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

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The reactivity and spectra of formaldehyde isomers and dimeric complexes between them are studied with *ab initio* methods. A large number of complexes between H₂CO, *trans*-HCOH, *cis*-HCOH is calculated. Infrared and Raman spectra of (H₂CO)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 H₂CO; the stabilization is due to classical hydrogen bonds. HCOH is a new example of an ambiphilic carbene. Addition products are formed from HCOH...H₂CO 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 (6-31G*) in favor of the unimolecular conversion. *cis*-HCOH - might be formed via a nonplanar transition state, where also stabilization at the carbenic center is possible. When higher concentrations of HCOH are available, a hydrogen exchange mechanism easily transfers hydroxycarbene back to H₂CO. 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 S₁ state by light absorption, and the final products are molecular and radical fragments:

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 Houston¹ and

Zughul² that a time lag is involved in the formation of CO photoproduct. At energies less than 1500 cm⁻¹ above the S₁ origin, the appearance time of CO light absorption is much longer than the corresponding decay time of S₁ 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 τ_{CO}^{-1} is at most 0.2 μsec⁻¹. This suggests that photochemistry cannot occur without collisions. As remarked by Weisshaar,³ 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,³ in principle, by a sequential coupling mechanism. The prepared single rotational level in S₁ is coupled with the set of high vibrational levels of S₀. These S₀^{*} levels are broadened to a "lumpy" continuum because of coupling with the continuum of H₂+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 Dijk⁴ and Heller.⁵ Weisshaar's conclusion is³ 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 S₁ state can be quenched to a nonfluorescing intermediate state X which requires a subsequent collision to give products:

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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 (S_0^*), the triplet state (T_1), 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.⁶⁻⁸ Diem⁶ 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 $p \rightarrow 0$. Extrapolation to zero pressure has only given an upper limit for τ_{CO}^{-1} .) In more higher concentrated matrices, Sodeau⁷ observed the formation of glycoaldehyde, methanol, and carbon monoxide. Also some evidence for hydroxyketene (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 Goddard⁹ and Pople¹⁰ place HCOH (S_0) at energies of 52.8 and 56.6 kcal/mol, relative to the formaldehyde ground state. So, the local S_0 minimum which corresponds to HCOH is, in principle, accessible from the first excited singlet of H₂CO ($ES_1 = 80.6$ kcal/mol). In an earlier paper,¹¹ we reported calculations on the electronic coupling elements between the S_1 and S_0 surfaces. These elements, which induce $S_1 \rightsquigarrow S_0^*$ 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 $\rightarrow$ HCOH reaction path is important, because it gives the molecule a maximal oppor-

tunity to leave the S_1 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 an 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 T_1 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

Scheme I

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 S_1 origin.¹² As will be discussed in Sec. V tunneling and/or bimolecular interactions give an effective lowering of this barrier beneath the S_1 origin. If we start, however, with a Fischer-type transition metal-carbene complex like

FIG. 1. Energies (kcal/mol) involved in the rearrangement $\text{H}_2\text{CO} \leftrightarrow \text{trans-HCOH}$.

the carbene ligand can split off from the metal. Then immediately a hydrogen shift occurs,¹³ yielding an aldehyde; there is no trace of RCOH at all. As remarked by Lucchese,¹⁴ this indicates that $\text{HCOH} \rightarrow \text{H}_2\text{CO}$ must be very easy. The carbene ligand might have some internal energy after the split off, but part of the HCOH molecules will relax to the vibrationless level at 52.8 kcal/mol. From there no unimolecular escape to H_2CO is possible because the energy barrier of ≈ 31 kcal/mol is too high. However, no HCOH is detected at all in transition metal chemistry. The way to escape from

the 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 program¹⁵; for the 6-31 G* calculations the GAUSSIAN 76 program¹⁶ was used.

III. COMPLEXES OF H₂CO 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 I. STO-3 G calculated complexes between H₂CO isomers. The intermolecular parameters are shown in Fig. 2.

