LASER CHEMISTRY, MOLECULAR DYNAMICS, AND **ENERGY TRANSFER**

Product Ratios in the Photolysis of cis- and trans-Glyoxal at Low Pressures: The Mechanisms of the Thermal and the Photochemical Decompositions[†]

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Values of the product ratio H_2/CO have been measured for the photolysis of *cis*-glyoxal excited at 488.0 nm and of *trans*-glyoxal excited at 454.5 nm for pressures of glyoxal ranging from 0.01 to 0.45 torr. In the low-pressure limit, ratios from the two isomers converge and rise toward a value of 0.5. It is concluded that the collision-free decomposition proceeds largely through crossing from the excited singlet state to high vibrational levels of the ground state, which then decomposes to $H_2 + 2CO$. With increasing pressure the H_2/CO ratio falls sharply, which is attributed to collisional deactivation of the vibrationally excited ground state and its consequent decomposition by a lower energy path to $H_2CO + CO$. These results and conclusions are compared with those found recently in the thermal decomposition and in a molecular-beam study of the dynamics of the photolysis. Product ratios were also measured in the infrared multiphoton decomposition of glyoxal, with a pulsed CO₂ laser. The results were similar to those found at 488.0 and 454.5 nm and support the conclusion that the vibrationally excited ground state decomposes by two channels.

Introduction

The spectroscopy¹ and photochemistry¹⁻⁴ of glyoxal, the prototype α -dicarbonyl compound, have been extensively studied. Biacetyl has also been thoroughly investigated,² while three other α -dicarbonyl compounds, oxalic,⁵ glyoxylic,⁶ and pyruvic⁷ acid, have been recently examined in this laboratory, all in the gas phase. All these compounds are planar (except for the methyl hydrogens), with barriers to rotation around the OC-CO bond of perhaps 10 or 15 kcal/mol, and are almost entirely in the trans configuration; in fact, only with glyoxal has the cis isomer been observed.⁸ Several decomposition reactions of these compounds, both thermal and photochemical, would appear however to proceed through cis configurations. With glyoxal, for example, the unimolecular decomposition into $H_2 + 2CO$ would require the cis isomer in the transition state. The concentration of cis-glyoxal in equilibrium with the trans isomer was estimated spectroscopically by Currie and Ramsay⁸ to be about 1 part in 1000 at room temperature, but a fortuitous coincidence of the 0-0 band with the strong 488-nm line from an Ar ion laser has permitted its selective excitation and thence several studies of its fluorescence and photophysics.8,9

The photodecomposition of cis-glyoxal has never been studied, and it was of some interest to see whether the dissociation to H₂ + 2CO might be enhanced relative to that in the photolysis of trans-glyoxal, particularly for the low-pressure collision-free photolysis recently shown to occur by Loge and Parmenter³ and by Hepburn et al.⁴ The present article describes a measurement of product ratios in the photolysis of cis-glyoxal excited at 488 nm. For comparison, the decomposition of trans-glyoxal excited at 454.5 nm was also examined. And finally, some experiments with the decomposition induced by a pulsed CO_2 laser, which should unambiguously excite the ground electronic state, are described.

Experimental Section

Photolyses at 488.0 and 454.5 nm were carried out in cylindrical Pyrex vessels about 1 m long, fitted with plane glass windows at

each end. Glyoxal pressures were varied from about 10 to 1000 mtorr, measured with a Baratron diaphragm gauge. At the higher pressures a vessel of 22-mm i.d. was used, while at lower pressures, one of 80-mm i.d. was employed to provide enough product for accurate measurement while staying at moderate conversions. Two different argon ion lasers were used, one of which delivered about 5 W at 488.0 nm and the other about 1 W at 454.5 nm. The laser beams were usually passed several times through the vessels by means of external mirrors.

