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A UNIMOLECULAR REACTION  $ABC \rightarrow A + B + C$  INVOLVING THREE PRODUCT MOLECULES AND A SINGLE TRANSITION STATE. PHOTODISSOCIATION OF GLYOXAL:  $OO \parallel \parallel HCCH \rightarrow H_2 + CO + CO$

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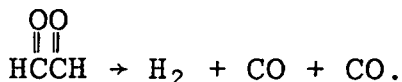
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Yoshihiro Osamura, Henry F. Schaefer III,  
Michel Dupuis, and William A. Lester, Jr.

July 1981

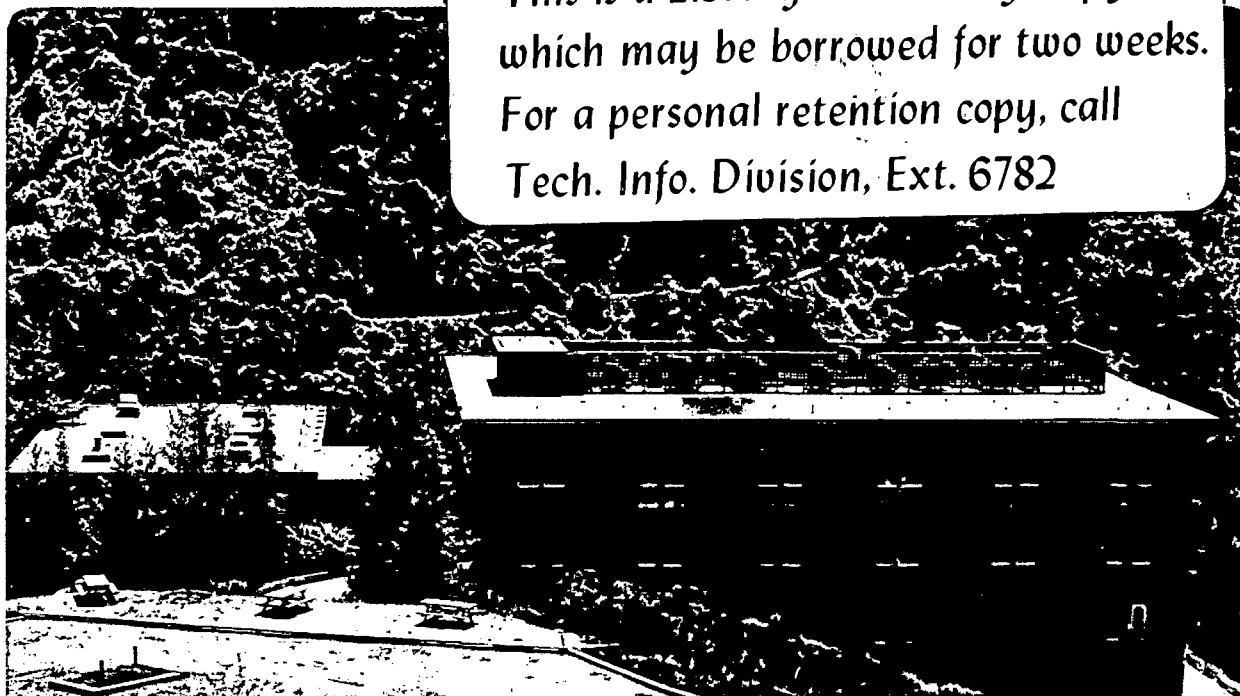
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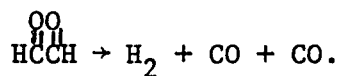


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A Unimolecular Reaction  $ABC \rightarrow A + B + C$  Involving Three Product Molecules  
and a Single Transition State. Photodissociation of Glyoxal:



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Abstract

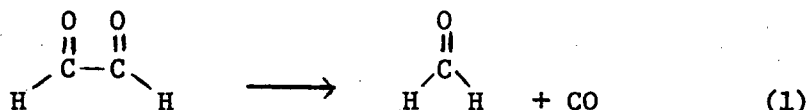
Following an earlier proposal [Y. Osamura and H. F. Schaefer, J. Chem. Phys. 74, 4576 (1981)], the unimolecular reaction  $\text{HCCH} \rightarrow \text{H}_2 + \text{CO} + \text{CO}$  has been examined via nonempirical molecular electronic structure theory. Specifically, the constrained symmetric (point group  $C_{2v}$ ) transition state for this  $\text{ABC} \rightarrow \text{A} + \text{B} + \text{C}$  reaction has been located at several levels of self-consistent-field (SCF) theory. Four different basis sets of contracted gaussian functions were used: an STO-3G minimum basis, the small split valence 3-21G basis, the standard C(9s 5p/4s 2p) double zeta (DZ) set, and a double zeta plus polarization (DZ+P) basis. Vibrational analyses of the four stationary point structures (all of which are geometrically similar) yield a remarkable variety of results. The STO-3G stationary point has three imaginary vibrational frequencies, 3-21G has one imaginary frequency (and thus is a genuine transition state), while the DZ and DZ+P structures yield two imaginary vibrational frequencies. For the latter two cases, one of the two imaginary vibrations is a very small bending frequency, while the larger frequency clearly connects glyoxal with the three products  $\text{H}_2 + \text{CO} + \text{CO}$ . This suggests the existence of a slightly nonplanar true transition state. To our knowledge such a unimolecular transition state is without precedent. Configuration interaction (CI) suggests that the barrier for this  $\text{ABC} \rightarrow \text{A} + \text{B} + \text{C}$  reaction is competitive with that for  $\text{HCCH} \rightarrow \text{H}_2\text{CO} + \text{CO}$ .

## I. Introduction

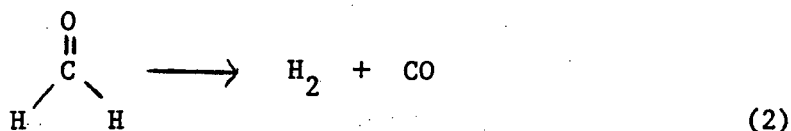
The spectroscopy of glyoxal ( $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ ) has been the subject of intensive experimental<sup>1-14</sup> and theoretical<sup>15-20</sup> study in recent years. This has led to many new insights, including for example the realization<sup>15,17</sup> that there is a reasonably low-lying  $\pi \rightarrow \pi^*$  triplet state and a second  $n \rightarrow \pi^*$  triplet state, both below  $30,000 \text{ cm}^{-1}$ . There has also been a smooth progression from the spectroscopy of glyoxal to its photophysics and photochemistry.<sup>21-45</sup> Perhaps most exhaustively studied has been the internal conversion (radiationless transition) from the lowest  $n \rightarrow \pi^*$  singlet state  $S_1$  to the vibrationally excited levels of the  $S_0$  ground state.<sup>33,40,41</sup> Additionally, while the intersystem crossing ( $S_1 \rightarrow T_1$ ) does not apparently occur under collisionless conditions, collisional quenching of  $S_1$  does produce  $T_1$  with nearly unit quantum yield.<sup>36,45</sup>

In light of the remarkable amount of dynamical information available concerning the decay of  $S_1$  glyoxal, it is perhaps surprising that a less complete mechanistic picture exists for the ensuing photodissociation. For example, McDonald and colleagues stated<sup>14</sup> early this year that "the excited electronic states (of glyoxal) decay by predissociation, although neither the dissociation threshold nor the detailed mechanism are precisely known". The most recent in-depth discussion of the experimental facts is that of Loge, Parmenter, and Rordorf.<sup>43</sup> They emphasize that, contrary to previous expectations,<sup>40</sup> glyoxal does appear to dissociate from the zero-point level in the absence of collisions. The observed independence of glyoxal pressure and linear dependence on laser power validates the idea that the dissociation is "a one-photon process with first-order  $S_1$  kinetics."

Loge, Parmenter, and Rordorf (LPR) report a mixture of products, of which H<sub>2</sub> and CO constitute the noncondensable fraction. The condensable product is identified mass spectrometrically as formaldehyde (or one of its isomers), suggesting for the primary photochemical step

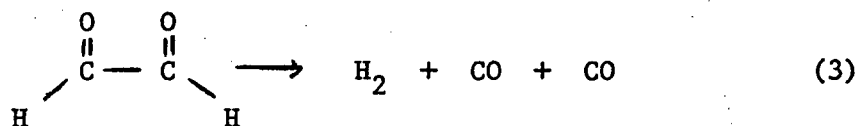


LPR note that "up to 180 kJ/mole" (43 kcal/mole) of vibrational energy is available for formaldehyde in (1), and conclude that this may lead to a second unimolecular decomposition



to yield the observed H<sub>2</sub>.

