barrier lowering described in Sec. VII A. This mechanism approaches a collision complex (chemical) model. Of course, also purely kinetic (physical) collisions can produce HCOH: Zughul showed that He, Ar, and Xe give CO nearly as rapidly as collisions with H$_2$CO itself. Houston reported, however, that Ar induces photoproducts from $D_2CO$ much slower than $H_2CO$ itself. At excitation energies higher than $\approx 90$ kcal/mol a direct production of (HCOH)$_2$ becomes possible via the exchange mechanism (see Table VII). We note that this mechanism also can play a role in the "strange" hydrogen shifts as, for instance, vinylalcohol-acetaldehyde. The high unimolecular barriers can be avoided by bimolecular hydrogen exchange. A similar problem exists in the H shift of $N_2H_2$.

Summarizing, the model offered in Scheme I explains a large number of experimental facts. Whether or not HCOH also plays a role in true collisionless experiments is uncertain. Miller showed that in that case a tunneling-induced interconversion HCOH → H$_2$CO might be rapid; products will be formed however, from the most reactive isomer. Above all things the question whether or not photoproducts are formed from a single molecule should be answered in an experimental way. In principle, once the issue of dimeric mechanisms is raised, other possibilities (like collision-induced radiationless transitions, etc.) should also be considered, but it is difficult to imagine how these more physical mechanisms can give, in a natural way, addition products. Of course, calculations alone cannot prove the existence of HCOH. Weisshaar measured infrared fluorescence after $\frac{4}{2}$ excitation of H$_2$CO in order to observe the intermediate state. It was not possible, however, to detect the short-lived emission of the hydroxy carbene OH stretch. This was due to the "quasicontinuum" emissions of highly vibrational $S_H^r$ states, which are produced after nonreactive quenching. (The quantum yield for product formation was about 0.7.) We suggest that hydroxy carbene might be detectable in interstellar space, where there are truly unimolecular conditions, without perturbations of emitting $S_H^r$ states. Formaldehyde is widely observed in the galaxy at radio wavelengths; it occurs in both high and relatively low density interstellar clouds. The H$_2$CO-HCOH situation can be analogous to the well-known HCN-HNC case. Hydrogen isocyanide was observed for the first time in interstellar space; in the laboratory the molecule rearranges easily to HCN. Also some other experiments are suggested from our theoretical results. Infrared and Raman frequencies of (H$_2$CO)$_2$ should be remeasured, preferably in a molecular beam. Matrix experiments with isotopic mixtures give information about the mechanism of addition reactions. Product formation as a function of excitation energy can clarify the relative importance of cis- and trans-HCOH. In this paper more attention is given to trans-HCOH, because this is the energetically most favored isomer. We feel that calculations on cis-trans interactions, as were done, e.g., by Pasto for N$_2$H$_4$, will have to wait until more experimental data are known. The unimolecular formation of gas-phase photoproducts from HCOH is another interesting topic for calculations.
describe the radical and molecular dissociation on an
equivalent level, the inclusion of correlation effects
will be necessary. We note that in matrix experiments7
no indication for the involvement of radicals is reported.

In this paper, we limited ourselves to relatively sim­
ple ab initio methods. For a starting point this is nec­
essary, because fairly large sections of the potential
energy surface of an eight-atom molecule have to be cal­
culated. Fortunately, however, the experimentally con­
trollable results (stabilization energies, infrared and
Raman spectra) are very good, while the cases where
we used several basis sets show that the results essen­
tially do not change in going from minimal STO-3 G to
6-31 G*.

Our results primarily concern gas-phase and matrix
studies. However, aqueous solutions of formaldehyde
also show very interesting reactions. In the so-called
formose reactions53 an aldol-type condensation results
in the formation of hydroxy aldehydes, hydroxy ketones,
and sugars. The interest in this reaction recently in­
creased, because of its possible importance in the pro­
duction of carbohydrates in spaceships.54,55 From this
reaction some investigators even concluded53 that for­
maldehyde is involved in photosynthesis. Especially the
origin of glycolate H2C(OH)CHOH was taxed many minds56
until the problem was solved by Tolbert.57 In most
formose experiments Ca(OH)2 is used as a catalyst,
but ultraviolet light can also be used for inducing the
reaction. The mechanism is an autocatalytic one; the
slow primary formation of glycoaldehyde is the rate
determining step. Once this C2 fragment is formed,
more formaldehyde molecules can be added to it. It
will be clear that our results suggest that HCOH can be in­
volved in these reactions, especially in the primary con­
densation to glycoaldehyde. Theoretical studies, how­
ever, will have to use semiempirical methods, because
the situation in the liquid phase is much more compli­
cated: the actual reactant in aqueous solution is not
H2CO, but hydrated formaldehyde (methyleneglycol).