The experiments with the pulsed CO₂ laser were done in a Pyrex vessel 1.2 m long and 40-mm i.d., fitted with plane NaCl windows. The unfocused beam from a Lumonics Model 203 pulsed CO₂ TEA laser was used, as previously described,¹⁰ at wavelengths of 9.174 and 10.674 µm.

After photolysis, products were removed for analysis through a trap at 77 K which removed formaldehyde and unreacted glyoxal. The remaining CO and H_2 were transferred by a Toepler pump into the pickup of a gas chromatograph. They were measured on a 2-m column of 5 Å molecular sieve operating at about 30 °C by using a thermal conductivity detector and argon carrier gas, which gave reasonable sensitivities for both products.

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Figure 1. Emission spectra of fluorescence excited at 488.0 nm. Arrows indicate origins of the 8_1^0 (19463 cm⁻¹) and the weak 4_0^1 bands of *cis*-glyoxal and of the 0–0 band of *trans*-glyoxal (21969 cm⁻¹). The upper spectrum is red-shifted relative to the lower one.

The gas chromatograph was calibrated frequently throughout the experiments with known mixtures in the same range of concentrations as the products.

Glyoxal was prepared in the usual way¹¹ by carefully heating the trimer with P_2O_5 , and was degassed thoroughly at 195 K before each experiment to remove any traces of formaldehyde, H_2 , or CO.

Results

Photolysis of cis-Glyoxal at 488.0 nm. Beyer and Lineberger⁹ have reported that excitation of cis-glyoxal with a dye laser at 487.5 nm also led to some excitation of trans-glyoxal from absorption in the overlapping $8_1^0 5_1^0 7_1^1$ hot band and found emission from the trans isomer comparable in intensity to that from cisglyoxal. To estimate the extent of this possible complication in the present work, we measured emission spectra from glyoxal at a pressure of 138 mtorr excited at 488.0 nm, using a double monochromator with photon-counting detection. Figure 1 shows scans of the emission in the 0-0 band of trans-glyoxal at 21973 cm^{-1} and the 8^0_1 band of *cis*-glyoxal at 19463 cm⁻¹, both known to be strong bands in fluorescence and conveniently displaced from the exciting wavelengths. The 7_1^1 sequence band of *trans*-glyoxal, expected since $v_{1} = 1$ was excited in the hot-band absorption, was also observed, but its emission intensity was about one-third that of the 0–0 band; evidently, the low-frequency v_7 torsional vibration was largely relaxed at the pressure of 138 mtorr employed, confirming similar observations by Beyer and Lineberger.⁹ The cis-glyoxal emission in the 8^0_1 band was perhaps 3 or 4 times more intense than that of the combined emission from the 0-0 and the 7_1^1 bands of *trans*-glyoxal. This ratio of cis-to-trans emission is appreciably higher than that reported by Beyer and Lineberger,⁹ who found about equal intensities from the two isomers. This can be attributed to the more selective excitation of *cis*-glyoxal by the Ar ion laser line, which is centered at 488.1223 nm and has a line width of about 0.005 nm. As noted by Currie and Ramsay,⁸ this coincides closely with a fairly strong rotational feature, and comparison with their spectra indicates a strong overlap with this feature. Beyer and Lineberger, on the other hand, used a dye laser with a bandwidth of about 0.1 nm centered at 487.5 nm, which would have overlapped several weak rotational features (and the gaps between them) so that excitation of underyling hot bands of trans-glyoxal would have been relatively much more important.

The faster internal conversion and the more efficient collisional quenching of the cis- S_1 state⁹ suggest a lifetime about 3 times



Figure 2. Product ratios from the photolysis of *cis*-glyoxal at 488.0 nm (circles) and that of *trans*-glyoxal at 454.5 nm (squares). Filled points are for the large reaction vessel. Triangles are data from Loge and Parmenter³ for *trans*-glyoxal.



