This is the result used in the text.

Appendix II

Our effective Hamiltonian is made by the following recipe. We project the 12 t_{2g} molecular orbitals onto the pure t_{2g} atomic orbital space. Let us call these projected orbitals $Q\Psi_n$ where n ranges from 1 to 12 and where

$$H_{\mathrm{eH}}\Psi_n = \lambda_n\Psi_n \qquad (21)$$

We require

$$H'_{\mathrm{eff}}Q\Psi_n = \lambda_n Q\Psi_n \qquad (22)$$

H'_{eff} is not a hermetian operator. Therefore we define

$$H_{\mathrm{eff}} = \tfrac{1}{2}(H'_{\mathrm{eff}} + H'^{\mathrm{T}}_{\mathrm{eff}}) \qquad (23)$$

It should be noted that the deviation of H'_{eff} from hermeticity has been found to be very slight.

The Unimolecular Triple Dissociation of Glyoxal: Transition-State Structures Optimized by Configuration Interaction and Coupled Cluster Methods

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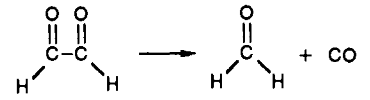
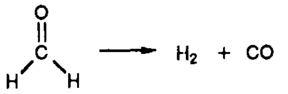
Abstract: Several high-level ab initio theoretical methods have been used to investigate the proposed (1980) "triple whammy" mechanism for the unimolecular dissociation of glyoxal. Basis sets of double zeta plus polarization (DZ+P) and triple zeta plus double polarization (TZ+2P) quality have been used in connection with CISD, CCSD, and CCSDT-1 theoretical methods. The theoretical studies show unambiguously that the triple dissociation mechanism is operative under conditions used in the laboratory to investigate glyoxal photochemistry. Also confirmed, contrary to existing experiments, is the early (1975) theoretical prediction of Dykstra that the C–C single bond distance of *cis*-glyoxal is longer than for *trans*-glyoxal. Vibrational frequencies for both *cis*- and *trans*-glyoxal are predicted and show good qualitative agreement with existing experimental data. The ordering (theory and experiment) of cis and trans C–C stretching frequencies is consistent with the theoretical structural predictions. The predicted energy difference between the cis and trans isomers of glyoxal falls within the error bars of the recent experiments by Parmenter's group.

Prior to 1981 it was generally agreed, following pioneering work by Parmenter,[1] that the photodissociation of glyoxal[2] to give molecular hydrogen proceeded via the two-step mechanism

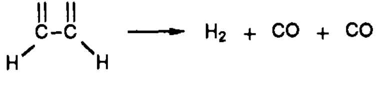


(1a)



(1b)

However, in 1981 Osamura and one of us (OS)[3] pointed out that the large barrier height for formaldehyde dissociation (eq 1b) precludes this two-step mechanism under typical conditions for glyoxal dissociation. Based on qualitative molecular orbital theory (Woodward–Hoffmann-like orbital correlation diagrams), OS suggested in place of (1) the unimolecular triple dissociation mechanism



(2)

The unconventional "triple whammy" proposal of OS[3] was subjected to quantitative theoretical examination later the same year by Osamura, one of us, Dupuis, and Lester (OSDL).[4] OSDL optimized the glyoxal stationary point structures at the self-consistent-field (SCF) level of theory, using basis sets as large as double zeta plus polarization (DZ+P). However, correlation effects were considered only at assumed geometries with the much smaller 3-21G basis set.[5] The Davidson-corrected[6] CISD (configuration interaction including all single and double excitations) barrier height for (2) is predicted to be 66 kcal/mol with the 3-21G basis set. OSDL[4] argued in addition that the effects of zero-point vibrational energy (ZPVE) would place the triple whammy activation energy below the experimental upper bound of 62.9 kcal. Thus the hypothesized[3] unimolecular triple dissociation gained substantial theoretical support.

