Ab Initio Studies of the Glyoxal Unimolecular Dissociation Pathways[†]

Denise M. Koch, Nam Huan Khieu, and Gilles H. Peslherbe*

Centre for Research in Molecular Modeling, and Department of Chemistry and Biochemistry,
Concordia University, Montréal, Québec, Canada H3G 1M8

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Glyoxal ($C_2H_2O_2$) unimolecular dissociation has been the subject of many experimental and theoretical studies, and some questions remain regarding the predominant pathway for dissociation. Molecular beam photodissociation studies identify the major pathway as that which leads to the formation of formaldehyde (CH_2O) and carbon monoxide (CO). Thermal decomposition experiments and theoretical studies, on the other hand, predict the *triple whammy* pathway that leads directly to $H_2 + 2CO$ to be predominant. The objective of this study is to elucidate this discrepancy by performing a thorough ab initio exploration of the free energy surface for glyoxal dissociation. Gaussian-3 (G3) theory was shown to be an appropriate method for studying glyoxal unimolecular dissociation since the calculated heats of reaction agree well with reliable experimental values. On the other hand, other *standard* model chemistries, including the popular hybrid-density functional theory methods, predict poor heats of reaction for glyoxal dissociation. Various pathways for ground-state glyoxal unimolecular dissociation were then explored with G3 theory. We identified nonplanar transition state structures that lie lower in energy than the previously reported planar stationary points for both the triple whammy and formaldehyde channels. Three pathways, i.e., the formaldehyde, triple whammy and hydroxymethylene channels, have activation free energies that fall below typical experimental glyoxal photoexcitation energies and are thus possible under the experimental conditions. The formaldehyde channel was shown to be predominant at low temperatures, in agreement with molecular beam experiments and in contrast to previous theoretical predictions. As temperature increases, however, the ordering of the activation barriers is reversed and the predominant channel becomes the triple whammy channel, as observed in high-temperature thermal experiments. The temperature dependence of the activation barriers is attributed to the vibrational structure of the transition states relative to that of glyoxal, which significantly affects the entropic contributions to the activation barriers. The present study ultimately reconciles various sets of experimental findings and theory.

1. Introduction

Prior to the 1980s, glyoxal ($C_2H_2O_2$) was studied extensively as a paradigm for investigating the molecular photophysics and photochemistry[1−8] of small molecules. The recognition of the importance of glyoxal in tropospheric chemistry[9,10] and in combustion chemistry[11] recently spawned renewed interest in many unresolved issues concerning its dissociation dynamics. The most important of these issues deals with the actual dissociation pathways for glyoxal.

Following the pioneering work of Parmenter,[5] it was generally accepted that photodissociation of glyoxal produced mainly formaldehyde (CH_2O) and carbon monoxide (CO). This was believed to occur from the first excited triplet state T_1 after collision-induced intersystem crossing from the first excited singlet state S_1. A low-pressure photochemical study performed by Rordorf et al.[12] shortly after provided strong evidence that glyoxal dissociates under collision-free conditions where triplet formation is precluded. This work was followed by two low-pressure photolysis studies[13,14] where predissociation, i.e. interconversion from the zero point level of the S_1 state to the vibrationally excited ground electronic state S_o level, was shown to occur prior to dissociation. Loge et al.[14] assigned an upper bound of 62.9 kcal/mol for the glyoxal unimolecular dissociation activation energy, which corresponds to the energy supplied by the 454.5 nm Argon excimer laser employed in the photolysis experiments. Another important finding stemming from these studies was the identification of H_2 as one of the major products of glyoxal photodissociation. Loge et al.[14] evaluated that the ratio for CH_2O:CO:H_2 products was approximately 1.4:2.5:1.0, and they proposed a two-step mechanism involving formaldehyde as an intermediate in order to account for the product ratios observed:

$$C_2H_2O_2 \rightarrow CH_2O^* + CO$$

$$CH_2O^* \rightarrow H_2 + CO$$

Shortly after this two-step mechanism was proposed, Osamura et al.[15,16] argued in a theoretical study that a concerted unimolecular mechanism could account for the presence of H_2 as a photodissociation product, leading directly from $C_2H_2O_2$ to $H_2 + 2CO$ via a pathway now known as the triple whammy channel. Since previous experimental[17−19] and theoretical[20−25] studies agreed on an activation energy for formaldehyde dissociation of ∼80 kcal/mol—which is much higher than the energy available for the glyoxal unimolecular dissociation

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* Corresponding author. E-mail: ghp@alcor.concordia.ca. Telephone: (514) 848−3335. FAX: (514) 848−2868.