	H atoms	R (Å)	ψ_1	ψ_2	ϕ_1	ϕ_2	Energy ^a (kcal/mol)	
H₂CO + H₂CO								
1	1234	3.72	70	70	0	0	-0.94	(A - 0.95) ^b
2	1234	3.59	53	71	0	90	-0.87	(D - 0.63) ^b
3	1234	3.44	0	180	0	0	-0.66	(C - 0.61) ^b
4	1234	4.07	101	48	0	0	-1.04	
5	1234	4.19	107	43	0	0	-1.04	(B - 1.04) ^b
6	1234	3.92	54	54	90	90	-0.63	(E - 0.44) ^b
H₂CO + <i>trans</i>-HCOH								
7	1238	4.06	74	56	0	0	-0.32	
8	1238	3.91	65	46	90	0	-0.56	
9	1247	5.93	0	0	0	0	-0.15	
10	1238	5.94	0	0	90	0	-0.11	
11	1247	4.51	191	322	90	0	-0.21	
12	1238	3.89	44	282	90	0	-4.41	
13	1247	4.14	54	18	0	0	-3.33	
H₂CO + <i>cis</i>-HCOH								
14	1248	3.47	66	282	90	0	-3.24	
15	1237	4.48	9	51	0	0	-6.14	
16	1237	4.59	8	50	90	0	-4.71	
17	1248	4.53	32	304	0	0	-5.24	
18	1248	3.67	125	128	0	0	-1.54	
19	1248	3.55	176	116	90	0	-0.86	
20	1237	3.54	120	264	90	0	-0.82	
<i>trans</i>-HCOH + <i>trans</i>-HCOH								
21	1674	2.77	68	68	0	0	-19.88	
22	2754	3.31	70	70	90	90	-0.77	

^aRelative to the sum of energies of the noninteracting molecules.

^bRelated complexes and energies as given in Ref. 17.

FIG. 2. Intermolecular coordinates for complexes between H_2CO isomers.

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 H_2CO dimers parallel qualitatively the results of Del Bene.¹⁷ 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 H_2CO 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 $\text{HCO}-\text{H}\cdots\text{OCH}_2$ 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 $\text{O}\cdots\text{H}-\text{O}$ bond. This is consistent with the general hybridization model of Del Bene,¹⁸ who studied $\text{ROH}\cdots\text{OCH}_2$ 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 density¹⁹ (IED) for the $\text{O}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{C}$ bonds. There is also a little 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 $\text{HCOH} \rightarrow \text{H}_2\text{CO}$ [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.²⁰ This is also the case for the stabilization energy²¹; for the most extensively studied dimers

(H_2O)₂ and (HF)₂, the STO-3 G 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,²² 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.*^{23,24} in studies on glyoxal and acrolein. He used a scale factor method²⁵ for the adjustment of diagonal force constants; he also used the so-called spectroscopic masses^{26,27} ($M_{sp} = M + 0.0795 M^{1/2}$) to allow for anharmonicity. The agreement between calculated and experimental frequencies is to within 2%. First, we investigated on the basis of H_2CO as to how such a procedure must be done for STO-3 G calculated force constants; then we calculated the spectra of (H_2CO)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.²⁸

H_2CO and HCOH . The results for H_2CO 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 Altona²⁵ 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 II. Calculated vibrational frequencies (cm^{-1}) for formaldehyde and HCOH . Diagonal stretching and bending constants were scaled down by factors 0.65 and 0.9, respectively. We used spectroscopic masses: $M_{sp} = M + 0.0795 M^{1/2}$.

	H_2CO	D_2CO	HDCO	HCOH
	2701.7	2005.2	2778.6	3275.4
	1754.2	1614.0	1665.2	2615.0
	1562.4	1209.0	1478.5	1626.1
	1043.6	845.9	949.9	1321.5
	2841.0	2138.1	2063.5	1166.9
	1240.5	990.6	1047.2	1082.8
Average deviation ^a from experiment	3.2%	4.6%	4.4%	

^aExperimental frequencies from H_2CO Ref. 29; D_2CO and HDCO , Ref. 30.