Figure 3. Product ratios from the multiphoton infrared decomposition of glyoxal.

shorter than for *trans*-glyoxal under our experimental conditions. There is also some evidence¹⁵ that the transition probability may be appreciably lower than that for *trans*-glyoxal, and taking this and the shorter lifetime into account, it appears that the quantum yield for emission from the S_1 state of *cis*-glyoxal could be 10 or 12 times lower than that for *trans*-glyoxal. The observed ratio of cis-to-trans emission would then correspond to only 2% or 3% excitation of *trans*-glyoxal, and assuming similar yields for dissociation,¹⁶ the products observed should have been largely derived from photolysis of *cis*-glyoxal. (While there are obvious uncertainties in these arguments, it is difficult to see how more than 10% or 15% (at the most) of the products could have come from photolysis of the trans isomer.)

Figure 2 shows the ratio H_2/CO formed in the photolysis of *cis*-glyoxal at 488.0 nm as a function of glyoxal pressure, together with similar data from the photolysis at 454.5 nm, which should have excited exclusively *trans*-glyoxal. At both wavelengths, data from the two reaction vessels are in good accord, and no systematic trend with conversion (which varied from 5% to 50%) was evident.

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Figure 4. Energy diagram (heats of formation) for the reagents, products, and intermediate states involved in the glyoxal decomposition.

Figure 3 shows values of H_2/CO from the decomposition of glyoxal induced by the pulsed CO_2 laser, plotted against pressure of glyoxal.

Discussion

It is clear from Figure 2 that values of the H_2/CO ratio produced by excitation of *cis*- and *trans*-glyoxal become indistinguishable, within the experimental scatter, at low pressures, and extrapolate smoothly to those of Loge and Parmenter,³ also plotted, and also obtained with 454.5-nm radiation. The data are also compatible with extrapolation to a zero-pressure collision-free value of 0.5, the theoretical limit corresponding to exclusive production of $H_2 + 2CO$, although a somewhat lower value cannot be ruled out. The data also show a significant difference in the product ratio from the two isomers at higher pressure, where the values of H_2/CO drop more rapidly with increasing pressure with *cis*glyoxal.

There is no convincing evidence that the photolysis of glyoxal at these wavelengths yields any final products other than H_2 , CO, and H_2CO . Secondary photolysis of H_2CO , or its sensitized decomposition, is impossible at these wavelengths, a conclusion supported by the independence of the H_2/CO ratio on conversion in this and earlier work.³ The following discussion will be based therefore on the assumption that the photolysis can be described by the two unimolecular processes

$$C_2H_2O_2 \rightarrow H_2CO + CO \tag{1}$$

$$C_2H_2O_2 \rightarrow H_2 + 2CO \tag{2}$$

The ratio H_2/CO is then a direct measure of the relative extent of the two processes, varying from 0.5 for reaction 2 alone to 0.0 for reaction 1, with the ratio of rates given by $R_2/R_1 = H_2/(CO - 2H_2)$.

Figure 4 shows energy levels of the states of *cis*- and *trans*glyoxal and the possible sets of reaction products; several features require some comment. It will be noted that the heats of formation of the excited singlet states of the two isomers are quite close (*cis*-glyoxal is 342 cm^{-1} lower), despite the separation of 1467 cm⁻¹ between the 0–0 bands of the two transitions. The difference is made up by the higher heat of formation of *cis*-glyoxal in the ground state, estimated by Currie and Ramsay⁸ to be 3.2 kcal/mol above that of *trans*-glyoxal. The broken lines joining the vibrational manifolds of the two ground states indicate the interchange between the two isomers that can occur when the vibrational energy exceeds the barrier for rotation around the C–C bond. At higher energies, this isomerization would become much faster than other reactions such as decomposition, and the two ground states would behave like a single freely rotating species. It should be noted that, in the present experiments, both *cis*- and *trans*-glyoxal were excited to the lowest vibrational levels of their excited singlet states. The torsional frequencies are higher than in the ground states,^{1,8} and the barriers to rotation are almost certainly higher. Isomerization between these excited states cannot occur without collisional activation; even with collisions, such thermal isomerization would be negligible during the expected lifetimes⁹ of these states of a few microseconds. This is borne out by the emission observed when *cis*-glyoxal was excited at 488.0 nm (Figure 1); the weak emission from *trans*-glyoxal here was almost certainly due to hot-band excitation of the latter rather than from isomerization.

