Photodissociation of glyoxal: Resolution of a paradox

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Photofragmentation of glyoxal, $C_2H_2O_2$, under collision free conditions proceeds by internal conversion from S_1 to vibrationally excited S_0, which is observed to dissociate into $H_2+CO+CO$ (28%), H_2CO+CO (65%), and $HCOH+CO$ (7%). Early molecular orbital calculations placed the barrier for the formaldehyde channel 12–20 kcal/mol above the three body fragmentation channel, contrary to what would have been expected from the branching ratios. The best calculational estimate of the barrier for the three body fragmentation was ≈ 8 kcal/mol higher than the reported activation energy for the thermal decomposition of glyoxal. These problems have been resolved by the more accurate *ab initio* molecular orbital calculations reported in the present note. With the complete basis set extrapolation method of G. Petersson and co-workers using an atomic pair natural orbital basis set (CBS-APNO), the calculated heats of reaction that are within 0.4–0.8 kcal/mol of the experimental values for glyoxal$\rightarrow H_2+2CO$, H_2CO+CO, and 2 HCO. The barrier computed for H_2CO+CO is 54.4 kcal/mol, in excellent agreement with the high pressure limit of the activation energy for thermal decomposition of glyoxal. The computed barrier for the three body fragmentation is 4.8 kcal/mol higher than the H_2CO+CO channel, in agreement with the observed lower yield for this channel. © *2001 American Institute of Physics.*
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The collisionless photofragmentation of glyoxal has been investigated for more than two decades by experimental and theoretical means.[1–12] The spectroscopy and photophysics of glyoxal has been studied extensively and is well understood (for leading references, see Ref. 1). After excitation to the lowest singlet, the dissociation products H_2CO, CO, and H_2 are observed.[1–5] Collisions promote intersystem crossing from the singlet to the lowest triplet, which fragments into formaldehyde and carbon monoxide.[8] Under collision free conditions, intersystem crossing is not observed, and S_1 has a lifetime of the order of 10^{-6} s,[2,9] returning to the ground state by fluorescence ($\approx 50\%$) (Ref. 6) and by internal conversion.[7] The photodissociation experiments typically excite the zero point level of S_1 or low lying vibrational bands such as 8_0^1. Internal conversion yields a highly excited ground state with 63–65 kcal/mol excess energy. With this energy, three channels for fragmentation are open,

$$C_2H_2O_2 \rightarrow H_2+CO+CO \tag{1}$$

$$\rightarrow H_2CO+CO \tag{2}$$

$$\rightarrow HCOH+CO. \tag{3}$$

The first reaction is an archetypal example of a three body fragmentation and has fascinated the experimental and theoretical communities alike.[1–12] The observation of H_2 as a product confirms this pathway, since there is not enough energy to produce H_2 by secondary fragmentation of HCOH or H_2CO (barrier of ≈ 80 kcal/mol or more).[13–16] Theoretical calculations have characterized the transition state for this three body fragmentation reaction[10–12] (whimsically termed the ''triple whammy'' reaction[10–12]). Calculations estimate that the barrier is low enough to permit this reaction under the experimental conditions.[10] The experimentally observed photofragmentation yields are 28% for reaction (1), 65% for reaction (2), and 7% for reaction (3) under collision free conditions.[3] However, previous calculations had placed the transition state for reaction (2) 12–20 kcal/mol higher than for reaction (1).[11] Therein lies the paradox. *How can the yield be higher for the reaction with the higher barrier?*

In the years since the last computational study of this system,[10] more accurate computational schemes have been developed. Methods such as G2,[17–19] CBS-APNO,[20] and various extrapolation techniques using the cc-VnZ basis sets and CCSD(T) (Refs. 14, 21) can calculate energy differences to chemical accuracy (1 kcal/mol or better). These three approaches agree very well for the heat of reaction and barrier height for formaldehyde dissociation, $H_2CO \rightarrow H_2+CO$.[14,15] The CCSD(T)/cc-VnZ extrapolation methods are too costly for glyoxal. Since the CBS-APNO method is more accurate and cheaper than G2,[20] we have used it to study the glyoxal system. The present calculations were carried out with the GAUSSIAN series of programs.[22]