In an earlier paper<sup>20</sup> primarily concerned with the glyoxal internal rotation barrier, we stated our skepticism concerning the importance of reaction (2) in glyoxal photochemistry. There we proposed that the H<sub>2</sub> product observed by Parmenter<sup>21</sup> might be explained in terms of the single reaction



To our knowledge, reaction (3) would be unique among experimentally understood processes in that it is a unimolecular reaction involving one transition state and three molecular products. The reverse

reaction is a termolecular association reaction, and all properly instructed physical chemists are taught at an early age that such termolecular reactions are generally unlikely.<sup>46</sup>

The purpose of the present research, then, is to theoretically explore the viability of reaction (3), an elementary unimolecular reaction with three molecular products. Although it cannot be stated unequivocally that (3) is the source of  $H_2$  in collisionless glyoxal photodissociation, this research provides firm theoretical support for the plausibility of such a molecular mechanism.



## II. A Qualitative Prediction for Theory

Here we develop in considerably more detail the qualitative prediction made earlier,<sup>20</sup> namely that molecular hydrogen may be formed from glyoxal via a single, concerted reaction, that is (3). This argument should be made in the light of Figure 1, which summarizes the known energetics of reactions (1), (2), and (3). Note first that glyoxal,  $H_2CO + CO$ , and  $H_2 + 2 CO$  all have about the same energy. It is relatively unusual for three fragments to have an energy comparable to that of the single molecule formed by attaching them with chemical bonds. Clearly this situation is due to the uniquely strong bond energy of the diatomic CO. Furthermore, the near degeneracy of the three channels ( $HCCH$ ,  $H_2CO + CO$ , and  $H_2 + 2 CO$ ) suggests<sup>20</sup> that the relative probabilities of decomposition will be determined by energy barriers rather than by enthalpy differences.

Critical to our discussion of Figure 1 is the energy imparted to the  $S_1$  first excited state of glyoxal. Since the 454.5 nm line of the argon ion laser is used for this purpose by Parmenter,<sup>43</sup> it is entirely reasonable to assume that the experiment begins with  $S_1$  glyoxal at an energy 62.9 kcal above the trans  $S_0$  ground state of glyoxal. Since it is generally agreed<sup>36,45</sup> that intersystem crossing (to  $T_1$ ) does not occur in the absence of collisions, one then logically assumes that the next step is internal conversion to the excited vibrational manifold of the  $S_0$  ground state. This radiationless transition leaves the molecule with the same 62.9 kcal of energy, but now in  $S_0$  internal energy. The ultimate question now becomes obvious:

over what barriers may ground state glyoxal with 62.9 kcal of internal energy pass?

Certainly the traditional answer<sup>21,47-49</sup> to the above question has been that glyoxal may pass over the barrier to formaldehyde plus CO. And it should be stated emphatically that we have no objection to this pathway. However, our primary contention is that without additional energy being put into the system, reaction (1) is a "dead end" street. Even if all the available energy [62.9 kcal plus the very small exothermicity of (1)] goes to the formaldehyde product, this is still inadequate (in the absence of collisions) to allow further reaction of H<sub>2</sub>CO. In particular, there is now agreement between experiment<sup>50-52</sup> and theory<sup>53,54</sup> that about 80 kcal of energy is required for formaldehyde to dissociate to H<sub>2</sub> plus CO, i.e., reaction (2). Since the formaldehyde emanating from reaction (1) has no more than 65 kcal, we are adamant in insisting that (2) plays no role in the collisionless photodissociation in the S<sub>1</sub> zero point level of glyoxal vapor.

The other avenue of disappearance available to formaldehyde short of dissociation to H + HCO (which requires about 87 kcal) is rearrangement to hydroxycarbene

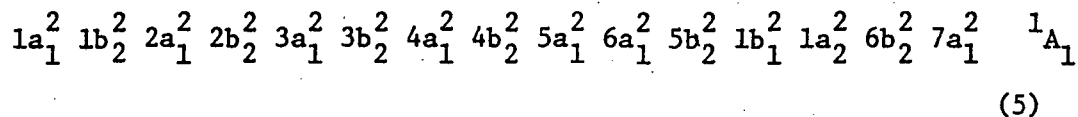


However HCOH is yet to be spectroscopically identified and theory<sup>53,54</sup> suggests an activation energy of ~ 80 kcal for (4). Thus we conclude that any H<sub>2</sub>CO formed via reaction (1) is blocked off from further reactive pathways of a unimolecular nature.

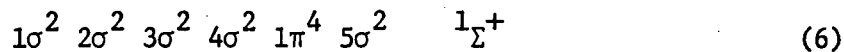
As noted in the brief earlier discussion<sup>20</sup> of the mechanism of

H<sub>2</sub> formation in glyoxal decomposition, it may be demonstrated that reaction (3) is allowed by orbital symmetry.<sup>55</sup> That is, the path from  $\begin{array}{c} \text{O} \quad \text{O} \\ || \quad || \\ \text{H} \text{C} \text{C} \text{H} \end{array}$  to H<sub>2</sub> + CO + CO is a concerted process which includes the synchronous decomposition of C-C and C-H bonds and the formation of the H-H bond. Such a pathway, of course, will begin (at least formally) from the cis isomer of glyoxal and maintain C<sub>2v</sub> point group symmetry throughout. This, it should be noted, is the highest possible symmetry conceivable for glyoxal photodissociation. If the high symmetry pathway is allowed, it follows that adjacent pathways of lower symmetry will also be allowed.

The ground state electron configuration for cis glyoxal is



while that for CO is



leaving for H<sub>2</sub>



When the three product molecules of reaction (3) are brought together to cis glyoxal in a concerted manner, the geometrical arrangement is qualitatively



The  $1\sigma_g$  orbital of  $H_2$  becomes a  $C_{2v}$   $a_1$  orbital, while the ten CO sigma orbitals become five  $a_1$  orbitals and five  $b_2$  orbitals. Similarly the two  $\pi$  orbitals resolve<sup>56</sup> as  $a_1 + a_2 + b_1 + b_2$ , leaving a total of seven  $a_1$  orbitals, one  $a_2$ , one  $b_1$ , and six  $b_2$ . Since this is exactly the breakdown of molecular orbitals in the cis glyoxal ground state (5), one concludes that the reaction is symmetry-allowed.<sup>55,57</sup> A correlation diagram for this process is given in Figure 2 and illustrates nicely the points made in the above discussion.

It should be emphasized that the symmetry-allowedness of reaction (3) does not carry with it any sort of prediction of the precise value of the barrier height (activation energy) of (3). However, it would generally support the idea (admittedly vague) that the barrier is not too high.

Finally, it may appear to the reader that a transition state of the general type (8) does not connect glyoxal to  $H_2 + CO + CO$ , but rather to  $H_2 + (CO)_2$ , the latter species being the carbon monoxide dimer. However, in the present case, this distinction is purely a semantic one. The closed-shell singlet potential energy surface of  $(CO)_2$  is known<sup>58</sup> to be repulsive, i.e., dissociative to  $CO + CO$ . This is to say that the only attraction between two  $^1\Sigma^+$  CO molecules is thought to be a van der Waals attraction with well depth less than 1 kcal.<sup>59</sup> Thus it is seen that (8) is indeed a plausible transition state for reaction (3).

### III. Theoretical Approach

It has been demonstrated that a structure of the general form (8) could be a transition state for the concerted dissociation of glyoxal to  $H_2 + CO + CO$ . What remains to be seen is whether this hypothesis holds up under detailed theoretical scrutiny. To this end, constrained  $C_{2v}$  stationary points of the general type (8) have been obtained at four distinct levels of self-consistent-field (SCF) theory.