The experimental upper bound to the activation energy requires a brief explanation. The glyoxal photodissociation experiments typically begin with the laser-excitation of ground-state-*trans*-glyoxal, S_0, to the zero-point vibrational level of the first excited singlet state, S_1. This zero-point level of S_1 is known to lie 62.9 kcal above the vibrational ground state of S_0 *trans*-glyoxal. Thereafter, there occurs a radiationless transition

$$S_1 \rightarrow S_0$$

to the upper vibrational manifold of the ground-state S_0 potential energy surface. The Hepburn experiments[7] show that dissociation

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to H_2 + CO + CO proceeds on the S_0 potential energy surface when this amount of energy is imparted to the system. In terms of energy conservation, precisely the same result would have been obtained by placing 62.9 kcal of energy directly into the cold S_0 ground state. Thus the 62.9-kcal figure is a true upper bound to the activation energy. We known that *trans*-glyoxal can and does dissociate when it is imparted 62.9 kcal of internal energy.

Experimental confirmation of the triple whammy mechanism for glyoxal photodissociation was provided in the 1983 experiments of Hepburn, Buss, Butler, and Lee (HBBL).[7] Using molecular beam photofragment translational spectroscopy, three distinct dissociation channels were identified, the major ones being (1a) and (2). In the experiments from Lee's laboratory,[7] the H_2CO channel (1a) represents 65% and the triple dissociation channel (2) 28% of the product yields. In a related study,[8] still apparently unpublished, Troe has examined the thermal dissociation of glyoxal. At the end of their 1983 paper, HBBL cite Troe[8] as finding yields for (1a) and (2) approximately equal, with barriers for both decompositions estimated to be about 50 kcal/mol.

Related to the unpublished work of Troe is the 1984 thermal unimolecular decomposition study by Saito, Kakumoto, and Murakami.[9] These authors, by following the disappearance of shock-heated glyoxal and the production of CO, conclude that the triple dissociation channel is more important than the reaction to give H_2CO + CO. Saito, Kakumoto, and Murakami[9] suggest activation energies of 47 kcal/mol for the triple dissociation (2) and 58 kcal for the reaction (1a) leading to formaldehyde. The most recent and final experimental paper pertinent to the glyoxal triple dissociation is that of Burak, Hepburn, Sivakumar, Hall, Chawla, and Houston (BHSHCH).[10] These authors investigated the photodissociation of glyoxal by monitoring the CO internal energy distribution using tunable vacuum UV laser-induced fluorescence. BHSHCH's analysis of the angular correlation between the velocity and angular momentum vectors showed that glyoxal dissociates predominantly from a planar geometrical configuration, in agreement with the ab initio stationary point structures of OSDL.[4]

The only theoretical study of the glyoxal triple dissociation since 1981 is the recent work by Kakumoto.[11] Although Kakumoto's research was done at modest levels of theory, it is of interest because it was carried out in parallel for three dicarbonyl compounds: glyoxal, oxalic acid, and glyoxalic acid.

In light of the strong experimental interest in the triple dissociation of glyoxal, this problem certainly deserves additional theoretical attention. Furthermore, we now have at our disposal theoretical methods (for example, the single and double excitation coupled cluster [CCSD] method[12]) which had not even been precisely formulated in 1981. Moreover, the speculations of OSDL concerning the role of ZPVE can now be readily evaluated. Therefore, in this paper we present a reasonably state-of-the-art theoretical description of the glyoxal triple whammy mechanism (2).

Theoretical Approach

The ab initio results presented here were obtained using in most cases the standard Huzinga-Dunning DZ+P basis set.[13,14a] Polarization function orbital exponents were $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.80$, and $\alpha_p(H) = 1.0$. All six d-like functions were included as polarization functions on carbon and oxygen. The hydrogen primitive Gaussian s functions were scaled by a factor of $(1.2)^2 = 1.44$.

Structural optimizations were carried out independently using SCF, CISD, and CCSD methods and employing analytic gradient techniques.[15,16] At the SCF level only, harmonic vibrational frequencies were evaluated using analytic second derivative methods.[17] All electrons were explicitly correlated in the DZ+P CISD and CCSD treatments; the number of single and double excitations for glyoxal in C_{2v} symmetry is 109 668. The saddle point for glyoxal internal rotation is of lower symmetry (C_2), and the CISD wave function includes 196 692 configurations. We report these numbers of configurations for the benefit of anyone subsequently attempting to precisely reproduce the present results.