The energy threshold of 55.1 kcal/mol for dissociation of ground-state *trans*-glyoxal into $H_2 + 2CO$ shown in Figure 4 is based on recent measurements of the thermal decomposition at 1100–1540 K in which apparently only reaction 2 was observed.¹² A lower threshold of 52 kcal/mol for reaction 1 was chosen rather arbitrarily, based on the lower activation energy found in the thermal decomposition at lower temperature where reaction 1 appeared to predominate.¹³ These thermal studies will be discussed later. A third decomposition channel to give HCOH + CO is shown with a threshold tentatively placed 5 kcal/mol above the estimated heat of formation of these products.⁴

The following reactions must be considered in the present systems:

$$\operatorname{cis-S}_0 + h\nu \to \operatorname{cis-S}_1$$
 (3)

$$trans-S_0 + h\nu \rightarrow trans-S_1 \tag{4}$$

 $\operatorname{cis-S}_1 \to \operatorname{cis-S}_0 + h\nu$ (5)

$$trans-S_1 \rightarrow trans-S_0 + h\nu \tag{6}$$

 $trans-S_1 \rightarrow HCOH + CO \tag{7}$

$$\operatorname{cis-S}_1 \to \operatorname{cis-S}_0^1$$
 (8)

$$trans-S_1 \rightarrow trans-S_0^{\ddagger} \tag{9}$$

(12) K. Saito, T. Kakumoto, and I. Murakami, J. Phys. Chem., 88, 1182 (1984).

(13) L. F. Lowden, Ph.D. Thesis, University of Oregon, 1972; Diss. Abstr. Int. B, 33, 2013 (1972).

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(15) Currie and Ramsay⁸ found that *cis*-glyoxal required a combination of path length and pressure about 1000 times greater than *trans*-glyoxal to give approximately equal absorption in the 0–0 bands of the two isomers at room temperature. The careful measurement by the same authors of the temperature dependence of the cis/trans ratio leads to a Boltzmann factor of about 220 at 300 K, suggesting that the absorption coefficient of *cis*-glyoxal, and hence the transition probability, is perhaps 4 times smaller than that of *trans*-glyoxal.

(16) Similar yields of dissociation are expected, especially at low pressures where Lineberger's studies⁹ indicate that the major loss process for both isomers is internal conversion to high levels of the ground state. It will be argued (see text) that, at these levels, cis-trans isomerization is fast compared to dissociation, so that it becomes immaterial which isomer was originally excited, and under these circumstances yields of dissociation must be similar, since the energies are similar (Figure 4). With increasing pressure, collisional quenching of the S₁ states begins to compete with internal conversion, and from Lineberger's measured rate constants for these processes,⁹ the yield of internal conversion would drop somewhat faster for *cis*-glyoxal than for *trans*-glyoxal. At the highest pressures used in the present experiments, the quantum yield of dissociation of *cis*-glyoxal should have been no less than half that of *trans*-glyoxal.

(17) A referee has suggested that collision-induced crossing to the triplet state could account for our observations if the quantum yield of dissociation of the triplet were much higher than that of the $S_1-S_0^{1}$ route. The observation by Loge and Parmenter of values of 0.6–0.7 for the latter leaves little leaway for an increase in the yield from the triplet and renders this explanation very unlikely.