(H₂CO)₂. From Sec. IIA it will be clear that cage dimers of formaldehyde are very interesting: It was shown by Diem and Lee⁶ that product formation is effected by the dimer; matrix isolated monomeric formaldehyde is not photochemically dissociated. Infrared and Raman spectra of formaldehyde in argon and nitrogen matrices were studied by Khoshkhoo and Nixon.³¹ 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 C_{2h} ; 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 , ψ_1 , and ψ_2). 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.³² 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 Bernstein³² 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,²² 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 $\nu_{\text{dimer}}(\text{infrared}) - \nu_{\text{dimer}}(\text{Raman})$ 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.³¹ 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.^{33,34} A

TABLE III. Experimental and calculated shifts (cm⁻¹) in infrared frequencies, due to A, dimer formation ($\nu_{\text{dimer}} - \nu_{\text{monomer}}$), and B, influence of matrix environment [$\nu_{\text{monomer}}(\text{matrix}) - \nu_{\text{monomer}}(\text{gas})$].

Mode ^a	H ₂ CO						D ₂ CO					
	Experiments					Calculated	Experiment					Calculated
	Solid ^b A + B	in N ₂		in Ar ^c		1 A	in Ar ^c		1 A	6 A		6 A
		B	A	B	A		B	A		B	A	
1	54	17.3	8.8	14.7	12.5	4.2	12.0	9.9	2.3	-3.7	-3.0	-3.0
2	-32	-6.2	-3.3	-4.0	-3.7	-10.7	-3.0	-6.1	-19.7	-6.1	-11.5	-11.5
3	-12	-0.6	-5.2	-1.3		-16.5	-2.2	-2.0	-5.0	-6.8	-1.5	-1.5
4	10	0.2	6.6	0.9			0.5					
5	16	21.4	6.2	19.6	10.0	2.9	16.5	10.6	1.9	-1.9	-1.5	-1.5
6	-33	-4.9	3.6	-4.5	3.6	-11.4	-0.5	2.6	-9.1	0.7	0.6	0.6

^aThe modes are derived from free H₂CO; the vibrations of (H₂CO)₂ differ only slightly from these.

^bReference 32.

^cReference 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.³⁵ 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 Steacie³⁶ 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.^{9,10} So,

the product formation can be easier if one starts with a complex between HCOH and H_2CO . 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 densities¹⁹ (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:

Scheme II

Mode ^a	H ₂ CO				D ₂ CO		
	Experiments		Calculated		Experiment	Calculated	
	in N ₂	in Ar	1	6	in Ar	1	6
1	-3.5	-0.4	0.3	-0.3	2.0	1.3	-2.5
2	4.6	6.3	5.7	-5.7	3.1	4.3	-11.9
3			-1.1	-8.9		-0.5	-0.6
4							
5		-1.0	0.3	0.0	0.4	0.1	0.0
6			-1.3	0.0		-1.7	0.0

^bReference 31.

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.

$$E = -3.24 \text{ kcal/mol}$$

$$E = +7.18 \text{ kcal/mol}$$

in O_2H_8 IED is slightly ahead of the formation of the C_1H_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.

$$E = -4.71 \text{ kcal/mol}$$

$$E = \text{high}$$

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 H_2CO and *trans*- HCOH as indicated below, and calculated

$$E = +35.1 \text{ kcal/mol}$$

reaction (6). It was necessary again to take a combination of two reaction parameters, C_1H_7 and O_2C_3 . If one only takes, for instance, the C_1H_7 distance as a reaction coordinate, the O_2C_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 O_4H_7 to C_1H_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, 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 ΔE : 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 effect⁴³ 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

TABLE V. Calculated energies (kcal/mol) for the formation of addition products from $\text{H}_2\text{CO} + \text{HCOH}$.