Final DZ+P basis values of the barrier height for the triple dissociation (2) were obtained via a higher level coupled cluster method that explicitly includes connected triple excitations. The triples are included in a linearized way via the CCSDT-1 method formulated by Bartlett and co-workers.[18] It will be seen that the connected triple excitations have a significant effect on the predicted barrier height. In general we have used *geometrically consistent* theoretical methods in this research. That is, full geometrical optimization of stationary points is independently carried out at each level of theory. However, this was not done with the highest level CCSDT-1 method. Nevertheless, CCSDT-1 total energies were evaluated at both the CISD and CCSD stationary points to provide a test of internal consistency. For the CCSDT-1 method only, the four core molecular orbitals were constrained to be doubly occupied and the four highest virtual SCF MOs were deleted.

It was also thought necessary to test the importance of extensions of the basis set beyond DZ+P. As will be seen, these extensions of the basis set have a major effect on the predicted triple whammy barrier height. The larger basis set used here was of triple-ζ plus double polarization quality. The TZ basis set is the Huzinaga–Dunning[13,14b] C,O(10s6p/5s3p), H(5s/3s) set. Polarization function orbital exponents were $\alpha_p(H) = 1.50, 0.35$; $\alpha_d(C) = 1.50, 0.35$, $\alpha_d(O) = 1.70, 0.40$. With this basis of 122 contracted Gaussian functions, there are 172 712 configurations in the CISD wave functions (C_{2v} symmetry, four core SCF MO's frozen, four highest virtual MO's deleted). With the TZ+2P basis, CCSD single point energies were evaluated assuming the DZ+P CCSD stationary point geometries.

Structures of *cis*- and *trans*-Glyoxal

Although not a primary goal of this research, our DZ+P CISD and DZ+P CCSD structures for *cis*- and *trans*-glyoxal are among the most reliable predicted to date theoretically. The only rival theoretical work in this particular respect is that of Saebo.[19] Saebo used a basis intermediate between DZ+P and TZ+2P sets. In fact, Saebo's basis is nearly of triple-ζ plus double polarization quality, and only slightly less complete than our TZ+2P basis set. The theoretical method used by Saebo[19] was fourth-order perturbation theory excluding triple excitations, i.e., MP4(SDQ). However, some additional approximations were made via the local correlation scheme of Saebo and Pulay.[20] Another recent (1988) study of the molecular structures of *cis*- and *trans*-glyoxal is that of Bock, Panchenko, and Krasnoshchiokov,[21] who used the 6-31G SCF method.

The present DZ+P SCF, CISD, and CCSD stationary points pertinent to glyoxal internal rotation are seen in Figure 1. Beginning with the 1975 ab initio study by Dykstra and one of us,[22] there has been a continuing conflict between theory and experiment concerning the relative values of the C–C bond distances in the cis and trans isomers of glyoxal. Dykstra[22] predicted r_e(C–C) to

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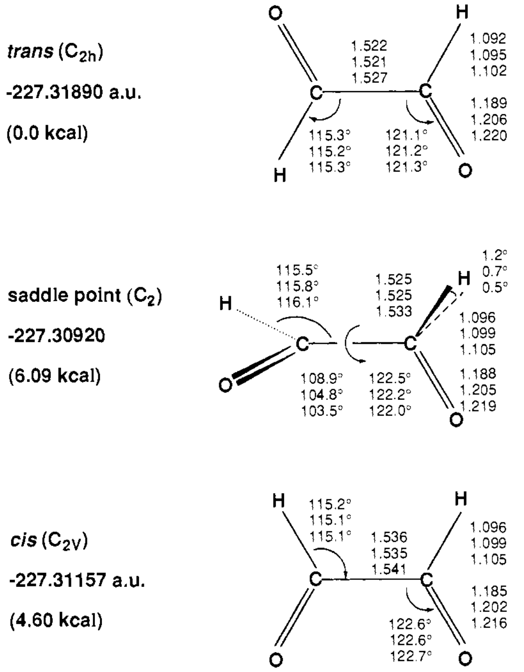

Figure 1. Theoretical molecular structures for *cis-* and *trans*-glyoxal and for the transition state connecting them via internal rotation. The total and relative energies are from DZ+P CCSD theory. As discussed in the text, a higher-yet level of theory (CCSDT-1) predicts a lower value (4.3 kcal/mol) for ΔE(cis–trans), and this prediction is further reduced to 4.25 kcal by zero-point vibrational energies. For each stationary point three levels of theory were used independently for the geometrical optimizations. The top, middle, and bottom entries represent the DZ+P SCF, DZ+P CISD, and DZ+P CCSD methods, respectively. All bond distances are reported in Å.