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products under the conditions used in the photochemical studies—further dissociation of CH_2O and production of H_2 via a two-step mechanism should be precluded. The triple whammy mechanism was postulated on the basis of ab initio optimizations of transition states that lead to dissociation via both the triple whammy and formaldehyde channels. Dissociation to $H_2 + 2CO$ was shown to proceed from the cis-isomer of glyoxal since the hydrogen atoms need to be relatively close together in the transition state to produce H_2. Osamura et al. found an activation energy for the triple whammy channel below the previously determined experimental upper bound for the dissociation activation energy (62.9 kcal/mol). Furthermore, the calculations placed the activation barrier for the triple whammy channel lower than that for the formaldehyde channel, thus suggesting that the triple whammy channel would be the predominant pathway in glyoxal dissociation.

The existence of the triple whammy channel was later confirmed in a molecular beam photodissociation experiment performed by Hepburn et al.,[26] in which glyoxal was excited to low-lying vibrational levels of the S_1 state. In fact, three major pathways for glyoxal dissociation were identified:

formaldehyde channel: $$C_2H_2O_2 \rightarrow CH_2O + CO \qquad (1)$$

triple whammy channel: $$C_2H_2O_2 \rightarrow H_2 + 2CO \qquad (2)$$

hydroxymethylene channel: $$C_2H_2O_2 \rightarrow HCOH + CO \qquad (3)$$

where channel 1 accounted for 65%, channel 2 for 28%, and channel 3 for 7% of the product yields. Since a 439.8 nm Nd :YAG excimer laser was employed, an upper bound of 65.0 kcal/mol can be assigned to the newly observed dissociation pathway leading to hydroxymethylene. Although this study provided strong evidence for the existence of the triple whammy channel, it was in contradiction with Osamura et al.'s conclusion that this channel would be the major dissociation pathway of vibrationally excited ground electronic state glyoxal.

Thermal decomposition experiments performed at temperatures below 800 K also showed the predominance of the formaldehyde channel over the triple whammy channel with a ratio of 5.25:1.00.[27] The high-pressure threshold for glyoxal dissociation was estimated to be around 52.6 kcal/mol. Later, Saito et al.[28] performed a low-pressure pyrolysis experiment at temperatures between 1100 and 1540 K. In contradiction to previous experimental studies, the predominance of the triple whammy pathway over the formaldehyde channel was observed with a ratio of 2.4:1.0. Kinetic analysis of the data yielded low-pressure activation barriers of 47 and 58 kcal/mol for channels 2 and 1, respectively. These findings suggested that the ordering of the formaldehyde and triple whammy channels may change under varying experimental conditions.

Accordingly, Roscoe and Back[29] studied the pressure dependence of H_2 to CO product ratios by selectively exciting either *trans*-glyoxal or *cis*-glyoxal. The latter is assumed to dissociate primarily via the triple whammy channel. Extrapolation of product ratio curves to zero pressure showed that collision-free dissociation of *cis*-glyoxal would proceed largely through the triple whammy channel. The formaldehyde channel became more important as pressure was increased, thus implying that collisional deactivation of vibrationally excited S_o glyoxal leads to dissociation via the lower energy formaldehyde pathway. Since the formaldehyde channel seemed to be precluded under collision-free conditions, in contrast with Hepburn et al.'s conclusions, it was proposed that a long-lived intermediate may have distorted the product yields obtained in the molecular beam experiment.

In response to this conjecture, Burak et al.[30] performed a time-resolved molecular beam photodissociation experiment aimed at elucidating the nature of this possible intermediate. The analysis of product translational and rotational energy distributions provided strong evidence that dissociation of glyoxal occurs immediately following interconversion from the S_1 to the S_o state, thus refuting the proposal that the presence of a long-lived intermediate state might have affected the product yields. Furthermore, these findings suggested that the extrapolation to zero pressure performed by Roscoe and Back was questionable since the formaldehyde channel is undoubtedly predominant under collision-free conditions.