In the CBS-APNO method, geometries are optimized at the QCISD/6-311G(d,p) level of theory. The optimized geometries are compared in Fig. 1. The triple whammy structure agrees well with earlier calculations at the CCSD/DZP level when the structure is constrained to be planar.[10] However, this is found to be a second order saddle point. Full optimization leads to a transition state with a dihedral angle of $\approx 90°$ between the carbonyl groups [Fig. 1(a)]. The potential energy surface is very flat and the twisted transition state is only 1.1 kcal/mol lower than the planar second order saddle point. Reaction path following at the MP2/6-311G(d,p) and B3LYP/6-311G(d,p) levels of
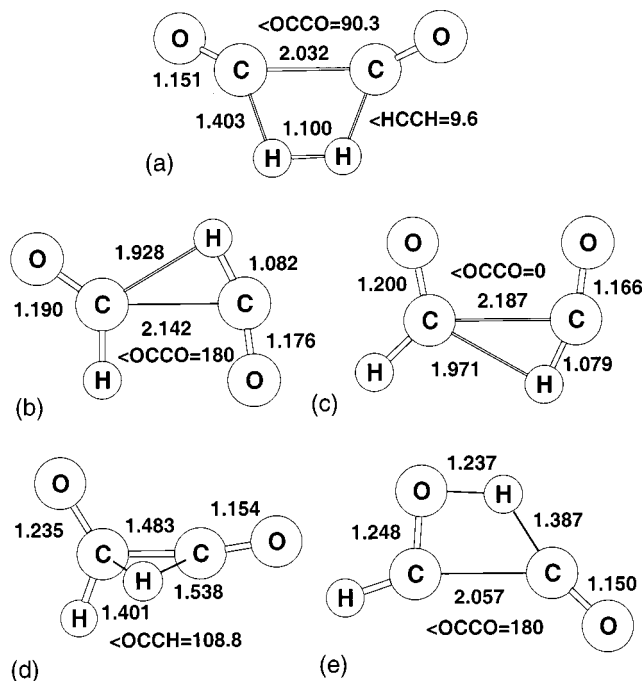
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FIG. 1. Transition state geometries for glyoxal dissociation optimized at the QCISD/6-311G(d,p) level of theory. (a) glyoxal→H_2+CO+CO, (b) and (c) structures on the glyoxal→HCO+HCO path (see text), (d) glyoxal→H_2CO+CO, and (e) glyoxal→HCOH+CO.

TABLE I. Enthalpies of reaction and barrier heights for the dissociation of glyoxal.[a]

	$\Delta H^0_{r,298}$	ΔH^t_{298}
$C_2H_2O_2 \rightarrow H_2 + CO + CO$		
MP2/6-311G(d,p)	−10.9	54.9
B3LYP/6-311G(d,p)	1.1	55.5
CBS-APNO	−1.8	59.2
experiment	−2.2±0.2	
$C_2H_2O_2 \rightarrow H_2CO + CO$		
MP2/6-311G(d,p)	−5.3	56.6
B3LYP/6-311G(d,p)	−0.2	51.6
CBS-APNO	−1.4	54.4
experiment	−1.8±0.2	
$C_2H_2O_2 \rightarrow HCOH + CO$		
MP2/6-311G(d,p)	50.5	59.3
B3LYP/6-311G(d,p)	52.8	56.5
CBS-APNO	51.2	59.7
$C_2H_2O_2 \rightarrow 2HCO$		
MP2/6-311G(d,p)	68.5	
B3LYP/6-311G(d,p)	65.2	
CBS-APNO	70.7	
experiment	71.5±0.2	

[a]Enthalpies at 298 K in kcal/mol; experimental data from Refs. 25–27.

theory confirms that this transition state connects glyoxal and H_2+CO+CO.