be 0.008 Å longer for *cis*-glyoxal than for the trans minimum. As noted by Bock, George, Mains, and Trachtman,[23] Dykstra's ab initio prediction is consistent with the simple qualitative idea that the oxygen lone pairs between the two C=O groups will try to avoid each other, hence lengthening the C—C distance for the cis isomer. In the present research, Dykstra's ordering of cis and trans C–C distances is confirmed. At every level of theory the cis C–C distance is longer, in fact, by 0.014 Å at each of the three distinct levels of theory reported here. Moreover, both of our predicted C–C distances from the DZ+P CCSD method agree to within 0.001 Å with those of Saebo.[19]

The theoretical predictions that $r_e(\text{C–C})_{\text{cis}} > r_e(\text{C–C})_{\text{trans}}$ have not resulted in a reassessment of the experimental conclusions. Although the 1987 paper by Rodler, Oldani, Grassi, and Bauder[24] reported new rotational spectra for both *cis-* and *trans*-glyoxal, those authors did not attempt to revise the experimental molecular structures. For *cis*-glyoxal the experimental C–C bond distances[25,26] are 1.505 and 1.514 Å, while for *trans*-glyoxal electron diffraction analysis[27] yields 1.525–1.526 Å. Following Dykstra and Schaefer[22] we conclude that the experimental ordering of these C–C bond distances must be incorrect.

Energy Difference between *cis-* and *trans*-Glyoxal

For *trans*-glyoxal, the DZ+P total energies obtained here are −226.644 05 (SCF), −227.227 54 (CISD), and −227.318 90 (CCSD) hartrees. The comparable cis total energies are −226.634 90 (SCF), −227.219 53 (CISD), and −227.311 57 (CCSD) hartrees. For the internal rotation transition state, the total energies are −226.633 45 (SCF), −227.217 44 (CISD), and −227.309 20 (CCSD) hartrees. Thus the predicted ΔE(cis–trans) values are 5.75 (SCF), 5.03 (CISD), and 4.60 (CCSD) kcal/mol. In a unit more frequently used by spectroscopists, the same energy differences are 2010 (SCF), 1760 (CISD), and 1610 (CCSD) cm^{-1}.

Our most reliable predictions of ΔE(cis–trans) are provided by the CCSDT-1 level of theory, which as discussed above includes connected triple excitations. Using the DZ+P CISD stationary point geometries, the DZ+P CCSDT-1 total energies are 227.279 72 (trans), −227.272 61 (cis), and −227.270 00 (transition state) hartrees. Assuming the DZ+P CCSD stationary point structures, the DZ+P CCSDT-1 total energies are −227.281 22 (trans), −227.274 16 (cis), and −227.271 53 (transition state) hartrees. The fact that the latter CCSDT-1 total energies are about 2 mhartrees lower confirms that the CCSD stationary point geometries are closer to the (unknown) optimum CCSDT-1 structures than are the CISD structures. The careful reader will note that the CCSDT-1 total energies actually lie *above* the CCSD energies because the latter correlation treatment includes all electrons, while the former is restricted to the valence electrons.

With the CISD geometries the CCSDT-1 value for ΔE(cis–trans) is 4.46 kcal/mol, or 1560 cm^{-1}. Assuming the CCSD geometries the CCSDT-1 method predicts 4.43 kcal/mol or 1550 cm^{-1} for the cis–trans energy difference. For a precise comparison with experiment, some inclusion of ZPVE should be made. In the present research, vibrational frequencies have been evaluated only with the DZ+P SCF method. At the DZ+P SCF level of theory the ZPVE's within the harmonic approximation are 25.53 kcal for *trans*-glyoxal and 25.35 kcal for *cis*-glyoxal. Thus at this level of theory ZPVE is predicted to reduce ΔE(cis–trans) by 0.18 kcal/mol. In this way the CCSDT-1 prediction for ΔE(cis–trans) is reduced to 4.25 kcal or 1490 cm^{-1}.