The experiments described hereabove established that the formaldehyde channel is predominant at both low and high pressures. At high temperatures on the other hand, Saito et al.'s results unambiguously demonstrate the predominance of the triple whammy channel, in accord with Osamura et al.'s theoretical predictions. However, the calculated activation energies for both the triple whammy and formaldehyde channels are in serious disagreement with the results of high-temperature thermal measurements, and theoretical studies to date even predict an ordering of the activation barriers that is opposite to what is observed experimentally. Finally, theoretical studies predict that the formaldehyde channel is precluded under typical experimental photochemical conditions, because of the very large activation barrier calculated for this pathway, in total contradiction with experimental findings.

Our goal is to perform a thorough investigation of the glyoxal free energy surface in order to resolve the discrepancies between various experiments on one hand and between experiment and theory on the other hand. Ab initio calculations are employed to characterize the glyoxal unimolecular dissociation pathways and the asssociated activation barriers. A major objective of this work is to determine a level of ab initio electronic structure theory reliable enough to properly describe glyoxal, its derivatives, and its dissociation pathways. We also investigate the temperature dependence of the activation barriers for all reaction pathways in order to make a connection between our theoretical predictions and actual molecular beam, photolysis, and thermal experiments.

The outline of this article is as follows. A brief description of the computational methodology employed to explore the glyoxal free energy surface and its range of validity is first given in section 2. Transition states and reaction pathways are then presented and discussed in section 3, where connection is made between our findings and those of previous experimental and theoretical studies. Concluding remarks follow in section 4.

2. Methodology

The ab initio calculations were performed using the Gaussian 98 suite of programs.[31] Reactant and product thermochemical properties were first determined by performing geometry optimizations and frequency calculations using various model chemistries. The resulting enthalpies and free energies are calculated using standard statistical thermodynamics within the harmonic oscillator-rigid rotor approximation.[32] The model chemistry best suited to explore the glyoxal free energy surface was chosen by comparing calculated heats of reaction with reliable experimental data.

Heats of reaction calculated with various standard model chemistries are listed in Table 1. It is remarkable that the very popular hybrid density-functional method using Becke3 exchange and Lee-Yang-Parr correlation (B3LYP) predicts endothermic reactions for glyoxal dissociation via the formal-

TABLE 1: Heats of Reaction (kcal/mol)[a]

	pathway			
	glyoxal isomerization	formaldehyde channel	triple whammy channel	formaldehyde dissociation
HF/3-21G	5.2	7.6	10.6	3.0
B3LYP/6-31G*	4.1	3.4	7.6	4.2
B3LYP/6-311+G**	4.3	2.9	0.0	57.9
MP2/6-31G*	4.2	2.2	6.5	4.4
MP2/6-311+G**	4.0	4.3	7.9	3.6
MP4(SDTQ)/6-311+G**//MP2/6-311+G**	3.6	6.8	12.9	6.1
QCISDT/6-311+G**//MP2/6-311+G**	4.1	6.1	10.7	4.6
G2	4.5	2.7	4.0	1.3
G3	4.7	1.7	2.3	1.6
experiment	4.8 ± 0.3[b]	1.7 ± 0.1[c]	2.2 ± 0.1[c]	2.1 ± 0.1[d]

[a] Heats of reaction are calculated relative to *trans*-glyoxal. [b] Reference 46. [c] Reference 53. [d] Reference 21.

dehyde and triple whammy reaction pathways, in contradiction with experimental results. On the other hand, the other model chemistries explored predict exothermic reaction pathways, in agreement with experiment, but they all tend to overestimate the reaction exothermicities. As anticipated from previous theoretical studies,[33] electron correlation is essential for describing the electronic structure of glyoxal and its dissociation products, and second-order Møller−Plesset (MP2) theory predicts heats of formation closer to experimental values than Hartree−Fock (HF) theory. Addition of polarization and diffuse functions in the basis set or using higher-level theories, such as fourth-order Møller−Plesset (MP4) and quadratic configuration interaction (QCISDT), does not seem to yield better heats of reaction, and most standard model chemistries fail to accurately describe the thermodynamics of glyoxal dissociation.