The first basis set used was the standard STO-3G minimum basis set.<sup>60</sup> Secondly, the small 3-21G split valence basis was adopted.<sup>61</sup> Third, the standard Huzinaga-Dunning double zeta (DZ) set<sup>62</sup>  $C,0(9s5p/4s2p)$ ,  $H(4s/2s)$  was chosen. Finally polarization functions [ $\alpha_d(C) = 0.75$ ,  $\alpha_d(O) = 0.80$ ,  $\alpha_p(H) = 1.0$ ] were added to all atoms, yielding a fourth basis, the double zeta plus polarization (DZ+P) set.<sup>63</sup> With each of these four basis sets the SCF geometries of cis and trans glyoxal and of the  $C_{2v}$  structure (8) were optimized using analytic gradient techniques.<sup>64,65</sup>

The four SCF constrained stationary points were then subjected to harmonic vibrational analyses, determined from the quadratic force constants in cartesian coordinates. The force constants were determined from the analytic forces via two-point (in addition to  $E_{min}$ ) central differencing, with increments of 0.01 bohr radius. The diagonalization of the 18 x 18 force constant matrix provides an immediate check on the accuracy and internal consistency of the force field, since six vibrational frequencies should be identically zero, corresponding to the three translational and three rotational degrees of freedom. In practice, the worst case proved to be the constrained transition state, for which the largest zero frequency was  $32 \text{ cm}^{-1}$ . Nevertheless, even for such cases, a

zero of this magnitude will not affect the nonzero frequencies to within  $\pm 1 \text{ cm}^{-1}$ , the accuracy reported.

Correlation effects are known to significantly lower barrier heights for many unimolecular reactions.<sup>66</sup> Therefore it was deemed important to consider the effects of electron correlation on the glyoxal barrier using one of the smaller basis sets. With the split valence 3-21G set, configuration interaction (CI) was carried out including all configurations differing by one or two orbitals from the SCF reference configuration (5). This amounts to 20,452 configurations ( $C_{2h}$  point group) for trans glyoxal and the same number for cis glyoxal and the constrained transition state (8).

IV. Results and Discussion for  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{H} \rightarrow \text{H}_2 + \text{CO} + \text{CO}$

A. Geometrical Structure of the Hypothesized Transition State

The four structures of the constrained  $\text{C}_{2v}$  transition states are predicted in Figure 3. In each case, the structure corresponds to a true stationary point, i.e., the gradient of the potential energy hypersurface is zero. Furthermore, it is seen by even a casual inspection that the four structures appear to describe the same stationary point. The largest difference is between the STO-3G C-C distance, 1.923 Å, and the 2.100 Å C-C distance predicted with the DZ+P SCF method. Although this difference of 0.177 Å is very large in the sense of quantitative predictions, the qualitative similarity is nevertheless evident.

For the most reliable level of theory, DZ+P SCF, it is fruitful to compare the stationary point structure in Figure 3 with the analogous equilibrium geometry<sup>20</sup> of cis glyoxal. The C-C single bond distance in cis glyoxal is 1.534 Å, and this is increased by 36.9% to 2.100 Å ( $\Delta r_e = 0.566$  Å) for the constrained transition state. A somewhat smaller fractional bond distance change (27.8%) is predicted for the C-H distances, which are 1.096 Å for cis glyoxal and 1.400 Å ( $\Delta r_e = 0.304$  Å) for the constrained transition state.

Consistent with the hypothesis<sup>20</sup> that the structures in Figure 3 approximate the transition state for dissociation to  $\text{H}_2 + \text{CO} + \text{CO}$ , the DZ+P CO bond distances (1.131 Å) are indeed significantly shorter than the predicted cis glyoxal C=O double bond distances of 1.185 Å. Moreover the largest fractional change of all occurs for the H-H

distance, which is a nonbonded  $2.464 \text{ \AA}$  in cis glyoxal. For the constrained  $C_{2v}$  transition state of Figure 3, this distance is reduced by 55.7% to  $1.091 \text{ \AA}$ . The latter value is of course much closer to the experimental bond distance<sup>67</sup> of  $H_2$ , namely  $r_e = 0.741 \text{ \AA}$ . Thus it is seen that the geometrical features of the stationary point predicted in Figure 3 clearly suggest that this structure is intermediate between cis glyoxal and the three separated products  $H_2 + CO + CO$ .

One feature of Figure 3 which cannot be trivially predicted from the hypothesis that this structure is an intermediate for reaction (3) is the C-C-O bond angle. For cis glyoxal this C-C=O is  $122.7^\circ$ , a typical angle about  $sp^2$  hybridized carbon. However, for the constrained stationary point, this  $C \cdots C=O$  bond angle has increased to  $152.1^\circ$ . A possible explanation for this difference could lie with the equilibrium geometry of the van der Waals molecule  $(CO)_2$ , but this must be considered speculative at the present time.

#### B. Vibrational Analyses of the Hypothesized Transition State

It was noted in Section III that the stationary point structures of Figure 3 have been characterized via their harmonic vibrational frequencies. As discussed by Murrell and Laidler,<sup>68</sup> a true transition state will have a single imaginary vibrational frequency at the saddle point. The present stationary point harmonic vibrational frequencies are presented in Table I.

From a purely theoretical perspective, the most remarkable result of the present research is the manner in which the characterization of the hypothesized transition state varies with the level of theory.



With the STO-3G basis, no fewer than three imaginary vibrational frequencies appear. For the split valence 3-21G basis, however, Figure 3 is a true transition state, having only a single imaginary normal mode. Although the 3-21G basis is expected<sup>61</sup> to be a reasonable approximation to the larger double zeta (DZ) set, a significant difference is found here, in that the DZ stationary point has two imaginary frequencies. It is somewhat encouraging (in terms of the consistency of the theory) that in adding polarization functions, the qualitative nature of the stationary point does not change. That is, both the DZ and DZ+P SCF methods yield two imaginary vibrational frequencies.

In light of the above-discussed variations in stationary point characterization, it would be premature to conclude that the constrained  $C_{2v}$  structure of Figure 3 definitely has two imaginary normal modes. The effects of electron correlation have been completely ignored in these vibrational analyses, and it is by no means inconceivable that further changes could take place at higher levels of theory. Nevertheless, in the absence of further information, the DZ+P SCF frequencies must be considered the most reliable and, accordingly, a standard by which to judge the smaller basis sets.

The two DZ+P SCF imaginary normal modes are 2161 i and 96 i and obvious greatly separated in any spectrum of vibrational frequencies. The larger imaginary vibration is sketched in Figure 4, which clearly indicates the connection between glyoxal and the three molecular products  $H_2 + CO + CO$ . If the vibration in Figure 4 were the only imaginary frequency, we would conclude that the  $C_{2v}$  structure is

indeed the hypothesized unimolecular transition state. However, one must also contend with the frequency at 96 i. Examination of the latter vibrational eigenvector shows that it is an out-of-plane bending vibration, and the exceptionally small magnitude (96 i  $\text{cm}^{-1}$ ) suggests to us that the true DZ+P SCF transition state lies nearby. That is, it appears that the transition state occurs for a nonplanar geometry displaced from Figure 3 in the general direction of the 96 i normal mode. Due to the extreme flatness of the potential hypersurface in the direction of the 96 i displacement, it seems likely that the true (nonplanar) saddle point energy will only be slightly less (perhaps  $\sim 1$  kcal) than that of the constrained  $C_{2v}$  stationary point. That is, although the  $C_{2v}$  structure is not a true transition state at the highest level of theory considered, it appears likely that a true nonplanar transition state, of qualitatively similar energy and structure, appears nearby in conformational space.

With the above discussion in mind, it is possible to evaluate the vibrational frequencies (Table I) predicted at the lower levels of theory. Comparison of the DZ and DZ+P frequencies show that for this system, the carbon d and hydrogen p functions are relatively unimportant. The largest absolute differences, 132  $\text{cm}^{-1}$  and 149  $\text{cm}^{-1}$ , occur as expected for the C-H stretching frequencies. The largest fractional difference occurs for the smaller imaginary frequency, for which the addition of polarization functions increases the DZ prediction of 41 i  $\text{cm}^{-1}$  to 96 i  $\text{cm}^{-1}$ . Turning to the split valence 3-21G basis, one finds reasonable agreement with the DZ+P frequencies except for the smaller imaginary frequency (96 i), which is no longer imaginary.

Nevertheless this  $a_2$  frequency is small ( $191 \text{ cm}^{-1}$ ) and thus concurs with the zeroth order prediction that the energy surface is very flat for excursions in this direction.

For the STO-3G basis, more serious problems occur for the vibrational frequencies. First, the lowest  $b_2$  vibration is imaginary ( $153 i$ ) and quite different from the (real) DZ+P prediction of  $305 \text{ cm}^{-1}$ . Equally disturbing is the fact that three of the higher frequencies differ by more than  $300 \text{ cm}^{-1}$  from the DZ+P predictions. The greatest such difference,  $337 \text{ cm}^{-1}$ , occurs for the larger  $a_2$  frequency. Such problems suggest that minimum basis sets may be of very limited usefulness in transition state vibrational frequency predictions.