(1976).
2M. B. Zaghlul, Ph. D. dissertation, University of California
at Berkeley, 1976.
3(a) J. C. Weisshaar, A. P. Baranovski, A. Cabello, and
C. B. Moore, J. Chem. Phys. 69, 4720 (1978); (b) J. C.
Weisshaar and C. B. Moore, ibid. 70, 5135 (1979); (c)
J. C. Weisshaar and C. B. Moore, ibid. 72, 2875 (1980);
(d) J. C. Weisshaar, Ph. D. dissertation University of
4J. M. F. van Dijk, J. H. Kemper, Hoeks, and Buck: Reactivity and spectra of H2CO and HCOH
5Due to a calculational error, the reported value in Ref. 9 of
89 kcal/mole, is incorrect and should be 84 kcal/mol. H. F.
Schaefer III at the Discussion meeting on “Photodissociation
1979.
Soc. 100, 298 (1978).
8W. J. Hehre et al., QCPE 11, 236 (1973).
9J. A. Pople et al., QCPE 11, 368 (1978). We thank Dr.
G. J. Visser for adaption of this program to the Burroughs
B7000 computer.
12Our GAUSSIAN 70 program calculates interatomic electron
densities (IED) between atoms a and b as $\Delta \rho_{ab} (\Delta N_{i} C_{i} C_{b})$
$\times 2\rho_{a}$. Here, j and k are the atomic orbitals on the atoms a
and b, respectively; i is a molecular orbital with occupation
number $N_{i}$ and coefficients $C_{i}$ $\Delta \rho_{a}$ is the overlap integral
(jk). This expression can be taken as a measure of the strength
of a bond between two atoms; it is half the so-called
Reduced Overlap Population as defined in A. G. Turner,
Methods in Molecular Orbital Theory (Prentice-Hall, New
Jersey, 1974).
13P. A. Kollman, Modern Theoretical Chemistry, edited by
14M. J. H. Kemper, thesis, Eindhoven University of Technology
1980.
15P. Pulay, in Modern Theoretical Chemistry, edited by H. F.
17Reference 23, p. 298.
18C. E. Blom and C. Altona, Mol. Phys. 31, 1377 (1976) and
related papers.
21E. B. Wilson, J. C. Decluis, and P. C. C. Wilson, Molecular
Vibrations (McGraw-Hill, New York, 1958). We thank Dr.
D. L. Vogel for making available the necessary programs.
(1979).
23V. A. Job, V. Sethuraman, and K. K. Innes, J. Mol.
24H. Khoshkhooh and E. R. Nixon, Spectrochimica Acta 29A,
603 (1973).
52, 13 (1956).
26L. A. Curtiss and J. A. Pople, J. Mol. Spectry. 48, 413
(1974).
27L. A. Curtiss and J. A. Pople, J. Mol. Spectry. 55, 1
(1975).
176 (1951).
31P. S. Skell and R. C. Woodward, J. Am. Chem. Soc. 78,
4496 (1956).
(1964).
35R. C. Dobson, D. M. Hayes, and R. Hoffmann, J. Am.
Chern. Soc. 93, 6188 (1971).
38J. A. Altmann, I. G. Csizmadia, K. Yates, and P. Yates,
This is easily seen by comparing our 4–31G calculated HOMO and LUMO energies of trans–HCOH (−9.81 and 3.53 eV, respectively) with the values given in Ref. 46. For the reaction with CH2=CHCN the difference HOMO–carbene/LUMO–reactant is small, so the carbene reacts in a nucleophilic way. The reaction with Me2C=CMe2 is electrophilic. The same arguments hold for cis-HCOH.


D. J. Pasto, J. Am. Chem. Soc. 101, 6852 (1979). The reaction 2 H2N2 (→) 2 trans–HNNH which is completely analogous to 2 H2CO (→) 2 trans–HCOH is not reported by the author. Our calculations show, that this rearrangement occurs very easily. [M. J. H. Kemper and H. M. Buck, Can. J. Chem. (to be published).]