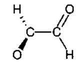
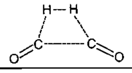
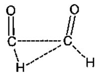
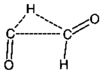
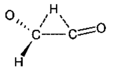
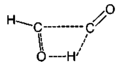
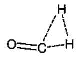
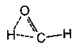
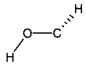
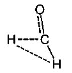
In contrast to standard model chemistries, the composite Gaussian-2 (G2)[34] and Gaussian-3 (G3)[35] methods, which typically correct energies determined with the MP2(Full)/6-31G* model chemistry by extrapolating to larger basis sets and higher levels of theory, yield heats of reaction that are in excellent agreement with experimental values. It should be noted that this is not a surprising result, since *trans*-glyoxal, formaldehyde, hydrogen, and carbon monoxide are part of the G2 and G3 training sets, and thus, one expects these methods to reproduce relatively well the experimental heats of formation for these compounds. *cis*-Glyoxal is not part of the G2 and G3 training sets, and it is very encouraging to see that yet the G2 and G3 enthalpy differences between the *cis*- and *trans*-isomers of glyoxal agree very well with experiment. Since the G3 method predicts heats of reaction within 1% of experimental values, we expect this model chemisty to accurately describe the glyoxal potential energy surface and thus, we chose that model chemistry to investigate the glyoxal free energy surface.[36]

In the G3 methodology,[35] the electronic energy is evaluated from a series of high-level calculations performed at the optimized MP2(full)/6-31G* molecular structure, while the less computationally intensive HF/6-31G* model chemistry is employed to compute frequencies and evaluate thermochemistry corrections. Since G3 employs MP2(full)/6-31G* molecular structures, we first performed an exhaustive search of transition states on the glyoxal potential energy surface, and we performed intrinsic reaction coordinate (IRC) calculations[37−39] to connect the various transition states to their respective reactants and products. We then evaluated the G3 free energies of the reactants, transition states, and products, in order to determine the actual activation energies for each reaction pathway.

3. Results and Discussion

The various pathways that we explored for glyoxal unimolecular dissociation are shown in Table 2, along with the transition state structures involved. The dissociation pathways for formaldehyde and hydroxymethylene were also included, to explore all possible avenues of H_2 production. The activation free energies predicted by G3 theory at 0, 300, and 1400 K are given in Table 3 for all pathways considered. As mentioned in the previous section, G3 theory applies a series of corrections to the energies of structures optimized at the MP2-(full)/6-31G* level of theory.[35] Thus, activation barriers calculated with the MP2(full)/6-31G* model chemistry have also been included in Table 3, in order to assess the extent of the corrections applied to the MP2 energies by G3 theory. In general, the values predicted by G3 theory are 7−15% lower than the corresponding MP2(full)/6-31G* values. This demonstrates again the importance of electronic correlation for this system.

TABLE 2: Glyoxal Unimolecular Dissociation Pathways and Transition States

	Reaction Channel	Transition state	
1	isomerization: *trans*-$C_2H_2O_2 \rightarrow$ *cis*-$C_2H_2O_2$	TS1	
2	triple whammy: *cis*- $C_2H_2O_2 \rightarrow H_2 + 2CO$	TS2	
3	formaldehyde: *trans*-$C_2H_2O_2 \rightarrow CH_2O + CO$	TS3a	
		TS3b	
		TS3c	
4	hydroxymethylene: *trans*-$C_2H_2O_2 \rightarrow HCOH + CO$	TS4	
5	formaldehyde dissociation: $CH_2O \rightarrow H_2 + CO$	TS5	
6	hydroxymethylene isomerization: $HCOH \rightarrow CH_2O$	TS6	
7	hydroxymethylene isomerization: *trans*-HCOH $\rightarrow$ *cis*-HCOH	TS7	
8	hydroxymethylene dissociation: $HCOH \rightarrow H_2 + CO$	TS8	

The first pathway explored, glyoxal isomerization, has 0 and 300 K activation barriers of 5.6 and 5.4 kcal/mol, respectively, which are in very good agreement with the average value of 5.5 kcal/mol obtained from previous experimental[40−46] and theoretical[15,33,47−51] studies. The rotational barrier is high enough

TABLE 3: Activation Free Energies (kcal/mol)

	MP2(full)/6-31+G*			G3		
	0 K	300 K	1400 K	0 K	300 K	1400 K
TS1[a]	6.4	6.3	8.7	5.6	5.4	8.1
TS2[a]	62.9	61.7	55.9	61.1	60.0	50.7
TS3a[a]	82.4	81.5	76.7	75.1	74.0	67.1
TS3b[a]	85.0	84.4	80.7	77.6	76.7	71.4
TS3c[a]	61.4	61.1	60.9	55.4	55.1	55.7
TS4[a]	66.0	65.3	63.0	60.7	60.3	58.3
TS5[b]	91.6	91.1	88.0	81.1	80.6	77.3
TS6[b]	89.5	89.0	87.2	82.5	82.0	78.9
TS7[c]	30.5	30.4	30.1	27.3	27.3	27.4
TS8[c]	30.2	30.2	29.1	28.9	28.8	27.8