The old (1971) experimental value for ΔE(cis–trans) is that of Currie and Ramsay,[28] who reported 1125 ± 200 cm^{-1}. The new (1987) experimental value, that of Butz, Johnson, Krajnovitch, and Parmenter,[29] is 1350 ± 200 cm^{-1}. Our most reliable theoretical value, 1490 cm^{-1}, is 140 cm^{-1} above the new experimental value of Parmenter and within his error bars. Glyoxal is a surprising[30] example of a situation in which electron correlation has a major effect on a barrier to internal rotation. The reduction in the classical (i.e., excluding ZPVE) barrier from SCF to CCSDT-1 is large, namely, 5.75–4.43 = 1.32 kcal/mol.

Extension of the basis set from DZ+P to TZ+2P has little effect on ΔE(cis–trans). The TZ+2P CCSD//DZ+P CCSD total energies are −227.380 82 (trans) and −227.373 28 (cis), yielding ΔE = 4.73 kcal. The analogous DZ+P CCSD//DZ+P CCSD difference noted above is 4.60 kcal/mol.

A related energetic quantity is the barier height for cis–trans isomerization. The theoretical predictions with the DZ+P basis set are 0.91 (SCF), 1.31 (CISD), and 1.49 kcal (CCSD). The CCSDT-1 predictions are 1.64 with CISD geometries and 1.65 kcal with CCSD geometries. Apparently there is no meaningful experimental value of the barrier to rotation for glyoxal. From the lower energy *trans*-glyoxal the present ab initio barrier heights are 6.65 (SCF), 6.34 (CISD), and 6.09 kcal (CCSD). The CCSDT-1 barriers from the trans side are 6.10 kcal with CISD and 6.08 with CCSD stationary point geometries. For eventual comparison with experiment, ZPVE should be considered. At the DZ+P SCF level of theory the ZPVE for the internal rotation transition state is 25.05 kcal/mol, less than that for either *cis-* and *trans*-glyoxal. Thus ZPVE reduces the predicted classical barriers to internal rotation by 0.30 kcal from the cis side and 0.48 kcal from the trans side.

Vibrational Frequencies

Two recent experimental papers, by Parmenter and co-workers[29] and by Engdahl and Nelander,[31] have significantly improved our

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Table I. Comparison of DZ+P SCF Harmonic Vibrational Frequencies with the Observed Fundamentals of *cis*- and *trans*-Glyoxal[a]

	trans-glyoxal-H_2			*cis*-glyoxal-H_2	
	ω(DZ+P SCF)	ν(expt)		ω(DZ+P SCF)	ν(expt)
$\nu_1(a_g)$	3229.3	2843	$\nu_1(a_1)$	3195	– (2841)
$\nu_2(a_g)$	2048	1745	$\nu_2(a_1)$	2040	1746 (1737)
$\nu_3(a_g)$	1501	1352	$\nu_3(a_1)$	1529	– (1369)
$\nu_4(a_g)$	1192	1065	$\nu_4(a_1)$	945	827 (817)
$\nu_5(a_g)$	607	551	$\nu_5(a_1)$	309	285
$\nu_6(a_u)$	909	801 (807, 813)	$\nu_6(a_2)$	849	–
$\nu_7(a_u)$	147	127	$\nu_7(a_2)$	74	91
$\nu_8(b_g)$	1188	1048	$\nu_8(b_1)$	1195	1049
$\nu_9(b_u)$	3228.5	2835 (2856, 2862)	$\nu_9(b_2)$	3165	–
$\nu_{10}(b_u)$	1996	1732 (1724)	$\nu_{10}(b_2)$	2037	– (1761)
$\nu_{11}(b_u)$	1456	1312 (1315)	$\nu_{11}(b_2)$	1514	–
$\nu_{12}(b_u)$	370	339 (335)	$\nu_{12}(b_2)$	881	–

[a] Experimental values are from the 1988 summary of Engdahl and Nelander.[31] Gas-phase fundamentals are given first, followed by argon matrix isolation results in parentheses.

understanding of the fundamental vibrational frequencies of *cis*- and *trans*-glyoxal. In fact, as noted by Butz, Johnson, Krajnovich, and Parmenter,[29] their work completes the measurement of all gas-phase fundamentals of *trans*-glyoxal in its electronic ground state. As stated earlier, in this research vibrational frequencies have been predicted only within the harmonic approximation at the DZ+P SCF level of theory. Nevertheless, a comparison with experiment is of interest and this is made in Table I.