Reactant		Product	E_{reactant}^a	ΔE^b	E_{product}^a
12	(1)	glycoaldehyde	43.2	high	-33.5
12	(2)	glycoaldehyde	43.2 (45.0) ^c	6.4 (6.1) ^c	-33.5
20	(3)	glycoaldehyde	52.7	42.2	-33.5
14	(4)	$\text{H}_3\text{COH} + \text{CO}$	50.3 (53.3) ^c	10.4 (14.5) ^c	-40.6
16	(5)	$\text{H}_3\text{COH} + \text{CO}$	48.8	high	-40.6
$\text{H}_2\text{CO} + \text{HCOH}$	(6)	methylformate	47.7	35.1	-54.6

^aRelative to 2 H_2CO (≈ -224.70870 a.u.).^cRecalculated with 4-31 G basis set.^b $\Delta E = E(\text{transition state}) - E_{\text{reactant}}$.

state. Fortunately, this turned out not to be the case; the superposition error as a function of the reaction coordinate is nearly a constant. All reported transition states are genuine stationary points on the energy surface. This follows from the fact that a vibrational analysis according to the methods of Sec. III B resulted in a single imaginary vibrational frequency. The calculated frequencies also showed that the differences in zero-point energy of reactants and transition state result in a small increase (< 1 kcal/mol) of the barrier heights.

The results in Table V clearly show that hydroxycarbene indeed is an attractive precursor to glycoaldehyde and methanol. The formation of methylformate is much more difficult; it asks for a high activation energy. This gets support from the matrix experiments; glycoaldehyde and methanol are easily formed, but no methylformate was detected.

It is interesting to note that the activation energies for reactions (2) and (4) are slightly higher than the dissociation energies of the starting complexes. This means that in gas phase the complexes will dissociate; free HCOH might then give molecular ($\text{H}_2 + \text{CO}$) and radical ($\text{H} + \text{HCO}$) products. When the complex is confined to a rigid matrix, dissociation is not possible and the lowest activation energy is the one leading to an addition product. Concerning the point that glycoaldehyde was only reported⁶ in relatively concentrated matrices, we note that it is possible that glycoaldehyde is also formed at higher dilutions, but that it is photolyzed itself⁷ to carbon monoxide and methanol.

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 $\text{H}_2\text{CO} \rightarrow \text{HCOH}$ 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.^{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 correc-

tions. 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,⁴⁴ 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 ($\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$) and for the hydroxycarbene rearrangement. As we wrote in an earlier paper,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 paper¹¹ 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.

FIG. 4. 4-31 G potential energy surface for $\text{H}_2\text{CO} + \text{HCOH}$. F=formaldehyde, T=*trans*-HCOH, C=*cis*-HCOH. The energy lines are given in kcal/mol relative to F.

We improved two aspects of our older study. All possible orientations of H_2CO , relative to HCOH , were studied and, if necessary, a larger basis set and complete optimization were implied. First, we calculated the energy surface for the unimolecular rearrangement $\text{H}_2\text{CO} + \text{HCOH}$ as a function of the angles θ and ψ [see Fig. 3(a)]. The other parameters were optimized. The 4-31 G result is shown in Fig. 4. Optimizations in critical regions with 6-31 G* showed that the characteristics of the surface are unchanged if one uses this larger basis set. Modes with an inversion of H_3 towards the other side of the molecule resulted in high energy barriers, as already found by Altmann *et al.*⁴⁵ 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*-HCOH.

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 ($-\dot{\text{C}}-$) and (b) directly at the shifting hydrogen.

(a) Moss *et al.*⁴⁶ recently introduced the concept of ambiphilicity in the carbenic selectivity spectrum. According to his criteria, hydroxycarbene is a second example of an ambiphilic carbene.⁴⁷ We took three structures on the "mountain ridge" between formaldehyde and HCOH : at out-of-plane angles $\theta = 0, 30$, and 70° (see Fig. 4). It can be shown²¹ that the planar transition state (TS-pl) has a nucleophilic interaction with H_2CO , while the interaction between H_2CO and the nonplanar transition states (TS-np) will be ambiphilic. An ambiphilic interaction leads to a larger number of stabilizing orientations.²¹