[a] Relative to *trans*-glyoxal. [b] Relative to formaldehyde. [c] Relative to *trans*-hydroxymethylene.

to produce a ratio of *trans*- to *cis*-glyoxal of 1000:1 at room temperature.[41] Since dissociation via the triple whammy pathway is known to proceed from *cis*-glyoxal, one might argue that the formaldehyde channel would be predominant at room temperature. However, under the experimental conditions employed in photolysis and pyrolysis studies, the population of each isomer is nearly equal,[29] such that dissociation from either isomer, that is via either the formaldehyde or triple whammy channels, is equally probable.

As mentioned earlier, the dissociation of *cis*-glyoxal to H_2 + CO, the triple whammy pathway, has been the subject of two previous theoretical studies.[16,33] Both studies explored a planar stationary point that was not a true transition state and was in fact a second-order saddlepoint. We were able to identify this planar second-order saddlepoint with the MP2(full)/6-31G* model chemistry. The largest imaginary frequency for that structure corresponds to the reaction coordinate, describing dissociation toward the triple whammy products, while the smaller imaginary frequency corresponds to an out-of-plane bending mode. The latter suggests that a true, nonplanar transition state lies lower in energy than the second-order saddlepoint. Therefore, we investigated a nonplanar transition state, hereafter referred to as TS2, that we found to lie less than 1 kcal/mol lower in energy than the planar saddlepoint structure. The 0 K activation barrier of 61.1 kcal/mol predicted by G3 theory for the triple whammy channel is 6.5 kcal/mol higher than the value reported earlier by Scuseria and Schaefer.[33] Inspection of the heats of reaction listed in Table 1 suggest that most model chemistries, including QCISD(T)/6-311+G** which is similar to that used by Scuseria and Schaefer, tend to overestimate the stability of the glyoxal dissociation products relative to the reactants. It is conceivable that similar arguments apply to the calculations of Scuseria and Schaefer, in which both the position of the reaction products and the activation barrier relative to that of the reactants would be lower than expected. Finally, the 1400 K barrier height of 50.7 kcal/mol predicted by G3 theory agrees well with the value of 47 kcal/mol obtained by Saito et al.[28] from thermal decomposition experiments.

Three transition states were considered for the glyoxal dissociation pathway leading to the production of CH_2O and CO. The first two transition states, referred to as TS3a and TS3b, correspond to the planar structures investigated by Osamura et al.[15,16] The G3 activation barriers at 0 K presented in Table 3 are 82.4 and 85 kcal/mol for the TS3a and TS3b pathways, respectively, and are significantly lower than previously calculated values of above 100 kcal/mol.[15] Nonetheless, these barriers are considerably higher than the upper bound for the activation energy of 62.9 kcal/mol[14] for the photolysis of glyoxal on the S_o state. Since the transition state for the triple whammy channel was shown to be nonplanar, we also explored a third nonplanar transition state, named TS3c, which turned out to be much lower in energy than the former two transition states. As a matter of fact, the activation energy for the TS3c formaldehyde pathway is lower than that for the triple whammy channel at room temperature, indicating that this pathway will be predominant in molecular beam and photolysis experiments. Moreover, the activation free energy for the TS3c pathway at 1400 K, i.e., 55.7 kcal/mol, is comparable to the low-pressure high-temperature value of 58 kcal/mol estimated by Saito et al.[28] This is, to our knowledge, the first theoretical study that provides viable predictions for the activation barrier of glyoxal dissociation via the formaldehyde pathway.

The final glyoxal dissociation pathway explored leads to the formation of HCOH and CO. Since this channel has not been addressed in previous theoretical studies, it was important, as a first step, to determine the most stable conformer of hydroxymethylene. Geometry optimizations performed with the MP2(full)/6-31G* model chemistries for both singlet and triplet states as well as *trans*- and *cis*-isomers yielded singlet *trans*-HCOH as the most stable conformer, in agreement with a previous theoretical study of singlet-state HCOH by Goddard et al.[23] Assuming that glyoxal will dissociate to the most stable HCOH conformer, a planar transition state, referred to as TS4, connecting *trans*-$C_2H_2O_2$ to *trans*-HCOH and CO was identified. The corresponding 0 K activation barrier of 60.7 kcal/mol predicted by G3 theory falls below the experimental upper bound of 65.0 kcal/mol,[26] thus confirming the possibility of glyoxal dissociation via the hydroxymethylene pathway in molecular beam experiments.

