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Author

Hepburn, J.W.

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A MOLECULAR BEAM STUDY OF THE PHOTOCHEMISTRY OF S_1 GLYOXAL

J. W. Hepburn,^a R. J. Buss, L. J. Butler and Y. T. Lee^b

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720

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ABSTRACT

The dissociation of glyoxal after excitation to low lying vibrational levels of the first excited singlet state has been studied using the method of molecular beam photofragment translational spectroscopy. Detection of products at masses 28, 29 and 30 provides unequivocal proof that the S_1 state of glyoxal predissociates in the absence of collisions. The product time of flight spectra show the presence of three distinct dissociation channels; the major ones being formation of $H_2CO + CO$ and the triple dissociation forming $2CO + H_2$. The third minor channel is attributed to the formation of CO plus an H_2CO isomer, possibly hydroxymethylene.

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- a. present address: Department of Chemistry and Department of Physics,
University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.
b. Miller Professor, 1981-1982.

INTRODUCTION

In several experimental studies, glyoxal has provided a good model system for investigating molecular photophysics and photochemistry. The first excited singlet state, the 1A_u state, has been the subject of many studies using diverse techniques. The $^1A_u \leftarrow ^1A_g$ spectrum has been thoroughly analyzed¹ and the photophysics of the S_1 state is well understood.² The photochemistry of this state is, however, only poorly known, in spite of a long history of study.³ Not until the recent work by Parmenter's group⁴ has there been a clear indication of photodissociation in the absence of collisions after excitation to the S_1 state. The products of this dissociation include H_2 , CO and H_2CO , but neither the detailed mechanism for their formation nor their relative yields were elucidated by these studies.

The mechanism for H_2 formation near the S_1 zero point is of particular interest as the production of H_2 by a sequential mechanism (i.e. formation of H_2CO followed by decomposition to $H_2 + CO$) is not allowed, because the potential energy barrier (>80 kcal/mole) for such a process⁵ is much higher than the maximum internal energy of H_2CO (~ 60 kcal/mole). Recent ab initio work by Osamura et al⁶ proposed a mechanism for H_2 formation in which the dissociation of glyoxal to yield $H_2 + 2CO$ occurs in a concerted fashion from a near planar cis-geometry transition state.

In an attempt to clarify the primary products and fragmentation mechanism, our study was carried out on the photofragmentation of glyoxal

molecules in a supersonic molecular beam. In this paper the photo-fragmentation process resulting from excitation of the 8_0^1 band of the $S_1 \leftarrow S_0$ system, especially the relative yields for the various product channels and the mechanism for H_2 formation, are discussed.

EXPERIMENTAL

The method of molecular beam photofragment translational spectroscopy has been previously reported.⁷ A supersonic beam of glyoxal was formed by expanding a mixture of 300 torr of He and ~50 torr of glyoxal (from a 0°C reservoir of the monomer) through a 0.13 mm diameter nozzle heated to 150°C. A conical skimmer was located 5 mm from the nozzle and the beam was defined to a 2° angular divergence by defining slits on the chamber walls of the two stages of differential pumping, before it was crossed by the unfocused output of a Nd:YAG pumped dye laser (Quanta-Ray). Photofragments were detected by a mass spectrometer which rotated in the plane of the two beams about the crossing volume. Product time of flight spectra were recorded at various angles using a multichannel scaler triggered by the laser. The mass spectrometer ionizer was located 20.8 cm from the crossing of the laser and molecular beams. Because of the defining slits between the detector ionizer and the beam-laser crossing, only photofragments originating in the crossing volume (~3 mm on a side) were detected.

In order to be certain that the photolysis laser was resonant with the glyoxal transition, fluorescence was collected by an f/0.67, 1.5" diameter lens (located below the beam laser crossing), spatially filtered, and detected by a phototube. For the data reported here, the laser was resonant with the band origin of the 8_0^1 band at 4398 Å. The output of the laser was 10 mJ/pulse in 0.5 cm^{-1} .

RESULTS AND ANALYSIS

For the 8_0^1 band of glyoxal, product time of flight spectra were taken at masses 28, 29 and 30. At mass 28, TOF spectra were recorded with the detector at 10° , 20° , 30° and 40° away from the glyoxal beam. For mass 29, data was collected at 7° , 10° , 15° , 20° , 30° and 40° . A mass 30 spectrum was recorded only at a detector angle of 10° .