(b) For the direct interaction with the shifting hydrogen charge effects will be important.²¹ The shifting atom H_4 has a positive net charge in the transition states;

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 H_2CO , 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 H_2CO and HCOH there is only one (18) where in the interaction the HCOH -carbon is involved. So, we expect that the direct interaction with H_4 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 orientations a second molecule and optimized the structure while θ and ψ 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 ψ , 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 H_2O , CO , and H_2 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 ($\theta = 30$, and $\theta = 70$), 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 H_2O , CO , and H_2CO . 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,¹¹ 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 C_1H_4 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 $\text{O}_2\text{C}_1\text{H}_4$ shifts to a slightly larger value. The IED values for C_1H_4 , O_2H_4 , and O_3H_4 show that in the transition state H_4 is shared by C_1 , O_2 , and O_3 : all three IED's are about the same. There is a significant charge transfer from the catalyzing formaldehyde to HCOH (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*-HCOH below the formaldehyde S_1 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 H_2CO (S_1) will be able however, to produce *cis*-HCOH; the larger number of stabilizing orientations can manifest itself then. In Sec. IV we showed that *trans*-HCOH is a suitable precursor to

TABLE VI. Uni- and bimolecular transition state H₂CO → HCOH. See Fig. 3(b) for the atom numbering.

	STO-3 G ^a	4-31 G/STO-3 G ^a	4-31 G	6-31 G*/4-31 G	6-31 G*
Unimolecular					
<i>E</i> (kcal/mol) ^b	128.4	109.4	110.2	105.1	104.6
O ₂ C ₁ H ₄	57.3	57.3	55.0	55.0	56.3
C ₁ H ₄ (Å)	1.208	1.208	1.266	1.266	1.219
Bimolecular					
<i>E</i> (kcal/mol) ^b	117.4	98.7	94.0 ^c	95.3	95.0
O ₂ C ₁ H ₄	60.4	60.4	55.0 ^c	55.0	59.0
C ₁ H ₄ (Å)	1.272	1.272	1.645 ^c	1.645	1.638
Stabilization					
in kcal/mol	11.0	10.7	16.2 ^c	9.8	9.6

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

^bEnergies relative to H₂CO.

^cPartially optimized results from Ref. 11: *E*=102.5; O₂C₁H₄=55; C₁H₄=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*-HCOH will be formed via the planar transition state. If, on the other hand, the out-of-plane vibration is highly excited, more *cis*-HCOH will be produced via a nonplanar transition state. Finally, if we recall the H₂CO + H₂CO complexes from Sec. IIIA, 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

(H₂CO)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: 2HCOH → 2H₂CO

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 H₂CO is practically impossible. Experimentally, however, no hydroxycarbene is detected. A bimolecular way to transform *trans*-HCOH into H₂CO is a hydrogen exchange mechanism:

In Sec. IIIA, we reported that two *trans*-HCOH form a very stabilized complex (complex 21 from Table I). This structure is very much like the transition state which we expect for 2HCOH → 2H₂CO. We took 21 as a starting point for our calculations. Table VII shows the results. We calculated the potential energy surface as a function of the C₁H₆ and C₃H₈ distances. At each combination of these parameters we optimized, as usual,

all other parameters. Two hydroxycarbenes give, without an energy barrier, complex 21. The stabilization energy is nearly the same in all basis sets: ≈ 19 kcal/mol. A further decrease of the CH distances leads to the transition state between 21 and 2H₂CO. As shown in the last column of Table VII, this transition state only lies a few kcal/mol above 21. So 21, (HCOH)₂, is a relatively shallow minimum on the energy surface. When

TABLE VII. Energies (kcal/mol) for the reaction 2 *trans*-HCOH → (HCOH)₂ → 2H₂CO.

Basis set ^a	2 <i>trans</i> -HCOH ^b	Complex 21 ^b	Barrier
		(HCOH) ₂	21→2 H ₂ CO
STO-3 G	95.3	75.5	1.4 (1.8) ^c
4-31 G/STO-3 G	105.5	83.7	7.4
4-31 G	102.3	84.8	2.9 ^c
6-31 G*/4-31 G	105.3	88.3	5.7 ^c
6-31 G*	103.9	85.4	

^aAs in Table VI.^bRelative to 2 H₂CO.^cFor a symmetrically exchange, see text.