To probe all possible avenues for H_2 production under photolysis and pyrolysis conditions, the formaldehyde and hydroxymethylene dissociation channels were also investigated. The calculated activation barrier for formaldehyde dissociation presented in Table 3 is 81.1 kcal/mol, not surprisingly in very good agreement with the average value of ~80 kcal/mol found in previous experimental[17−19] and theoretical[20−25] studies. For all temperatures considered, the barrier height lies at least 14 kcal/mol above typical photochemical glyoxal excitation energies (62.9 kcal/mol), thus precluding this pathway for H_2 production in photochemical experiments.

Since hydroxymethylene is a very reactive carbene species, it is likely that it will react promply after formation. Under collision-free conditions, the only possible reaction pathways for hydroxymethylene are isomerization to formaldehyde via TS6 or dissociation to H_2 and CO via TS8. The isomerization pathway has been the subject of two previous theoretical studies[22,23] in which 0 K activation barriers of 81.4 and 84.0 kcal/mol were reported. The G3 value reported in Table 3 of 82.5 kcal/mol agrees well with the earlier theoretical predictions.

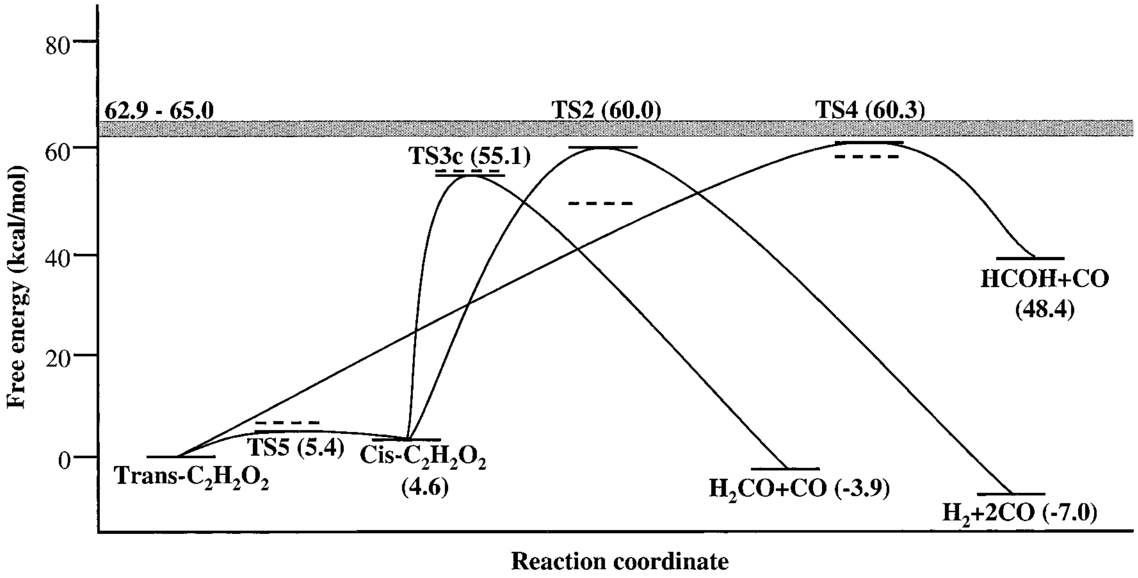


Figure 1. Free energy surface for glyoxal unimolecular dissociation. Solid lines indicate activation barriers at 300 K with values indicated in parentheses. Dashed lines correspond to activation barriers at 1400 K.

Because of the high barrier, isomerization of hydroxymethylene cannot contribute to the product yields of CH_2O.

The dissociation of hydroxymethylene has, to our knowledge, never been studied. As for the triple whammy channel, the hydrogen atoms need to be relatively close to each other in order to form the dissociation products. For this reason, we addressed the isomerization of *trans*- to *cis*-HCOH, via TS7, in their most stable singlet states. The 0 K rotational barrier of 27.3 kcal/mol for *trans*- to *cis*-isomerization is only slightly lower than the activation barrier of 29 kcal/mol for hydroxymethylene dissociation itself, via TS9. This suggests that hydroxymethylene may dissociate rapidly after isomerization. However, since the free energy of hydroxymethylene relative to glyoxal is estimated at 48.4 kcal/mol with G3 theory, both the isomerization and dissociation barriers lie far above typical photochemical glyoxal excitation energies, precluding any hydroxymethylene dissociation pathway under experimental conditions.