Figure 1 shows the time of flight spectra of masses 28, 29 and 30 obtained at 10° detector angle. With the laser powers used in these experiments, both the fluorescence signals and the photofragment signals were linear in laser power, indicating that the observed photochemistry was the result of a single-photon process. Although signal from a small amount of dimer in the beam was detected in the product TOF spectra, the dimer photochemistry was shown not to contribute to the main features of the results by repeating the measurements using beam conditions for which the dimer signal was eliminated, and observing no change in the product TOF spectra (other than the disappearance of the dimer peak).

The solid lines drawn through the data are the TOF spectra calculated using the product translational distributions $P(E)$'s shown in Fig. 2. The dotted line spectra shown in Fig. 1 give the result of each $P(E)$ in Fig. 2, considered separately. The $P(E)$ were determined by a trial and error fitting procedure, with the assumption that the center-of-mass angular distribution of product is isotropic and uncoupled from the $P(E)$.

The only fragmentation channels allowed energetically are as follows:



As HCOH has not yet been directly observed, there is no experimental heat of formation available. Recent theoretical work,^{5a,b} however, has indicated that the hydroxymethylene channel is energetically accessible. The radical channels, such as formation of two HCO radicals, are not allowed energetically.⁸

The TOF spectra at mass 29 and mass 30 show contributions from two primary channels with the channels becoming better resolved at larger angles. The only source of ions at mass 29 (HCO^+) and 30 (H_2CO^+) is some isomer of H_2CO . The individual peaks in the mass 30 spectra must have an identical shape to those in the mass 29 spectra, as a consequence of the common parent. Using the two $P(E)$'s shown in Fig. 2 and with isotropic center of mass angular distributions it was possible to fit the mass 29 data at all angles. The quality of the fit was very sensitive to both the peak position and widths of the distributions chosen (peak ± 0.5 kcal/mole, width ± 10 percent); and the relative probability of the two channels was found to be 9:1 (channel 3: channel 1).

The TOF spectrum for mass 28 (CO^+) does not have the same shape as the mass 29 and mass 30 spectra. An additional feature appears as a shoulder on the slow side of the major peak. The source of this extra signal cannot be the CO from the $\text{CO} + \text{H}_2\text{CO}$ channels because the velocity distribution of this CO is fixed by linear momentum conservation in the center of mass coordinate system to be very similar to that of the H_2CO . The shoulder on the major peak must arise from a dynamically distinct channel producing CO with a velocity intermediate to that formed in the previously discussed channels.

An energy distribution for this new channel that must be introduced to fit the mass 28 data is shown in Fig. 2. It is not possible to fit the mass 28 data by using the two distributions which fit the mass 29 data, even if their relative intensities are varied. In obtaining a P(E) to fit the third channel, it was assumed that the two channels observed in the mass 30 data contribute to the mass 28 spectra the same relative amounts. The relative yield for the three channels was obtained from the signal intensities after correcting for kinematic effects, and noting that channel 2 produces twice the signal at mass 28 while channel 1 and 3 give a contribution by direct ionization of the CO and the dissociative ionization of the H₂CO product. The resulting branching ratio was found to be 3.5:9:1 (channel 2: channel 3: channel 1).

DISCUSSION

These data show that excitation to low-lying vibrational states in the S_1 state of glyoxal leads to dissociation in the absence of collisions. Although not shown here, similar data have also been obtained for several low lying vibrational bands including the zero point level of S_1 , which suggests that all vibrational states of S_1 predissociate. The TOF data show the presence of three product channels at the photon energy used, 65 kcal/mole.

Of particular interest is the product channel which can be seen only in the mass 28 TOF spectrum. This implies that a fragmentation channel exists which gives CO but not formaldehyde (or formaldehyde isomer) and this is likely to be: $H_2C_2O_2 + h\nu \rightarrow H_2 + 2CO$, suggested by Osamura et al.⁶

In a sequential dissociation process for which the first step is the formation of $CO + H_2CO$ followed by fragmentation of the formaldehyde, the maximum energy available for internal excitation of the H_2CO is 56 kcal/mole. However, it has been well established, both theoretically and experimentally⁵ that the barrier to decomposition of formaldehyde to $H_2 + CO$ exceeds 80 kcal/mole. Therefore sequential dissociation is prohibited at these excitation energies.