Broadly speaking the agreement between the DZ+P SCF harmonic vibrational frequencies and the gas-phase fundamentals is quite good. Except for the torsional frequency for *cis*-glyoxal every theoretical harmonic frequency lies above the analogous observed fundamental. Even for the cis torsional frequency the agreement between theory (74 cm^{-1}) and experiment (91 cm^{-1}) is good in light of the extreme nature of the harmonic approximation for such floppy degrees of freedom. For the 17 fundamentals known in the gas phase (both cis and trans), the average difference between DZ+P SCF ω values and experimental ν values is 13.8%, a value not unexpected from past experience.[32]

Among the glyoxal vibrational degrees of freedom, the carbon–carbon stretching modes are of particular interest. DZ+P SCF theory agrees with the experimental assignments[29,31] that this C–C vibration lies significantly higher for *trans*- ($\nu_4\,a_g$) than for *cis*-glyoxal ($\nu_4\,a_1$). Specifically the difference between the two C–C theoretical harmonic vibrational frequencies is (1192 – 945) = 247 cm^{-1}, while the difference between the two observed fundamentals is (1065 – 827) = 238 cm^{-1}. We think that this relatively simple level (DZ+P SCF) of theory is doing a good job of reproducing an important recent experimental discovery.[29] Parmenter has noted[29] that intuition (Badger's rule) supports the idea that *trans*-glyoxal, with the higher C–C stretching vibrational frequency, ought to have the shorter C–C bond distance. As discussed above, this is precisely the position that theory has consistently taken since the 1975 work by Dykstra.[22]

The infrared spectrum of *cis*-glyoxal is much less completely characterized than that of the more abundant trans isomer. A reasonable question to ask is whether those fundamentals of *cis*-glyoxal which have never been observed are predicted by theory to have low IR intensities. Of the two C–H stretches only the a_1 mode has been observed, and that only via matrix isolation. This is consistent with the fact that the a_1 mode has a the theoretical (DZ+P SCF) intensity, 146 km/mol, that is more than three times more intense than the b_2 mode, 44 km/mol. The fact that the a_2 vibrational frequency predicted by DZ+P SCF theory at 849 cm^{-1} has not been observed is certainly consistent with the theoretical prediction $I(\nu_6\,a_2)$ = 0.05 km/mol. Similarly $\nu_{11}(b_2)$ has not been assigned experimentally and has a predicted DZ+P SCF IR intensity of only 1.8 km/mol. What is, however, very puzzling is the inability of experiment to date to identify $\nu_{12}(b_2)$. From DZ+P SCF theory, this is predicted to be the third most intense fundamental of *cis*-glyoxal, with $I(\nu_{12}\,b_2)$ = 106 km/mol. We suspect that a new experimental search for ν_{12} of cis glyoxal might be successful near 800 cm^{-1}.

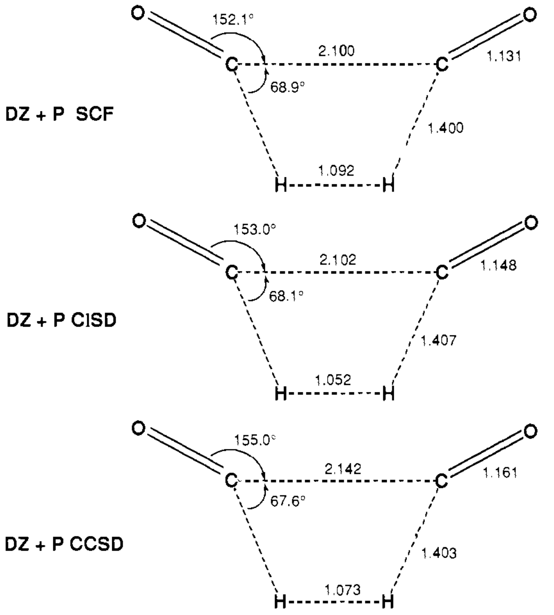

Figure 2. Theoretical predictions of the geometry of the planar stationary point corresponding to unimolecular triple dissociation of glyoxal. The three levels of theory all use a double zeta plus polarization (DZ+P) basis set. The methods adopted were self-consistent-field (SCF) theory, configuration interaction including all single and double excitations (CISD), and coupled cluster including all single and double excitations (CCSD). All bond distances are given in Å.