(18) Beam velocity is not reported in ref 4, but assuming it to be the same as in ref 14 (it may have been somewhat higher), the 3-mm sampling zone was traversed in 2.36 μ s. The average time spent in the sampling zone after irradiation should have been just half this, or about 1 μ s.

$$\operatorname{cis-S_0^{\ddagger}} \to \operatorname{trans-S_0^{\ddagger}}$$
 (10)

(11)

$$\operatorname{cis-S_0}^{\ddagger} \to \operatorname{H}_2 + 2\operatorname{CO}$$
 (11)
 $\operatorname{cis-S_*}^{\ddagger} \to \operatorname{H}_2\operatorname{CO} + \operatorname{CO}$ (12)

$$\operatorname{trans-S_0}^{\ddagger} \to \operatorname{HCOH} + \operatorname{CO}$$
(12)

trans-
$$S_0^{\dagger} \rightarrow HCOH + CO$$
 (13)
trans- $S_0^{\dagger} \rightarrow H_2CO + CO$ (14)

$$\operatorname{cis-S_0}^{\ddagger} + M \to \operatorname{cis-S_0} + M$$
 (15)

$$trans-S_0^{\dagger} + M \rightarrow trans-S_0 + M$$
(16)

$$cis-S_1 + M \rightarrow cis-T_1 + M$$
 (17)

$$\operatorname{trans-S}_1 + M \to \operatorname{trans-T}_1 + M \tag{18}$$

$$\operatorname{cis-T_1} \rightarrow \operatorname{cis-S_0}^{\ddagger}$$
 (19)

trans-
$$T_1 \rightarrow \text{trans-}S_0^{\ddagger}$$
 (20)

Two main conclusions can be drawn from the present study: (1) We conclude, in agreement with Loge and Parmenter,³ that the collision-free photolysis in the low-pressure limit proceeds by radiationless transition to high vibrational levels of the ground state which decompose largely (80%-100%) to $H_2 + CO$ (reactions 8-11). Strong support for this comes from the fact that both isomers decompose in this way, although the cis configuration is required to form these products. As noted above, the excited singlet state cannot undergo cis-trans isomerization at the levels excited, but interconversion of the vibrationally excited ground states, S_0^{\dagger} , would be fast compared to their decomposition.

(2) The initial decrease in the H_2/CO ratio with increasing pressure *cannot* be explained by the well-established² collisioninduced crossing to the triplet state (reactions 17 and 18) which then decomposes to yield $H_2CO + CO$, as suggested by Saito et at.¹² Comparison with the rate of the collision-induced disappearance of both excited singlet states, carefully measured by Beyer and Lineberger⁹ via their fluorescence, reveals that this process is much too slow to account for our results.¹⁷ This is most clearly shown in Figures 5 and 6, where the decrease in the ratio $R_2/(R_1 + R_2)$ with pressure for each isomer is compared with values calculated from the data of Beyer and Lineberger, assuming that the collision-free decomposition proceeds only by channel 2 and the triplet decomposition only by channel 1. The only reasonable explanation of the much faster observed decrease of $R_2/(R_1 + R_2)$ with pressure is that at low pressures this is due largely to collisional deactivation of the vibrationally excited ground state (reactions 15 and 16), with decomposition via channel 1 occurring at a lower energy threshold (and lower frequency factor) than channel 2.

It can be seen from Figures 5 and 6 that at the higher pressures the ratio $R_2/(R_1 + R_2)$ appears to be leveling out at some nonzero value which is somewhat higher for *trans*- than for *cis*-glyoxal. Plots of the same ratio against reciprocal pressure show highpressure intercepts of 0.076 and 0.150 for the cis and trans isomers, respectively. This is to be expected from the proposed mechanism, in which S_0^{\dagger} is produced by reactions 8 and 9 at energies above the thresholds for both decomposition channels and loses vibrational energy by multiple collisions which progressively reduce its energy first below the threshold for channel 2 (reaction 11) and then below that for channel 1 (reactions 12 and 14). With increasing pressure, as deactivation through the reactive energy range becomes more rapid, the ratio of the integrated yields of the two channels will tend toward a constant, but nonzero, value, favoring the lower energy channel. The lower limiting ratio apparently found for cis-glyoxal may be partly due to the slightly lower initial energy of $\operatorname{cis-S_0}^t$, but an additional effect might be a contribution to channel 1 from decomposition via the triplet (reactions 17-20 and then 12 and 14) which sets in at a lower pressure with the cis isomer (Figures 5 and 6). At sufficiently high pressure, of course, reaction via the triplet state will predominate, and if this proceeds largely by channel 1, as seems probable, the $R_2(R_1 + R_2)$ ratio will finally fall again toward zero. We suggest that the triplet decomposes by crossing to the ground