In fact, the energetics observed are those expected for a single step decomposition. The CO TOF spectrum determines the translational energy of CO, from which the total translational energy can be obtained only in the case of fragmentation to two products (mass 28 and mass 30). In the case of a fragmentation to three products, the analysis is more complicated⁹ and the conservation laws are not sufficient to allow exact determination of the

product translational energy unless measurements are carried out on all three fragments. Because the mass of H_2 is so small compared to that of CO, there are kinematic constraints restricting the geometries of decomposition. In order to conserve energy and linear momentum, the concerted decomposition which results in CO product separating symmetrically with respect to the H_2 velocity with 7.5 kcal/mole of translational energy (the experimentally observed most probable) must result in the angle between the velocity vector of the two CO molecules being $>144^\circ$. If you allow the transition state to be nonsymmetric, the angle between the two CO molecules must be $>141^\circ$. The average decomposition results in 15 kcal/mole in translation of the two CO molecules and 41 kcal/mole which are shared among H_2 translation and internal excitation of the three species. It is likely as in many other four-center eliminations, that the H_2 is vibrationally excited.

Unfortunately, due to the extreme difficulty of H_2 detection in a beam experiment, it was not possible to obtain a meaningful TOF spectrum at mass 2, so the actual total translational energy is not known. However, if we assume an impulsive energy being channeled into product translation, we would in fact predict the observed behavior of the channel 2 $P(E)$,⁹ with a mean 8 kcal/mole in CO translation, and a maximum of 15 kcal/mole.

The most probable fragmentation channel gives $CO + H_2CO$ as products, with about 60 percent of the available energy remaining in product internal excitation. While the identities of this product channel and the $H_2 + 2CO$ channel are unambiguous, the lowest translational energy channel is more difficult to assign. The products are CO and a formaldehyde isomer, but the energetics are completely different from the $CO + H_2CO$ channel.

There are two possible explanations for this low translational energy channel. The first one is that the products are also $\text{CO} + \text{H}_2\text{CO}$, but there is a microscopic branching¹⁰ which leads to the bimodal energy distribution; i.e., there are two quite different pathways on the potential hypersurface to the $\text{CO} + \text{H}_2\text{CO}$ product. If this is true, the less probable path to the $\text{CO} + \text{H}_2\text{CO}$ product would have to deposit almost 90 percent of the available energy into internal excitation of the products. Since there is no low lying electronic state to take up some of the internal energy, this explanation also implies that all the energy in the product internal excitation is vibrational or rotation.

The other more likely possibility for this channel is the formation of $\text{CO} + \text{hydroxymethylene, HCOH}$. Reliable theoretical calculations place HCOH 50 kcal/mole higher in energy than formaldehyde.⁵ This would give the $\text{CO} + \text{HCOH}$ channel ~15 kcal/mole of excess available energy, which is consistent with the product translational energy observed for this channel.

Further evidence for an unstable product such as HCOH is provided by Parmenter's recent work⁴ in which mass analysis of the condensable product resulting from low pressure photolysis of $\text{H}_2\text{C}_2\text{O}_2$ gave the stoichiometry as $\text{C}_{1.7}\text{H}_{2.0}\text{O}_{1.7}$, rather than CH_2O which would be expected if formaldehyde was the only condensable product. In light of this additional evidence, we tentatively ascribe this low translational energy channel to formation of $\text{CO} + \text{HCOH}$.

From the mass 28 TOF, the relative yields of the three channels has been determined to be: $\text{H}_2\text{CO} + \text{CO}$, 67 percent; $2\text{CO} + \text{H}_2$, 26 percent; $\text{HCOH} + \text{CO}$, 7 percent.

In a recent study by J. Troe's group on the thermal decomposition of glyoxal¹¹ the yields for the $\text{H}_2\text{CO} + \text{CO}$ and $2\text{CO} + \text{H}_2$ channels were found to be approximately equal, and the barriers for both decompositions were found to be ~ 50 kcal/mole. Although these two sets of experimental results cannot be compared directly because different initial excitation energies were used, both agree that one of the major channels is formation of $2\text{CO} + \text{H}_2$ as has been predicted theoretically.