Planar Stationary Point for Unimolecular Triple Dissociation

As with *cis*- and *trans*-glyoxal and the internal rotation transition state, three distinct levels of theory have been used to optimize the structure of the planar stationary point corresponding to triple dissociation. The three structures are shown in Figure 2. At the simplest level of theory (DZ+P SCF), the planar stationary point is *not* a transition state. As discussed by OSDL,[4] the DZ+P SCF stationary point has two imaginary vibrational frequencies, corresponding to two negative diagonal quadratic force constants in normal coordinates. With our DZ+P basis set, these SCF harmonic vibrational frequencies are 2161i and 96i cm^{-1}. The former vibrational frequency corresponds to the expected reaction coordinate for *cis*-glyoxal $\rightarrow$ H_2 + CO + CO. The smaller (96i cm^{-1}) imaginary vibrational frequency is of a_2 symmetry and corresponds to out-of-plane motion analogous to the torsional vibration of *cis*-glyoxal. Following this 96i vibrational motion will lead to the true (nonplanar) transition state for triple dissociation. Given the very flat nature of the potential energy hypersurface in this direction, the true DZ+P SCF transition state for triple dissociation will lie only slightly energetically below the

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Table II. Ab Initio Quantum Mechanical Predictions for the Activation Energy for the Glyoxal Triple Dissociation *trans*-HCOHCO → H_2 + CO + CO[a]

basis set	DZ	DZ+P	TZ+2P
theoretical method			
SCF	89.0	79.3	(75.4)[f]
CISD	75.4	72.3	(67.6)[d]
Davidson-corrected CISD	(70.9)[b]	(68.0)[d]	(62.5)[d]
CCSD	69.3	65.9	(60.4)[e]
CCSDT-1	(61.8)[c]	(60.1)[e]	(54.6)[g]

[a] All results are given in kcal/mol and should be compared with the experimental upper limit[7,31] of 62.9 kcal/mol. Unless indicated by parentheses, all classical barrier heights were obtained by theoretically consistent methods; i.e., the structures of *trans*-glyoxal and the planar triple dissociation stationary point were optimized at the same level of theory. The zero-point vibrational energy correction obtained at the DZ+P SCF level of theory has been included. [b] Using DZ CISD stationary point geometries. [c] Using DZ CCSD stationary point geometries. [d] Using DZ+P CISD stationary point geometries. [e] Using DZ+P CCSD stationary point geometries. [f] Using DZ+P SCF stationary point geometries. [g] Estimated by subtracting the DZ+P CCSDT-1 correction from the TZ+2P CCSD result.

planar stationary point displayed in Figure 2.

Figure 2 shows that the effects of electron correlation on the geometry of the planar stationary point for triple dissociation are small. The C–C bond being ruptured is predicted to have length 2.100 (SCF), 2.102 (CISD), and 2.142 (CCSD) Å. The two C–O bond distances (about to become separated carbon monoxide molecules) are 1.131 (SCF), 1.148 (CISD), and 1.161 Å (CCSD). These may be compared with analogous results for diatomic CO, namely, 1.118 (DZ+P SCF), 1.141 (CISD), and 1.148 Å (CCSD). The triple whammy planar stationary point C–O distances are longer than those of isolated CO by 0.013 (SCF), 0.007 (CISD), and 0.013 Å (CCSD). Similarly, the C–H bonds being broken and the H–H bond being made are relatively little affected by correlation effects.

The primary purpose of this research was to make a definitive prediction of the activation energy for triple dissociation. For the triple whammy mechanism to be operative, this activation energy must be less than 62.9 kcal. The latter energy is the zero-point energy of the electronically excited S_1 state of *trans*-glyoxal.[33] Excitation of *trans*-glyoxal was unambiguously shown by Hepburn, Buss, Butler, and Lee[7] to lead to triple dissociation in the absence of collisions. Although the triple whammy mechanism is best visually understood[4] as proceeding from *cis*-glyoxal, the zero of energy must for this reason be taken to be *trans*-glyoxal.