The results presented above indicate that, under typical experimental conditions—which involve excitation energies in the range of 62.9−65.0 kcal/mol, glyoxal may dissociate via the formaldehyde, triple whammy and hydroxymethylene channels and that the resulting dissociation products cannot undergo any further dissociation. Figure 1 depicts the free energy surface for glyoxal dissociation and the activation barriers for the three possible pathways at 300 and 1400 K. At 300 K, the activation energy for the formaldehyde channel (via TS3c) is clearly lower than that of both the triple whammy (via TS2) and hydroxymethylene (via TS4) channels. The ordering of the activation barriers at this temperature support the product yields obtained in the molecular beam experiments performed by Hepburn et al.[26] and Burak et al.,[30] the thermal decomposition experiment performed by Lowden[27] as well as Loge et al.'s photolysis experiments.[13,14] The small energy difference between the triple whammy and hydroxymethylene channels, which we should point out is within the range of accuracy of our ab initio calculations, cannot really account for the large difference in product yields of 28 and 7%, respectively, found by Hepburn et al.[26] In fact, based on the energy difference between the two activation barriers, a ratio of H_2 to HCOH of around 1.5:1.0 would be expected instead of the observed 3.9:1.0 ratio. As discussed previously, HCOH will not have enough internal energy after the dissociation from glyoxal to either isomerize or dissociate. It is conceivable, however, that the preference for the triple whammy channel over the hydroxymethylene channel stems from a very large driving force for the former channel, as its reaction products lie much lower in free energy compared to the transition state, which is not the case for the hydroxymethylene. Finally, we note that previous studies have been mainly concerned with the predominance of either the formaldehyde or the triple whammy channels, not so much that of the hydroxymethylene channel, which has been postulated and not unambiguously demonstrated experimentally so far. Our present calculations do support the existence of this channel, but they may overemphasize its importance in molecular beam experiments.

We now turn our attention to the thermal decomposition experiment performed by Saito et al.[28] at temperatures between 1100 and 1540 K. Our theoretical predictions of the activation barriers at 1400 K are given in Table 3 and are shown in Figure 1. It is remarkable that, at this high temperature, the barriers for the formaldehyde and triple whammy channels are reversed, compared to the room-temperature situation. This suggests that the triple whammy channel is predominant under high-temperature conditions with an estimated H_2 to CH_2O ratio of 2.5:1.0 at 1400 K, in excellent agreement with Saito et al's findings.

To elucidate the reversal in the barrier heights for the formaldehyde and triple whammy channels, we analyzed the temperature dependence of the activation free energies. A closer look at the barrier heights for TS3c and TS2 in Table 3 reveals that the barrier for the formaldehyde channel is nearly independent of temperature, whereas that for the triple whammy channel decreases with increasing temperature. To understand these differing behaviors, we list in Table 4 the changes in activation enthalpies and entropies as a function of temperature (relative to the 0 K values) for the formaldehyde and triple whammy channels. Clearly, the temperature dependence of the activation barriers for both channels is governed to a large extent by the changes in entropy, and the entropy change is actually much larger for the triple whammy channel. This is not too surprising, considering that the triple whammy channel produces three products whereas the formaldehyde channel produces two, and thus, the triple whammy channel must involve a transition state with a larger number of loose modes relative to glyoxal.

Various contributions to the activation entropy changes are

TABLE 4: Contributions to the Activation Free Energies for the Triple Whammy (TS2) and Formaldehyde (TS3c) Channels[a]

	TS2		TS3c	
	300 K	1400 K	300 K	1400 K
$\Delta H^{\ddagger}$	0.76	2.18	0.22	0.98
$T\Delta S^{\ddagger}$	1.92	12.56	0.03	1.32
$\Delta S^{\ddagger}$	6.39	8.97	0.09	0.94
$\Delta S^{\ddagger}_{\text{trans}}$	0.00	0.00	0.00	0.00
$\Delta S^{\ddagger}_{\text{rot.}}$	0.88	0.88	1.58	1.58
$\Delta S^{\ddagger}_{\text{vib}}$	5.51	8.09	1.50	2.53

[a] Activation enthalpies $\Delta H^{\ddagger}$ and entropy contributions $T\Delta S^{\ddagger}$ are in kcal/mol, while activation entropies $\Delta S^{\ddagger}$, translational $\Delta S^{\ddagger}_{\text{trans}}$, rotational $\Delta S^{\ddagger}_{\text{rot.}}$, and vibrational $\Delta S^{\ddagger}_{\text{vib}}$ activation entropies are in cal/(mol·K). All values are calculated relative to *trans*-glyoxal and relative to 0 K values.