ACKNOWLEDGMENTS

This work was inspired by the theoretical prediction of "triple whammy" of Osamura, Schaefer, Dupuis and Lester.⁶ Stimulating discussions with Schaefer, Parmenter and their coworkers are gratefully acknowledged. This work 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 No. DE-AC03-76SF00098.

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FIGURE CAPTIONS

- Fig. 1. Time of flight spectra taken with detector 10° from molecular beam. Data taken at masses 28, 29 and 30 are given as points, while fits to data are shown as solid lines. Fits show result from energy distributions given in Fig. 2. Contributions to total due to each channel are shown as dotted lines.
- Fig. 2. Translational energy distributions used to obtain calculated time of flight spectra shown in Fig. 1 for a) mass 28 and b) masses 29 and 30.

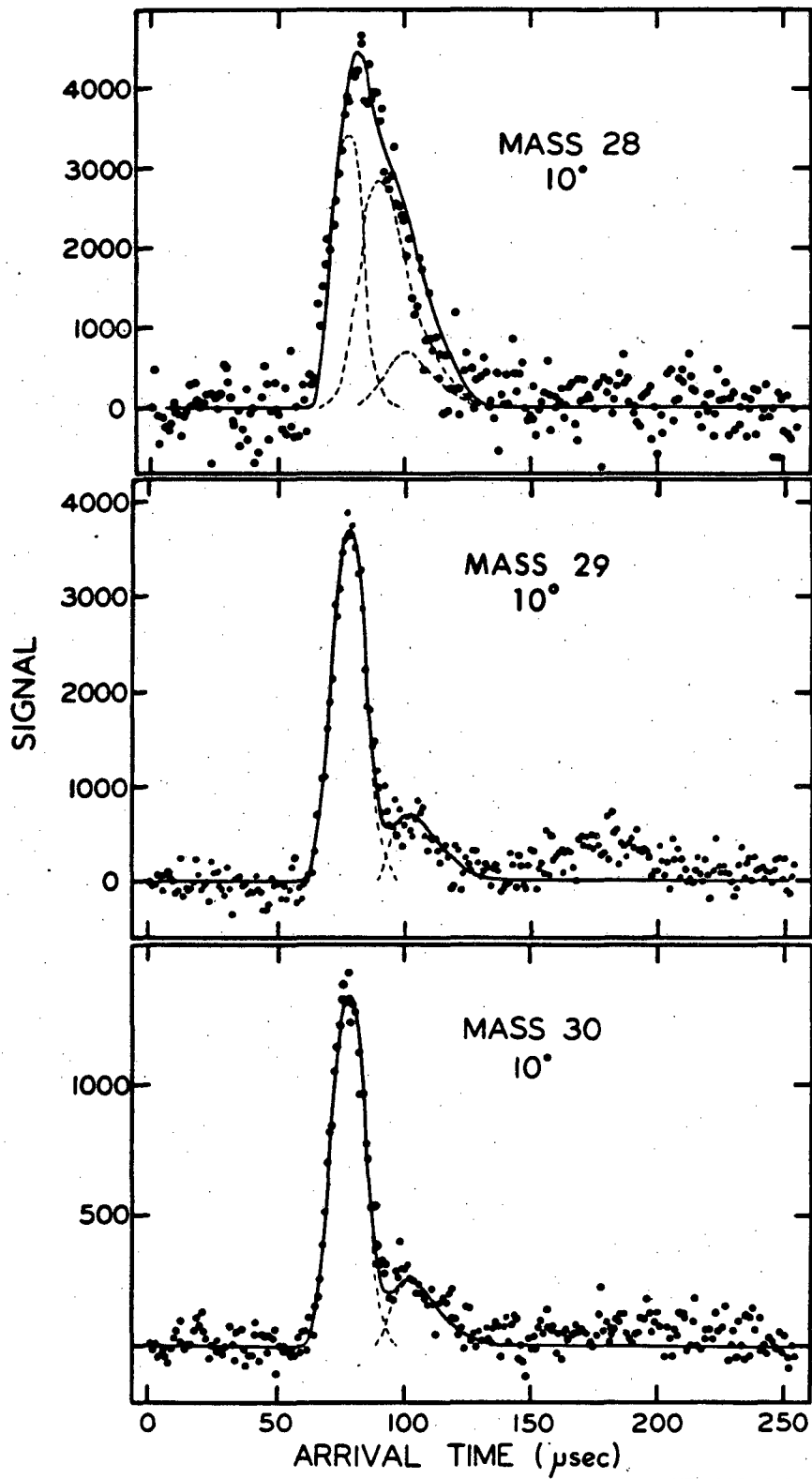


Fig. 1

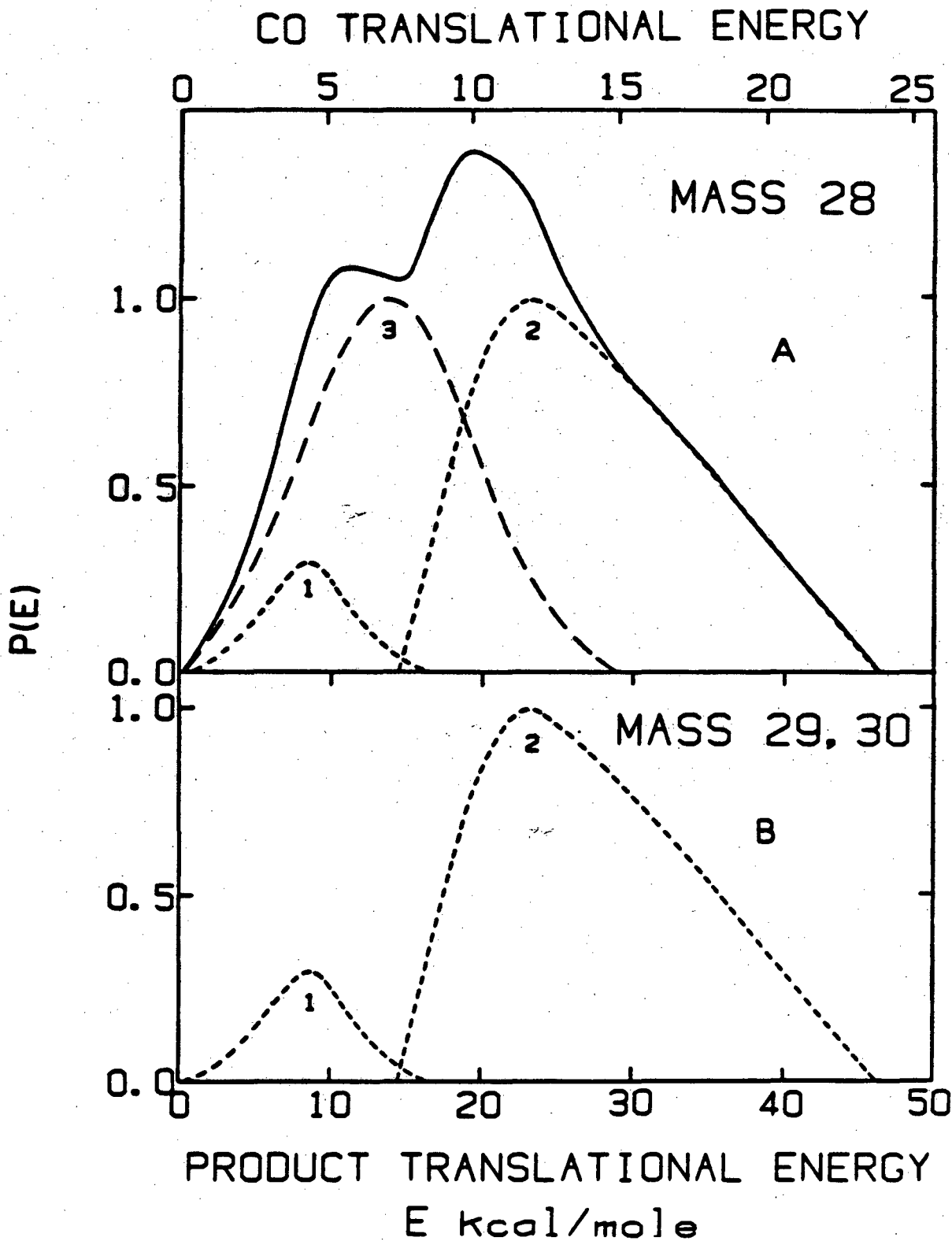


Fig. 2

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