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 (C₁H₆ ≈ C₃H₈ during the reaction). The STO-3 G barrier for the completely symmetric (C_{2h}) exchange is only slightly larger than the asymmetric one. For the larger basis sets we limited our calculations to C_{2h} symmetry. We also determined the infrared and Raman frequencies of 21 according to the method described in Sec. III 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 H₂CO 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 tunneling⁴⁴ might give a possible way to reach HCOH from the vibrationless S₁ level. In the nonzero pressure mechanism an alternative (or additional) lowering occurs: the bimolecular interactions described in Sec. V A lower the barrier to hydroxycarbene 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 hydroxycarbenes occurs [reaction (4)]. This offers a low energy path for HCOH → H₂CO. If one irradiates H₂CO, the concentration of HCOH will be too low to make such an exchange likely. In that case the HCOH...H₂CO 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 H₂CO configuration again⁴⁴; it is also possible that subsequent collisions are involved.⁴ In a rigid matrix dissociation of HCOH...H₂CO 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. V A. This mechanism approaches a collision complex (chemical) model. Of course, also purely kinetic (physical) collisions can produce HCOH: Zughul² showed that He, Ar, and Xe give CO nearly as rapidly as collisions with H₂CO itself. Houston¹ reported however, that Ar induces photoproducts from D₂CO much slower than D₂CO itself. At excitation energies higher than ≈ 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.⁴⁸ The high unimolecular barriers can be avoided by bimolecular hydrogen exchange. A similar problem exists in the H shift of N₂H₂.^{49,50}

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. Miller⁴⁴ showed that in that case a tunneling-induced interconversion HCOH-H₂CO 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. Weisshaar³ measured infrared fluorescence after 4₁¹ excitation of H₂CO in order to observe the intermediate state. It was not possible, however, to detect the short-lived emission of the hydroxycarbene OH stretch. This was due to the "quasicontinuum" emissions of highly vibrational S₀^{*} states, which are produced after nonreactive quenching. (The quantum yield for product formation was about 0.7.) We suggest that hydroxycarbene might be detectable in interstellar space, where there are truly unimolecular conditions, without perturbations of emitting S₀^{*} states. Formaldehyde is widely observed in the galaxy at radio wavelengths; it occurs in both high and relatively low density interstellar clouds.⁵¹ The H₂CO-HCOH situation can be analogous to the well-known HCN-HNC case. Hydrogen isocyanide was observed for the first time in interstellar space⁵²; in the laboratory the molecule rearranges easily to HCN. Also some other experiments are suggested from our theoretical results. Infrared and Raman frequencies of (H₂CO)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 importances 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 Pasto⁵⁰ for N₂H₂, have to wait until more experimental data are known. The uni- and bimolecular formation of gas-phase photoproducts from HCOH is another interesting topic for calculations. To

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 simple *ab initio* methods. For a starting point this is necessary, because fairly large sections of the potential energy surface of an eight-atom molecule have to be calculated. Fortunately, however, the experimentally controllable results (stabilization energies, infrared and Raman spectra) are very good, while the cases where we used several basis sets show that the results essentially 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 reaction⁵³ an aldol-type condensation results in the formation of hydroxy aldehydes, hydroxy ketones, and sugars. The interest in this reaction recently increased, because of its possible importance in the production of carbohydrates in spaceships.^{54,55} From this reaction some investigators even concluded⁵³ that formaldehyde is involved in photosynthesis. Especially the origin of glycolate H₂C(OH)COOH 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 involved in these reactions, especially in the primary condensation to glycoaldehyde. Theoretical studies, however, will have to use semiempirical methods, because the situation in the liquid phase is much more complicated: the actual reactant in aqueous solution is not H₂CO, but hydrated formaldehyde (methylene glycol).

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