### C. Relative Energies for the Constrained $C_{2v}$ Transition States

Total and relative energies for the  $C_{2v}$  structures connecting glyoxal with  $H_2 + CO + CO$  are given in Table II. It would be very difficult even with the current theoretical state-of-the art to make a quantitatively reliable prediction (say  $\pm 2 \text{ kcal}$ ) of the  $C_{2v}$  constrained barrier height for (3). Nevertheless, one can make plausible estimates of this barrier by at least two ab initio schemes. Of these the most direct is the 3-21G basis configuration interaction procedure (20452 configurations) described in Section III above. This yields a barrier of  $69.6 \text{ kcal}$ , which is reduced to  $65.6 \text{ kcal}$  after application of the Davidson correction<sup>69</sup> for unlinked clusters. Note, of course, that the position of the stationary point was not redetermined at the latter two levels of theory, so the true theoretical barriers here will differ somewhat, perhaps by  $\pm 2 \text{ kcal}$ .

A second approach to estimating the  $C_{2v}$  barrier to  $H_2 + CO + CO$  uses the DZ+P SCF barrier of  $88.0 \text{ kcal}$  and attempts to guess the correlation correction to the barrier. This is obviously a treacherous

business and such a prediction must be viewed with considerable skepticism. Nevertheless, we note that for the formaldehyde dissociation process (2), the DZ+P SCF barrier is 106 kcal, and reduced to  $\sim 88$  kcal when state-of-the-art correlated wave functions are brought to bear on the problem.<sup>53,54</sup> If the same electron correlation lowering of the barrier ( $\sim 18$  kcal) were to be found for glyoxal, the estimated barrier would be  $\sim 70$  kcal.

Irrespective of which estimate of the classical barrier is accepted, a further correction for the effects of zero-point energy (ZPE) is required if comparison with experiment is to be made. In any case the zero-point vibrational energy of the transition state will be significantly less than that for trans glyoxal. For example, for formaldehyde this difference is 5.3 kcal.<sup>53</sup> When this magnitude of ZPE correction is subtracted from the ab initio predicted barrier of 65.6 kcal, it is evident that the predicted activation energy falls below the 62.9 kcal available to  $S_0$  glyoxal following internal conversion from the  $S_1$  origin.<sup>43</sup>

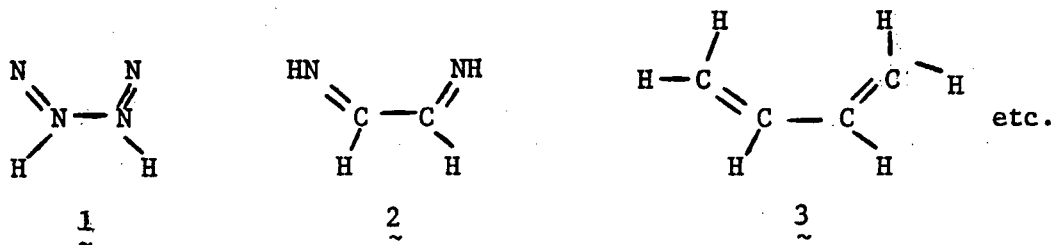
It should be emphasized that this prediction that the ZPE corrected barrier for glyoxal  $\rightarrow H_2 + CO + CO$  lies below the  $S_1$  origin is not a definitive one. However, it does represent a very great improvement over our early qualitative hypothesis that such a unimolecular transition state could in principle exist. Furthermore, the idea that the activation energy for (3) and the  $S_1$  origin are roughly isoenergetic is consistent with the experimental finding<sup>43</sup> that only a fraction of zero-point  $S_1$  glyoxal molecules dissociate to  $H_2$  in the absence of collisions.

D. Qualitative Discussion for the Synchronous Decomposition

It is interesting to consider why the synchronous bond breaking and bond forming is possible, starting from cis glyoxal. Note first that the two highest occupied molecular orbitals are the symmetric ( $n_+$ ) and antisymmetric ( $n_-$ ) combinations of two oxygen lone pair orbitals.

These two lone pair orbitals are located in such a manner as to interact favorably with both CC and CH antibonding orbitals, and Figure 5 illustrates two modes of orbital interaction among them. Figure 5a illustrates the notion that electron delocalization from the  $n_-$  orbital to the CC antibonding one causes the CC bond rupture. The other type of intramolecular charge transfer interaction leads to the CH bond breaking and HH bond formation at the same time (Figure 5b). Together these interactions stabilize the transition state and make the decomposition reaction favorable.

Since the correlation diagram shows that the reaction from glyoxal to  $H_2 + CO + CO$  is symmetry-allowed as described in Figure 2, the decomposition path to three molecules in the same fashion as glyoxal would be also symmetry-allowed for other isoelectronic molecules which have  $C_{2v}$  symmetry, e.g.,



In the case of molecule 1, the analogous decomposition process would be able to occur;  $1 \rightarrow H_2 + 2N_2$ . However, once the reactant molecule 2 or 3 decomposed to three species ( $H_2 + 2 HNC$  or  $H_2 + 2 H_2C=C:$ ), the products would be unstable (particularly <sup>66</sup> 3) with respect to further rearrangement. Moreover, the orbital interactions discussed above may not be applicable for such isoelectronic molecules.

V. The Dissociation  $\overset{\text{OO}}{\text{HCCH}} \rightarrow \text{H}_2\text{CO} + \text{CO}$

An exhaustive theoretical study of the photodissociation of glyoxal would include a detailed examination of reaction (1), the dissociation to formaldehyde. Such a detailed examination is beyond the scope of the present research. However, it was deemed important to get a qualitative idea whether the  $S_0$  dissociation to  $\text{H}_2\text{CO}$  was more or less competitive energetically with the much more unconventional unimolecular dissociation to three molecular products. Therefore planar models for the transition states connecting trans and cis glyoxal to formaldehyde were adopted and pursued in detail at the lower levels of theory.

The predicted  $C_s$  constrained transition states are illustrated in Figure 6. The qualitative geometrical structures of these transition states are relatively independent of the level of theory adopted. Moreover, the key structural feature, the dissociating C-C distance is roughly the same as the 2.1 Å discussed earlier for the transition state to  $\text{H}_2 + \text{CO} + \text{CO}$ . It is also clear from Figure 6 that the larger 3-21G and DZ basis sets yield more spatially extended transition states than does the STO-3G minimum basis. Otherwise, at least in hindsight, there is little that is particularly shocking about these transition states. A reasonable description is that they represent two formyl (HCO) radicals loosely associated and preparing to undergo an abstraction reaction to  $\text{H}_2\text{CO} + \text{CO}$ . Note however (see below) that the final predicted energy of this transition state is below the energy (see Figure 1) of two separated formyl radicals.

Vibrational analyses for the constrained transition states to formaldehyde are summarized in Table III. As with the  $C_{2v}$  transition

state to  $H_2 + CO + CO$ , the STO-3G and 3-21G characterizations of this stationary point are qualitatively different. The minimum basis set predicts two imaginary vibrational frequencies while the split valence basis predicts the  $C_s$  stationary points to be true transition states. With the 3-21G basis the single imaginary vibrational frequencies are sizeable ( $\sim 1750\text{cm}^{-1}$ ) and do indeed connect glyoxal with formaldehyde plus carbon monoxide.

The relative energies of the transition states to formaldehyde are seen in Table II. These show that the transition state commencing from trans glyoxal lies  $\sim 2-3$  kcal below the analogous cis transition state. Moreover, at each level of theory considered, this transition state lies energetically above the much less conventional transition state from glyoxal to  $H_2 + CO + CO$ . However, the  $C_s$  transition states to  $H_2CO$  have not been studied using correlated wave functions, so one cannot make an unequivocal prediction in this regard. It is also conceivable that there is another (lower energy) transition state (connecting glyoxal with formaldehyde) that we have unintentionally neglected in the present research.



### Concluding Remarks

This ab initio theoretical research provides support for the qualitative theoretical prediction<sup>20</sup> that the mechanism for H<sub>2</sub> production in collisionless glyoxal photochemistry may be the elementary unimolecular reaction  $(\text{HCO})_2 \rightarrow \text{H}_2 + \text{CO} + \text{CO}$ . The predicted activation energy for this extraordinary reaction appears to be comparable to the energy of S<sub>1</sub> glyoxal, namely 62.9 kcal. Moreover, this barrier for unimolecular dissociation to three molecular products may be no higher than the barrier to the often-discussed  $(\text{HCO})_2 \rightarrow \text{H}_2\text{CO} + \text{CO}$  reaction, which cannot lead to H<sub>2</sub> if one begins with zero-point S<sub>1</sub> glyoxal and prevents collisions.