Figure 5. Values of $R_2/(R_1 + R_2)$, the fraction decomposing via reaction 2, for the photolysis of cis-glyoxal at 488.0 nm. The upper curve is calculated from fluorescence quenching data;9 see text.



Figure 6. Values of $R_2/(R_1 + R_2)$, the fraction decomposing via reaction 2, for the photolysis of *trans-glyoxal* at 454.5 nm. Filled circles are data from Loge and Parmenter.³ The upper curve is calculated from fluorescence quenching data.9

state (reactions 19 and 20, perhaps induced by collision) rather than directly, this being more consistent with the behavior of analogous systems, such as formaldehyde, and with the fact that direct decomposition of S_1 is not an important process.

While the suggested mechanism seems the only reasonble way to explain the present observations, there are two apparent conflicts with other studies of the glyoxal decomposition. The first of these is with the molecular-beam experiment of Hepburn et al.,⁴ who photolyzed trans-glyoxal at 439.8 nm (and also apparently at 454.5 nm with "similar" results). They observed channels 1 and 2 with a ratio $R_2/(R_1 + R_2) = 0.30$, far below the low-pressure limiting value of 0.8-1.0, which we found (Figure 6). They also found evidence for a third channel, yielding HCOH + CO, about 10% of channel 1. A tentative explanation of the difference between these results and ours lies in the sampling time of the beam experiments, which appears to have been about 1 μ s.¹⁸ Beyer, Zittel, and Lineberger⁹ measured a collisionless lifetime of 0.87 μ s for the trans-S₁ state excited to the 8¹ vibrational level, thought to be largely determined by radiationless transition to S_0^{\dagger} . Thus, the appearance of products from the subsequent decomposition of S_0^{\dagger} would show an induction period with a duration comparable to the sampling time of the beam experiments. Further, from our measured pressure dependence of H_2/CO , the lifetime for decomposition of S_0^{\dagger} can be estimated as 3-5 μ s, and while it may be somewhat less at the higher energy of the 439.8-nm excitation, the net result of these effects is that the beam experiments would sample only a small initial fraction of the decomposition of S_0^{t} . This would not matter if S_0^{\dagger} were the only source of products, but if at the same time a small fraction of S_1 decomposed directly to $H_2CO + CO$ in competition with reaction 9, this process would be more heavily weighted, relative to the slower sequential decomposition of S_0^{t} , by the shorter sampling time of the beam. Such internal transfer of H atoms appears to occur directly from the excited singlet states of other α -dicarbonyl compounds⁵⁻⁷ and could also account for the small yield of HCOH + CO observed by Hepburn et al.⁴ It is intriguing also that the 8^1 level of trans- S_1 glyoxal showed an abnormally low collision-free lifetime,9 and direct decomposition might well contribute to this. With or without the sampling-time effect, the excitation of the 8¹ level in the beam experiments may be a factor in the observed channel ratios, although the authors report "similar data" (but no channel ratios) from excitation in the 0-0 band. The sampling-time effect would be greater at the latter wavelength, as the lifetime of S_1 is 2.41 μ s, but the direct dissociation might be less. Measurement of accurate product ratios at 439.8 nm would obviously be desirable.