Two transition states have been reported for reaction (2),[11] with the one arising from *trans*-glyoxal being 2–3 kcal/mol lower than the one from *cis*-glyoxal. These were calculated to be 12–20 kcal/mol higher than the structure for the triple whammy channel.[11] The present calculations confirm this at the CBS-APNO level [Figs. 1(b) and 1(c)]. However, SCF stability calculations indicate that these structures have sizable singlet–triplet instabilities. Starting from these structures, optimizations using spin unrestricted MP2 calculations lead back to glyoxal without a barrier. Examination of the geometry suggests that these structures may be on the glyoxal→2HCO pathway. The energetics discussed below support this conjecture.

The correct transition structure for reaction (2) is shown in Fig. 1(d). It is a 1,2 hydrogen shift across the C–C bond, with the CCO angle for the departing CO nearly linear and the HCO group in the nascent formaldehyde rotated to accept the shifting hydrogen. The C–H distances for the migrating hydrogen are typical for 1,2 hydrogen shifts,[23,24] and the C–C bond is still intact, similar to other 1,2 hydrogen shifts.[24] Reaction path following confirms that this transition structure connects glyoxal and H_2CO+CO. SCF stability calculations show that it is stable with respect to spin unrestricted calculations. This transition state is 4.8 kcal/mol lower than the triple dissociation transition state at the CBS-APNO level. *This resolves the paradox between the observed photofragmentation yields and the calculated barrier heights.*

The calculated energetics for reactions (1)–(3) are col-

lected in Table I. The reaction enthalpies computed at the CBS-APNO level are in very good agreement with the available experimental data.[25–27] The B3LYP energetics are also in good agreement. Similar trends in the quality of the calculated energetics were obtained for $H_2CO \rightarrow H_2 + CO$.[15]

The barrier height for reaction (1) calculated at the CBS-APNO level is ≈5 kcal/mol higher than the extrapolated value of Scuseria and Schaefer for the planar structure.[10] Transition state theory using the MP2/6-311G(d,p) results indicates that at 298 K, the activation energy, E_a, is 0.6 kcal/mol higher than the barrier enthalpy. The calculated barrier height for reaction (2) is 4.8 kcal/mol lower than for reaction (1). Transition state theory again places the activation energy 0.6 kcal/mol above the barrier enthalpy. The reported experimental activation energy for the thermal decomposition of glyoxal is 47 kcal/mol,[28] considerably lower than the calculated value. However, this frequently quoted activation energy was based on a fit of the experimental data at high temperatures to a reaction mechanism and rate constants. This made use of the results of earlier calculations to estimate the difference in the activation energy of reactions (1) and (2) (the authors did note that some of the resulting numbers were anomalous[28]). A direct comparison with the experimental high pressure rate constant [$E_a = 55$ kcal/mol (Ref. 28)] shows excellent agreement with the present calculations.

The ''barriers'' computed for structures in Figs. 1(b) and 1(c) are 75.4 and 77.3 kcal/mol, respectively, with closed shell, spin restricted CBS-APNO, i.e., 16–18 kcal/mol higher than the transition state for the triple dissociation channel, similar to the earlier calculations.[11] Problems with these structures were described above. Their energies at CBS-APNO are close to the energy of HCO +HCO (70.7 kcal/mol), supporting the suggestion that

these structures belong to the glyoxal→HCO+HCO channel, which is energetically inaccessible under the experimental conditions. The barrier for reaction (3) has not been studied previously. The transition structure is shown in Fig. 1(e) and the barrier at the CBS-APNO level is 0.5 kcal/mol higher than for the triple dissociation channel.

In summary, the present calculations resolve the discrepancy between the observed photofragmentation yields and the theoretical barrier heights. Further investigations of these reactions by *ab initio* classical trajectory calculations are in progress.[29]

Note added in proof. D. M. Koch, N. H. Khieu, and G. H. Peslherve have recently submitted to J. Phys. Chem. a more extensive study of glyoxal unimolecular decomposition. Their calculations at the G3 level of theory and the present work at CBS-APNO are in excellent agreement.

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