### Acknowledgements

This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48 and by the National Science Foundation Grant CHE80-09320. We are grateful to Professors William H. Miller and C. Bradley Moore for many helpful discussions.

References

1. J. Paldus and D. A. Ramsay, *Canad. J. Phys.* 45, 1389 (1967).
2. F. W. Birss, J. M. Brown, A. R. H. Cole, A. Loftus, S. L. N. G. Krishnamachari, G. A. Osborne, J. Paldus, D. A. Ramsay, and L. Watman, *Canad. J. Phys.* 48, 1230 (1970).
3. G. N. Currie and D. A. Ramsay, *Can. J. Phys.* 49, 317 (1971).
4. J. R. Durig, C. C. Tong, and Y. S. Li, *J. Chem. Phys.* 57, 4425 (1972).
5. D. A. Ramsay and C. Zauli, *Acta Phys. Acad. Sci. Hung.* 35, 79 (1974).
6. A. R. H. Cole, Y. S. Li, and J. R. Durig, *J. Mol. Spectrosc.* 61, 346 (1976).
7. C. Cossart-Magos, *Spectrochim. Acta* 34A, 415 (1978).
8. D. Dougherty, P. Brint, and S. P. McGlynn, *J. Amer. Chem. Soc.* 100, 5597 (1978).
9. B. F. Rordorf and C. S. Parmenter, *J. Mol. Spectrosc.* 69, 365 (1978).
10. G. H. Atkinson, R. A. Malstrom, and M. E. McIlwain, *J. Mol. Spectrosc.* 76, 164, 182 (1979).
11. G. J. Verhaart and H. H. Brongersma, *Chem. Phys. Lett.* 72, 176 (1980).
12. M. Lombardi, R. Jost, C. Michel, and A. Tramer, *Chem. Phys.* 46, 273 (1980).
13. G. W. Loge and C. S. Parmenter, *J. Chem. Phys.* 74, 29 (1981).
14. M. Gurnick, J. Chaiken, T. Benson, and J. D. McDonald, *J. Chem. Phys.* 74, 99 (1981).

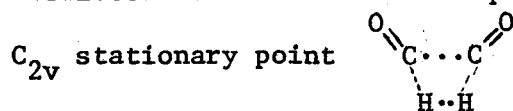
15. C. E. Dykstra, R. R. Lucchese, and H. F. Schaefer, J. Chem. Phys. 67, 2422 (1977).
16. W. B. Mueller, J. F. Harrison, and P. J. Wagner, J. Amer. Chem. Soc. 100, 33 (1978).
17. R. R. Lucchese and H. F. Schaefer, J. Chem. Phys. 68, 769 (1978).
18. C. W. Bock, P. George, and M. Trachtman, J. Mol. Spectrosc. 78, 248 (1979).
19. D. C. Rawlings and E. R. Davidson, J. Chem. Phys. 72, 6808 (1980).
20. Y. Osamura and H. F. Schaefer, J. Chem. Phys. 74, 4576 (1981).
21. C. S. Parmenter, J. Chem. Phys. 41, 658 (1964).
22. L. G. Anderson, C. S. Parmenter, H. M. Poland, and J. D. Rau, Chem. Phys. Lett. 8, 232 (1971).
23. J. T. Yardley, G. W. Holleman, and J. I. Steinfeld, Chem. Phys. Lett. 10, 266 (1971).
24. J. T. Yardley, J. Chem. Phys. 56, 6192 (1972).
25. R. A. Beyer and W. C. Lineberger, Chem. Phys. Lett. 20, 600 (1973).
26. L. G. Anderson, C. S. Parmenter, and H. M. Poland, Chem. Phys. 1, 401 (1973).
27. A. Frad and A. Tramer, Chem. Phys. Lett. 23, 297 (1973).
28. R. A. Beyer, P. F. Zittel, and W. C. Lineberger, J. Chem. Phys. 62, 4016 (1975); R. A. Beyer and W. C. Lineberger, J. Chem. Phys. 62, 4024 (1975).
29. R. van der Werf, E. Shutten, and J. Kommandeur, Chem. Phys. 11, 281 (1975).
30. E. Photos and G. H. Atkinson, Chem. Phys. Lett. 36, 34 (1975).

31. A. Matsuzaki and S. Nagakura, Chem. Phys. Lett. 37, 204 (1976).
32. H. G. Kuettner, H. L. Selzle, and E. W. Schlag, Chem. Phys. Lett. 48, 207 (1977); Israel J. Chem. 16, 264 (1977); Chem. Phys. 28, 1 (1978).
33. P. F. Zittel and W. C. Lineberger, J. Chem. Phys. 66, 2972 (1977).
34. C. S. Parmenter, and R. F. Rordorf, Chem. Phys. 27, 1 (1978);  
C. S. Parmenter, A. E. W. Knight, and R. F. Rordorf, Chem. Phys. 27, 11 (1978).
35. G. H. Atkinson, M. E. McIlwain, and C. G. Venkatesh, J. Chem. Phys. 68, 726 (1978).
36. C. Michel and A. Tramer, Chem. Phys. 42, 315 (1979).
37. H. L. Selzle, S. H. Lin, and E. W. Schlag, Chem. Phys. Lett. 62, 230 (1979).
38. H. M. TenBrink, J. Langelaar, and R. P. H. Rettschnick Chem. Phys. Lett. 62, 263 (1979).
39. B. Soep and A. Tramer, Chem. Phys. Lett. 64, 465 (1979).
40. R. Naaman, D. M. Lubman, and R. N. Zare, J. Chem. Phys. 71, 4192 (1979); J. Mol. Struct. 59, 225 (1980).
41. B. G. MacDonald and E. K. C. Lee, J. Chem. Phys. 71, 5049 (1979).
42. G. DeLeeuw, J. Langelaar, and R. P. H. Rettschnick, J. Mol. Struct. 61, 101 (1980).
43. G. W. Loge, C. S. Parmenter, and B. F. Rordorf, Chem. Phys. Lett. 74, 309 (1980).
44. C. Michel and C. Tric, Chem. Phys. 50, 341 (1980).
45. C. S. Parmenter and M. Seaver, Chem. Phys. 53, 333 (1980).
46. H. S. Johnston, Gas Phase Reaction Rate Theory (Ronald Press, New York, 1966).

47. R. G. W. Norrish and J. G. A. Griffiths, J. Chem. Soc. 1928, 2829.
48. F. E. Blacet and R. W. Moulton, J. Amer. Chem. Soc. 63, 868 (1941).
49. J. G. Calvert and G. S. Layne, J. Amer. Chem. Soc. 75, 856 (1953).
50. J. C. Weisshaar and C. B. Moore, J. Chem. Phys. 72, 2875 (1980).
51. M. Diem and E. K. C. Lee, Chem. Phys. 41, 373 (1979).
52. M. R. Berman, "Competing Reaction Channels in IR Laser Induced Unimolecular Reactions," Ph.D. Thesis, University of California, Berkeley, January, 1981.
53. J. D. Goddard and H. F. Schaefer, J. Chem. Phys. 70, 5117 (1979);  
J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. 74, 0000 (1981); S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, J. Amer. Chem. Soc. 103, 1900 (1981).
54. L. B. Harding, H. B. Schlegel, R. Krishnan, and J. A. Pople, J. Phys. Chem. 84, 3394 (1980).
55. R. B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry (Verlag Chemie, Weinheim/Bergstr., Germany, 1970).
56. G. Herzberg, The Electronic Structure of Polyatomic Molecules (D. Van Nostrand, Princeton, New Jersey, 1967).
57. D. H. Liskow, C. F. Bender, and H. F. Schaefer, J. Chem. Phys. 61, 2507 (1974).
58. R. C. Haddon, D. Poppinger, and L. Radom, J. Amer. Chem. Soc. 97, 1645 (1975).
59. S. H. Linn, Y. Ono, and C. Y. Ng, J. Chem. Phys. 74, 3342 (1981).
60. W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. 51, 2657 (1969).