Our proposed mechanism is also in conflict with the two reported studies of the thermal decomposition of glyoxal, which are also in serious conflict with each other. In a shock tube study at temperatures from 1100 to 1540 K, Saito et al.12 observed only channel 2 and found an extrapolated high-pressure Arrhenius expression of $k_{\infty} = 10^{14.03} \exp(-55.1 \, (\text{kcal/mol})/RT) \, \text{s}^{-1}$ for the disappearance of glyoxal. Earlier, Lowden¹³ had reported that at temperatures from 703 to 783 K, in a static system, $R_2/(R_1$ $+ R_2$ = 0.14 and had found an extrapolated high-pressure rate constant for glyoxal disappearance given by $k_{\infty} = 10^{13.14} \exp(-52.6)$ (kcal/mol)/RT s⁻¹. At first sight these two studies seem qualitatively in accord with the high-energy channel 2 predominant at high temperatures and the lower energy channel 1, with a lower frequency factor, taking over at low temperatures. Quantitatively, however, the differences in the measured frequency factors and activation energies are much too small. A change from 14% channel 2 at 743 K to 90% at 1320 K (the latter based on a generous upper limit for the formaldehyde product that could have escaped detection in the shock tube) requires that $E_2 - E_1 = 13.6$ kcal/mol and $A_2/A_1 = 1700$, which may be compared with experimental values from the two studies of 2.5 and 7.7, respectively. The disagreement hinges on measurements of both the rate of disappearance of glyoxal and the product ratios and seems well beyond the apparent combined uncertainties in these measurements. Both studies, however, required long extrapolations to reach the limiting high-pressure values of the rate constant, and

the low-temperature experiments were complicated by surface effects; it seems possible that unsuspected systematic errors in one or both systems may account for their disagreement.

Our proposed interpretation of the present results probably requires a ratio A_2/A_1 of at least 25 and a value of $E_2 - E_1$ of from 3 to 6 kcal/mol. Given the uncertainty and disagreement in the thermal decomposition measurements, such values are perhaps not incompatible with the latter. Our brief study using the pulsed CO_2 laser lends some support to these conclusions. There seems little doubt that, at the low pressures employed, we were observing the unimolecular decomposition of ground-state glyoxal molecules pumped above the thresholds for dissociation by multiphoton absorption, rather than the bulk thermal decomposition of a heated gas. The decrease in the H_2/CO ratio with increasing pressure was much like that found with photoexcitation at 488.0 and 454.5 nm and can be attributed to the same cause, collisional deactivation of S_0^{\dagger} molecules, in this case both during and after the infrared pulse. Lacking absorption measurements and absolute probabilities of decomposition per pulse, quantitative interpretation of the system is difficult, but the infrared data clearly confirm our conclusion that the unimolecular decomposition of S_0^{\dagger} proceeds by both channels 1 and 2 and that channel 2 has the higher energy threshold and a higher frequency factor. The multiphoton infrared decomposition of glyoxal clearly deserves a more detailed study as an interesting example of a two-channel system and as a clarification of the uncertainties in the thermal decomposition.

Concluding Remarks

The primary conclusion of the present study is that the photolysis of *cis*-glyoxal in the 0–0 band approaching the low-pressure limit is very similar to that of *trans*-glyoxal, from which it follows that the collision-free decomposition of both isomers proceeds largely (\geq 80%) through radiationless transition to high vibrational levels of the ground state, S₀[‡], in which the two isomers interchange rapidly compared to the decomposition. It is further concluded that S₀[‡], whether formed via the excited singlet states, by infrared multiphoton pumping, or by thermal excitation, decomposes unimolecularly by two channels, giving H₂CO + CO and H₂ + 2CO, respectively, with the latter having a higher threshold energy and a higher frequency factor. The molecular-beam experiments of Hepburn et al.⁴ suggest that direct decomposition of the excited singlet state, trans-S₁, might make some contribution to the photochemistry at 439.8 nm.

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