Although OSDL[4] hypothesized the importance of zero-point vibrational energy (ZPVE) for the triple dissociation mechanism, this hypothesis was not tested. As we have noted above, the ZPVE for *trans*-glyoxal is predicted to be 25.53 kcal/mol at the DZ+P SCF level of theory within the harmonic approximation. Similarly the sum of the 10 real vibrational frequencies for the triple whammy planar transition state is 16.77 kcal/mol. The difference (25.53 − 16.77) = 8.76 kcal is the gap between the classical barrier height and the activation energy predicted within the DZ+P SCF harmonic approximation. The reader should recall that the DZ+P SCF method was the only one used in this work to evaluate vibrational frequencies. Since the experimental 62.9-kcal upper limit to the activation energy necessarily includes ZPVE, we have substracted the ZPVE correction 8.76 kcal from all our ab initio classical barrier heights to allow direct comparison with experiment.

The predicted activation energies for the triple dissociation of *trans*-glyoxal are given in Table II. Although we have not reported DZ basis set results elsewhere in this paper, they have been obtained systematically in this research and are reported for the activation energy. Since the DZ+P basis set is the largest for which CISD and CCSD stationary points have been structurally optimized, we emphasize these results. The effect of CISD is to reduce the predicted SCF activation energy by (79.3 − 72.3) = 7.0 kcal/mol. Beyond CISD a further decrease of (72.3 − 65.9) = 6.4 kcal is found with the CCSD method. The Davidson-corrected CISD method[6] may be viewed as an approximation to CCSD, and it predicts an activation energy (68.0 kcal) somewhat closer to CCSD than to CISD.

With the DZ+P CCSD optimized geometry, the TZ+2P CCSD total energy is −227.270 65 hartrees. This translates to a predicted activation energy of 60.4 kcal for triple dissociation. It would have been desirable to carry out TZ+2P CCSDT-1 computations at the same geometry, but it was not feasible with 122 contracted functions. However, in Table II we have estimated the TZ+2P CCSDT-1 activation energy from the difference in DZ+P activation energies obtained between the CCSD and CCSDT-1 methods.

The estimated TZ+2P CCSDT-1 activation energy of 54.6 kcal falls comfortably below the rigorous experimental upper bound[7,33] of 62.9 kcal/mol. Thus we may confidently state that the triple whammy mechanism is operative under the experimental conditions for the photodissociation of glyoxal. The ab initio prediction agrees with the rough, unpublished estimate by Troe[8] (cited by Hepburn, Buss, Butler, and Lee[7]), of $E_a \sim 50$ kcal/mol. Our 54.6-kcal prediction is also in the ball park of the experimental 47-kcal estimate for E_a(triple whammy) by Saito, Kakumoto, and Murakami.[9]

Concluding Remarks

Coupled cluster methods are increasingly becoming a significant contributor to mainstream ab initio quantum chemistry.[34] These methods provide a way, short of multireference configuration interaction, of treating higher than double excitations. The results presented here show conclusively that these higher excitation correlation effects can have a dramatic impact on predicted activation energies. For the glyoxal triple dissociation, the effect of going from CISD to CCSD is to reduce the barrier height by 6.4 kcal/mol. Going further from CCSD to the CCSDT-1 method, which includes all triple excitations, results in an additional decrease in the barrier height by 5.8 kcal.

A common, useful, and very simple method for the estimation of higher excitation correlation effects has been Davidson's correction.[6] This work shows that for the triple dissociation barrier height the CCSDT-1 prediction lies 7.9 kcal below the Davidson-corrected CISD result. It is clear that high-level theoretical methods such as CCSDT-1 will be required for quantitative theoretical predictions of activation energies for chemical reactions. Beyond any question, the present research establishes the triple whammy mechanism for fragmentation as operative under the experimental conditions for glyoxal photodissociation. Further experiments to distinguish between reaction 2, leading to molecular hydrogen, and reaction 1, leading to formaldehyde, could be very insightful.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811. Since the 1980 hypothesis of the triple whammy mechanism we have enjoyed fruitful discussions with Professors Charles Parmenter, Yuan Lee, John Hepburn, and Laurie Butler.

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