61. J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Amer. Chem. Soc. 102, 939 (1980).
62. S. Huzinaga, J. Chem. Phys. 42, 1293 (1965); T. H. Dunning, J. Chem. Phys. 53, 2823 (1970).
63. H. F. Schaefer, The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results, (Addison-Wesley, Reading, Massachusetts, 1972).
64. P. Pulay, pages 153-185 of Volume 4, Modern Theoretical Chemistry, editor H. F. Schaefer (Plenum, New York, 1977).
65. M. Dupuis and H. F. King, J. Chem. Phys. 68, 3998 (1978).
66. See, for example, Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, J. Amer. Chem. Soc. 103, 1904 (1981).
67. K. P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).
68. J. N. Murrell and K. J. Laidler, Trans. Faraday Soc. 64, 371 (1968).
69. E. R. Davidson, pages 17-30 of The World of Quantum Chemistry, editors R. Daudel and B. Pullman (D. Reidel, Dordrecht, Holland, 1974).

Table I. Predicted SCF vibrational frequencies for the constrained

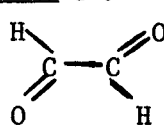
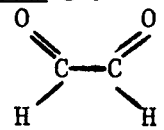
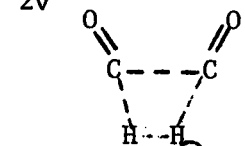


Basis Set	STO-3G	3-21G	DZ	DZ+P
$a_1$	2484	2221	2176	2308
$b_2$	2400	2219	2148	2297
$a_1$	2149	1769	1801	1829
$a_2$	1712	1435	1388	1375
$b_2$	1708	1432	1391	1393
$b_2$	1370	1094	1116	1169
$a_1$	989	749	705	720
$b_2$	153 i	349	308	305
$b_1$	125	306	222	179
$a_1$	178	201	168	165
$a_2$	262 i	191	41 i	96 i
$a_1$	2791 i	2135 i	2181 i	2161 i

$b_1, a_2$  ... out-of-plane (symmetric, asymmetric) motion

$a_1, b_2$  ... in-plane motion

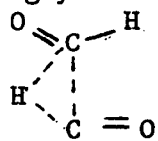
Table II. Total energies (in hartrees) and relative energies (in kcal/mole relative to trans glyoxal) for glyoxal and several constrained transition states for reactions (1) and (3). The circled numbers which appear as superscripts indicate the number of imaginary vibrational frequencies found for each constrained transition state.

Theoretical Method	<u>trans</u> -glyoxal	<u>cis</u> -glyoxal	$C_{2v}$ transition state	decomposition to $H_2CO + CO$	
				from <u>trans</u>	from <u>cis</u>
STO-3G	-223.582301 (0.0)	-223.579915 (1.5)	-223.397323 <sup>③</sup> (116.0)	-223.375419 <sup>②</sup> (129.7)	-223.372783 <sup>②</sup> (131.4)
3-21G	-225.306961 (0.0)	-225.298755 (5.2)	-225.177445 <sup>①</sup> (81.2)	-225.143913 <sup>①</sup> (102.3)	-225.138575 <sup>①</sup> (105.6)
3-21G CI	-225.696303 (0.0)	-225.689433 (4.3)	-225.585297 (69.6)	--	--
Davidson Corrected CI	-225.740593 (0.0)	-225.734156 (4.0)	-225.636020 (65.6)	--	--
DZ	-226.5182 <sup>a</sup> (0.0)	-226.5088 <sup>a</sup> (5.9)	-226.362464 <sup>②</sup> (97.7)	-226.343052 (109.8)	--
DZ + P	-226.644054 (0.0)	-226.634896 (5.7)	-226.503716 <sup>②</sup> (88.0)	--	--

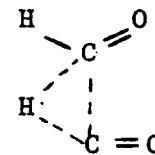
<sup>a</sup>C. E. Dykstra and H. F. Schaefer, J. Amer. Chem. Soc., 97, 7210 (1975).



Table III. Predicted vibrational frequencies for the  $C_s$  stationary points in Figure 6. These constrained  $C_s$  structures connect glyoxal with  $H_2CO + CO$ .



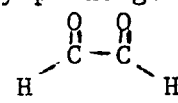
from trans glyoxal



from cis glyoxal

	STO-3G	3-21G	STO-3G	3-21G
a'	3490 $cm^{-1}$	3200 $cm^{-1}$	3533 $cm^{-1}$	3303 $cm^{-1}$
a'	3313	2682	3333	2896
a'	2087	1984	2102	2071
a'	2065	1894	2032	1770
a'	1497	1308	1519	1381
a''	914	1051	953	1094
a''	728	772	656	705
a'	885	755	813	630
a'	464	358	648	501
a'	274	220	184	217
a''	75 i	162	45 i	162
a'	2303 i	1739 i	2343 i	1764 i

Figure Captions

1. Schematic energy relationships for the decomposition of glyoxal.
2. Orbital correlation diagram for the unimolecular reaction:  
glyoxal  $\rightarrow$  H<sub>2</sub> + CO + CO. Decomposition process of cis glyoxal conserves C<sub>2v</sub> symmetry (left hand side) and that of trans glyoxal conserves C<sub>2h</sub> symmetry (right hand side). Both of these processes are allowed under their respective symmetries. The symbols; ss, sa, as and aa express the orbital symmetry associated with  $\sigma_s$  (reflection through the plane of the molecule) and  $\sigma_v$  planes in C<sub>2v</sub> and  $\sigma_s$  plane and C<sub>2</sub> axis in C<sub>2h</sub> symmetry.
3. Predicted constrained C<sub>2v</sub> stationary point geometries, possible transition states for the reaction   $\rightarrow$  H<sub>2</sub> + CO + CO.
4. Reaction coordinate ( $\nu = 2161$  i) for the DZ + P SCF C<sub>2v</sub> constrained transition state for glyoxal  $\rightarrow$  H<sub>2</sub> + CO + CO. Note that this normal mode clearly connects the reactant with the three product molecules.
5. Two modes of orbital interaction pertinent to the synchronous decomposition glyoxal  $\rightarrow$  H<sub>2</sub> + CO + CO. (a) is the  $n_- \rightarrow \sigma_{CC}^*$  interaction, while (b) represents the  $n_+ \rightarrow \sigma_{CH}^*$  interaction.
6. Predicted constrained C<sub>s</sub> stationary point geometries, possible transition states for the reaction glyoxal  $\rightarrow$  H<sub>2</sub>CO + CO.