TABLE 5: Vibrational Frequencies (cm^{-1}) of the TS2, TS3c, and *trans*-Glyoxal Structures

TS2	TS3c	*trans*-glyoxal
		156
81	235	372
171	564	612
223	740	909
342	948	1118
718	1078	1197
1054	1343	1465
1405	1487	1506
1412	1599	2015
1772	1785	2054
2321	2336	3227
2322	3261	3230

listed in Table 4. Since the translational and rotational entropy changes are constant at a given temperature, the entropy change with temperature depends entirely on the vibrational modes of each species. The magnitude of the vibrational entropy change is much larger for the triple whammy channel than that for the formaldehyde channel. This can simply be traced back to the fact that the transition state for the triple whammy channel (TS2) is much looser than *trans*-glyoxal, whereas that for the formaldehyde channel (TS3c) has a vibrational structure similar to that of glyoxal. As shown in Table 5, the frequencies of TS2 are considerably lower than those of *trans*-glyoxal, whereas those of TS3c are of similar magnitude to those of glyoxal.[52] This results in a large positive entropy change for the triple whammy channel and a negligible entropy change for the formaldehyde channel. This explains why the barrier for the triple whammy channel significantly decreases with increasing temperature, while that for the formaldehyde channel is nearly independent of temperature.

4. Concluding Remarks

A number of ab initio model chemistries were tested by comparing calculated heats of reaction for glyoxal dissociation with their experimental counterparts. Most standard model chemistries, including the popular B3LYP method, fail to describe properly the thermodynamics of glyoxal dissociation. On the other hand, composite G2 and G3 methods seem to be adequate for that purpose. We then explored all possible pathways for ground-state glyoxal unimolecular dissociation with G3 theory. Transition-state structures were optimized and reaction pathways were computed with MP2(full)/6-31G*, which is the model chemistry employed in G3 theory for molecular structures. Nonplanar transition states that lie lower in energy than planar stationary points are reported for the first time for both the formaldehyde and triple whammy channels. Activation free energies were then calculated with G3 theory. Our results indicate that, under typical experimental photochemical conditions—where the glyoxal excitation energy is in the range of 62.9−65.0 kcal/mol−the formaldehyde, triple whammy and hydroxymethylene channels are all possible dissociation channels, and that the freshly generated formaldehyde and hydroxymethylene cannot undergo further dissociation. The calculated activation free energies at high temperatures are also in very good agreement with previous experimental results.

Further, the temperature dependence of the activation free energies allows one to resolve discrepancies between molecular beam and high-temperature thermal decomposition experiments regarding the predominance of the formaldehyde and triple whammy channels. Our calculations show that the barrier for the formaldehyde channel is lower than that for the triple whammy channel at 0 and 300 K, but it is higher at 1400 K. In fact, the activation free energy for the formaldehyde channel is essentially independent of temperature, whereas that for the triple whammy channel significantly decreases with increasing temperature. The temperature dependence can be traced back to the difference in the vibrational activation entropies. The latter is significant for the triple whammy channel, which involves a transition state much looser than glyoxal, while it is negligible for the formaldehyde channel, which involves a transition state with a vibrational structure similar to that of glyoxal. As a result of the temperature dependence of the activation free energies and the reversal of the activation barrier ordering, the triple whammy channel is found to be predominant at high temperatures, in agreeement with what is observed in high-temperature thermal experiments, while the formaldehyde channel is predominant at low temperatures, in agreement with the product yields reported in molecular beam studies. This theoretical study gives, for the first time, a viable explanation for the differing findings reported in molecular beam and thermal decomposition experimental studies.

Note Added in Proof. After this article was submitted for publication, a note appeared in the *Journal of Chemical Physics* (Li, X.; Schlegel, H. B. *J. Chem. Phys.* **2001**, *114*, 8) which reported investigations of glyoxal unimolecular photodissociation at the CBS-APNO level of theory. Our room-temperature results with G3 theory are in excellent agreement with the CBS-APNO calculations.

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