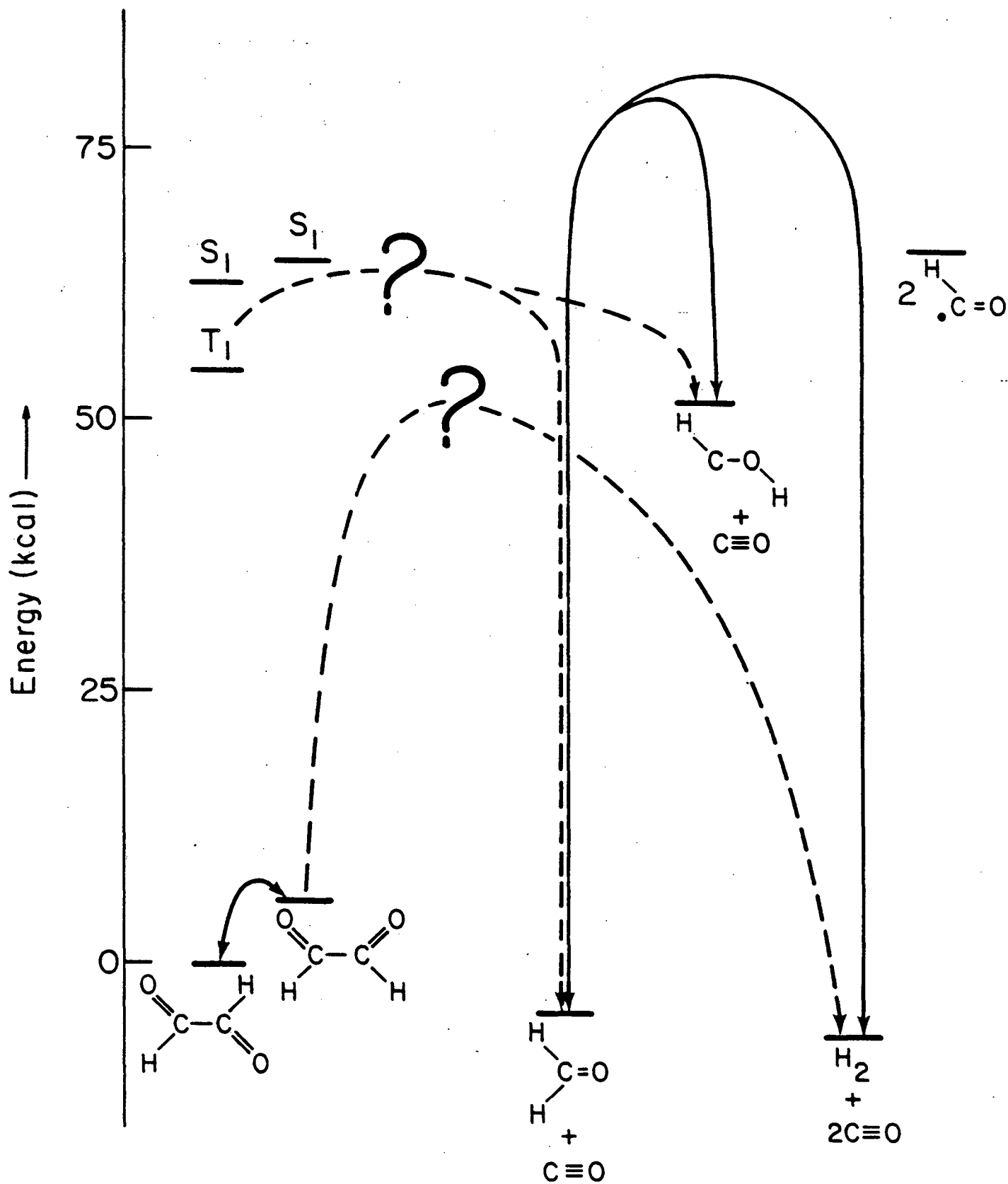
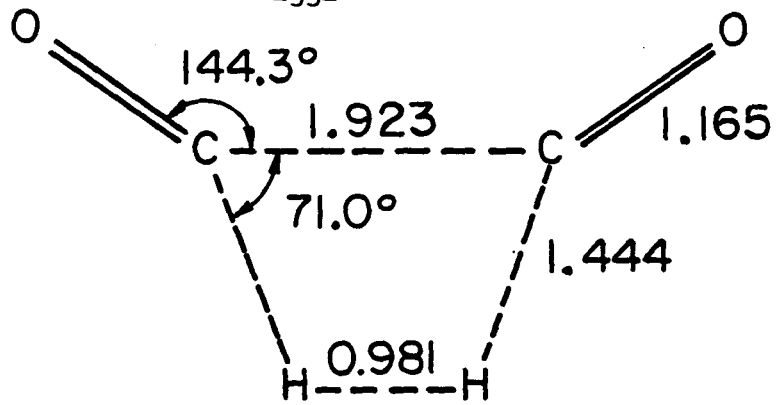


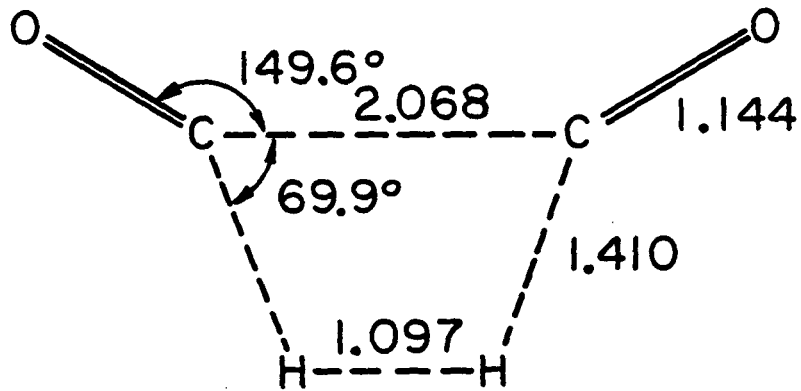
Figure 1



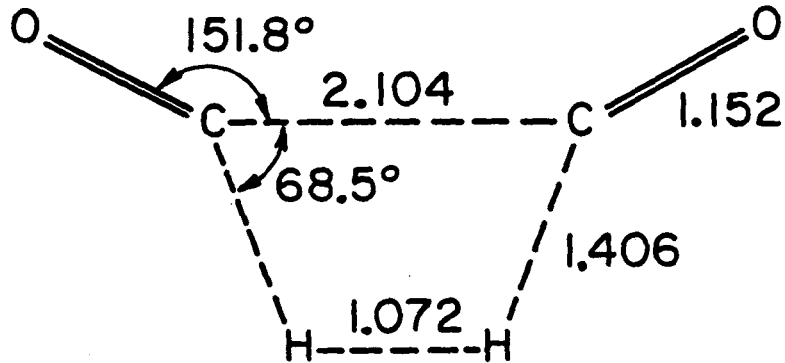
STO-3G



3-21G



DZ



DZ + P

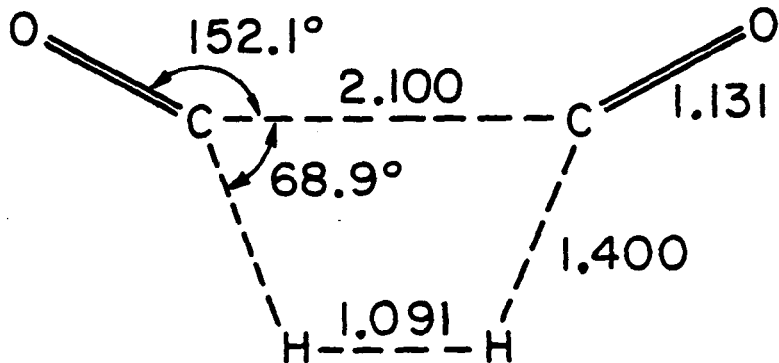


Figure 3

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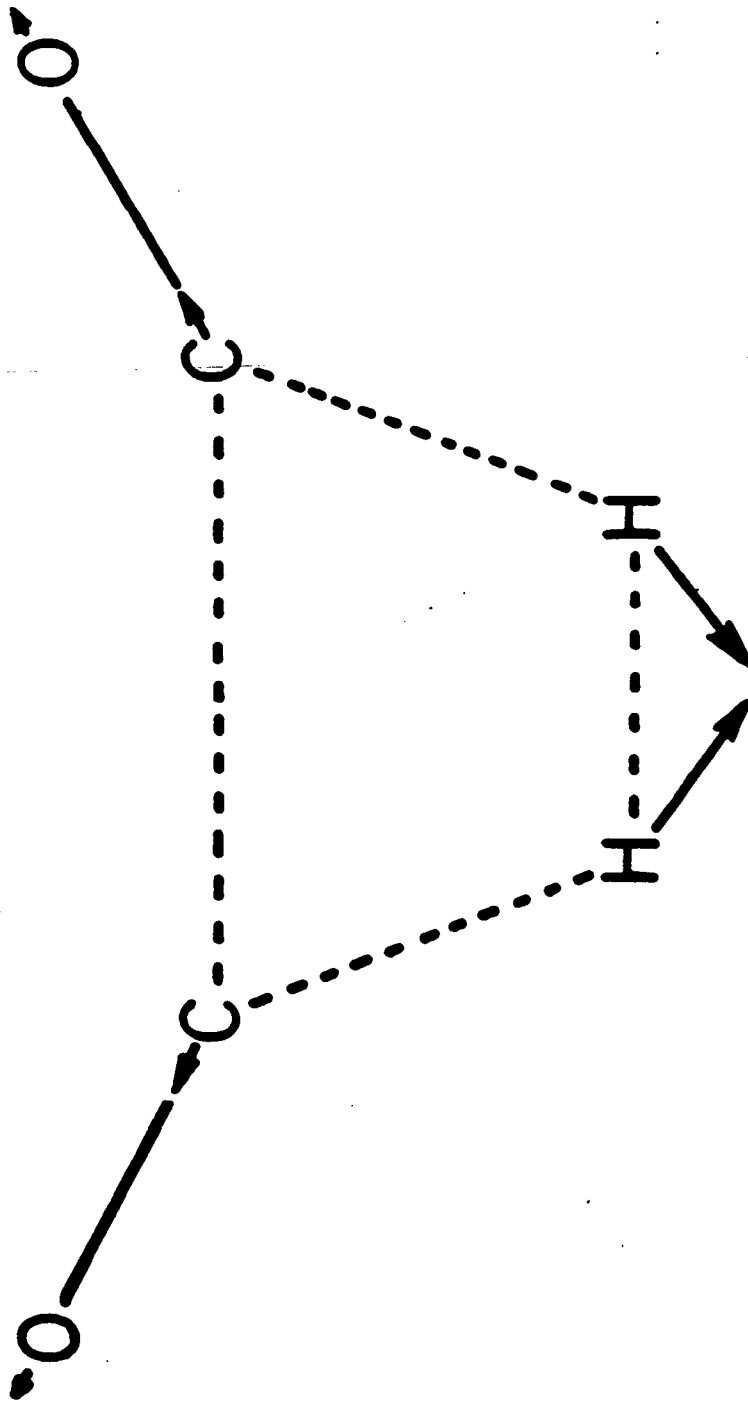


Figure 4

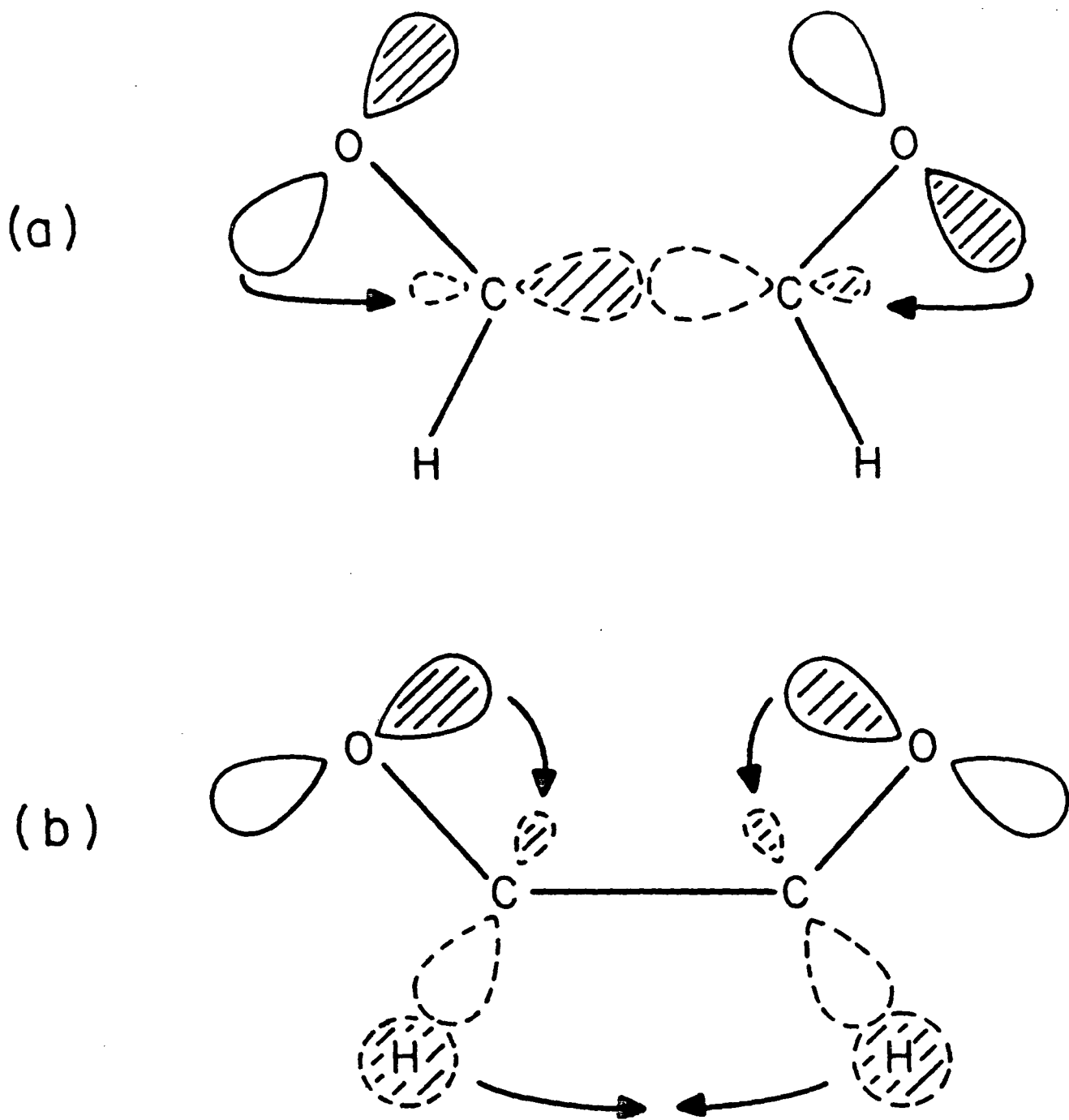
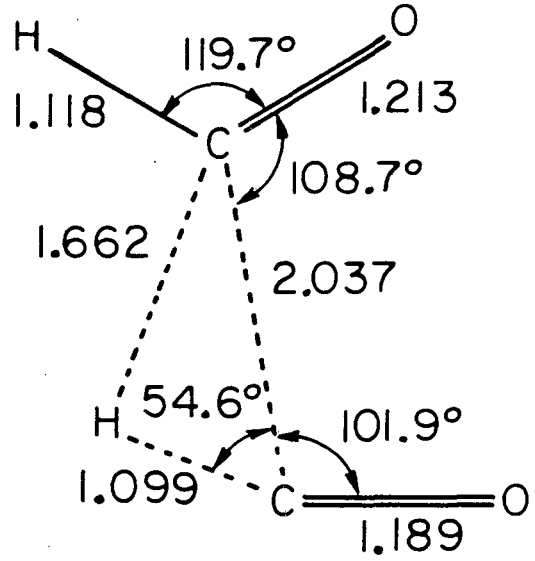
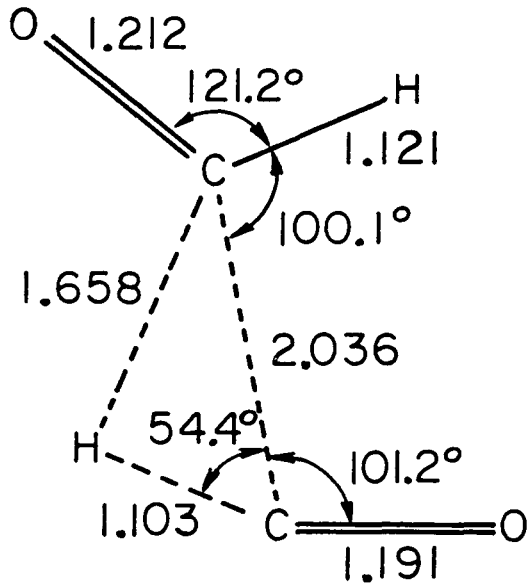
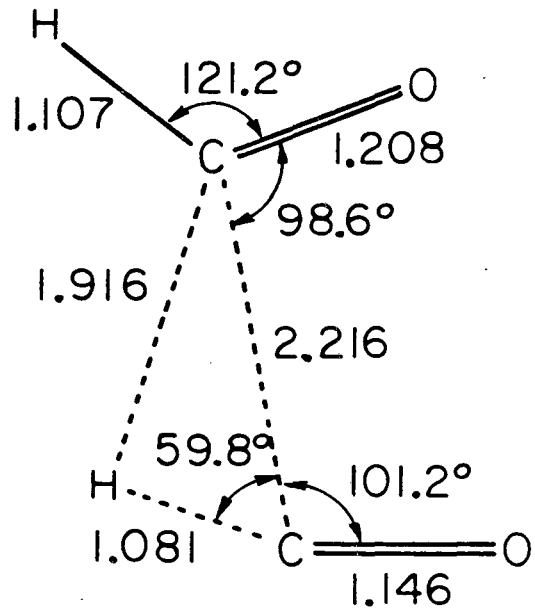
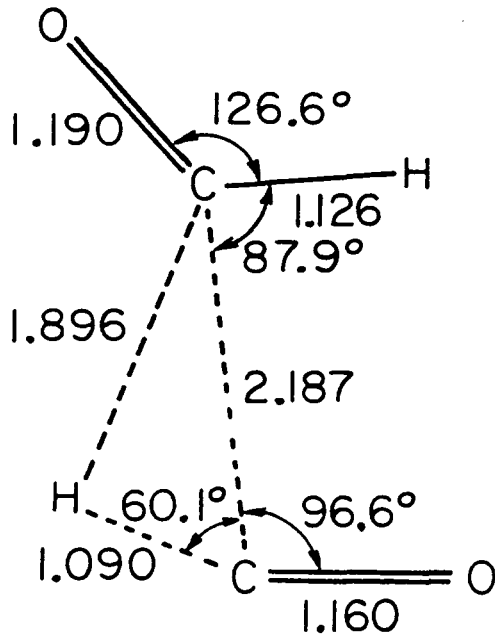


Figure 5



STO-3G



3-21G

XBL816-3910

Figure 6



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