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Energy Disposal in the Photofragmentation of Pyruvic Acid in the Gas Phase

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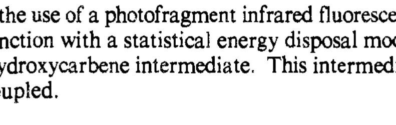
Abstract: The photochemical decarboxylation of pyruvic acid has been studied with the use of a photofragment infrared fluorescence method. The dependence of observed emission on excitation wavelength, in conjunction with a statistical energy disposal model, suggests that the loss of CO_2 occurs in concert with the formation of an unstable hydroxycarbene intermediate. This intermediate undergoes isomerization to acetaldehyde only after nascent products are uncoupled.

The distribution of available energy among the nascent products of a chemical reaction implicitly contains information on the transition-state structure and any interactions between the separating product fragments in the exit channel.[1] This follows from work on both atom–diatom metathesis[2] and photofragmentation reactions,[3] suggesting that energy-disposal studies can provide a means for deducing mechanistic information unencumbered by the ensemble averaging that normally accompanies conventional kinetics experiments. In the case of typical organic reactions, the resolution of product-state distributions becomes relatively complex as the number of product ro-vibrational modes increases. Energy-disposal measurements in polyatomic reactions are then most likely to yield mechanistically useful data when some subset of product degrees of freedom can be identified as particularly "relevant". For example, the HF rotational and vibrational modes can be so identified in the hydrogen-abstraction reactions of fluorine atoms with hydrocarbons where HF infrared chemiluminescence has been used as a probe of the reaction dynamics.[4] In the case of the unimolecular fragmentation of some cyclic azo compounds, it has been suggested that vibrational excitation in the N_2 product should be a useful mechanistic probe.[5] An analogous hypothesis might be formulated for decarboxylation reactions: The reaction dynamics can strongly influence the degree of vibrational excitation in the CO_2 product based in part on the extent to which the bond lengths and angles associated with the developing CO_2 molecule change as the transition state turns into products. We have initiated a study of the energy disposal associated with the photochemical decarboxylation of some carboxylic acids in the gas phase. By comparing results for a mechanistically homologous series of reactions, some insight may ultimately be obtained regarding the relationship between energy-disposal dynamics and reaction mechanism. In this paper, we discuss our initial work on the photodecarboxylation of pyruvic acid with the use of photofragment infrared fluorescence methods.

The photochemistry of pyruvic acid has been studied by Leermakers and Vesley.[6,7] In the gas phase they found that acetaldehyde and CO_2 were the isolable products and suggested that their results were consistent with either of two mechanisms: a five-center process leading to the formation of an intermediate hydroxycarbene (reaction 1) or a four-center process where acetaldehyde and CO_2 are formed directly (reaction 2). The same products are formed when pyruvic acid is pyrolyzed in the gas phase[8,9] and CO_2 is also observed as a product of it's infrared multiphoton dissociation,[10] where infrared emission from the CO_2 product has been resolved.

(1)



(2)

Photofragment infrared (IR) fluorescence methods have seen recent application in characterizing energy partitioning in photodissociation reactions.[11,12] Although product energy distributions can sometimes be determined with good resolution, no generalized, ab initio theoretical model for energy disposal in polyatomic systems has been developed. Experimental results are normally analyzed by comparing them with predictions made on the basis of simple, limiting case models, e.g., impulsive, or various statistical models. Results from energy-partitioning studies of the photofragmentation of polyatomic species may ultimately provide some basis for refining theoretical models in molecular dynamics by providing useful "calibration" points. We describe here an experimental approach for studying decarboxylation reactions via CO_2 product infrared fluorescence and discuss a simple statistical model for energy partitioning and its application in characterizing the mechanism by which pyruvic acid undergoes decarboxylation.

Experimental Procedure

A schematic diagram of our experimental configuration is shown in Figure 1. Pyruvic acid is flowed through an aluminum fluorescence cell either neat or diluted with argon. In most cases, a small amount of argon is admitted through an additional inlet port in order to purge the volume near the quartz window through which the UV laser beam enters the cell. The UV source employed here is a rare gas-halide excimer laser (Lambda Physik EMG 101) whose pulse width is ca. 15 ns. The laser repetition rate is held below 5 Hz in order to minimize any photolysis of reaction products. The laser beam is passed through a circular aperature in front of the fluorescence cell to give a beam 12 mm in diameter which appears homogeneous when viewed against a fluorescing target. Photofragment IR fluorescence is observed at 90° relative to the excimer laser beam through a CaF_2 window. A 77 K InSb detector (50 mm^2, 7 μm cut-off) views the IR emission through an evacuable cold gas filter (CGF) cell[13] whose path length is 1 cm, a silicon window which serves as a 1.2-μm long-pass filter, and a 4.3-μm band-pass filter (0.67 μm fwhm). Following amplification, the detector output is processed with a boxcar

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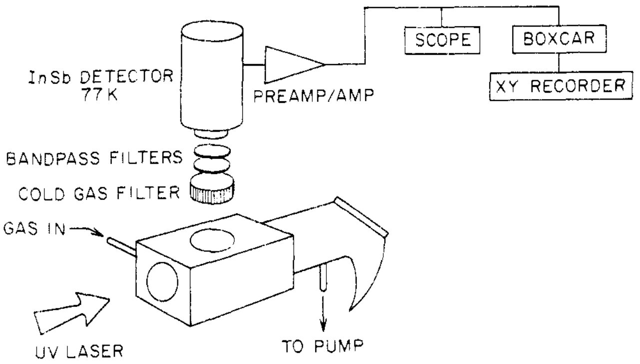

Figure 1. Schematic diagram of the experimental configuration used for photofragment infrared fluorescence studies.

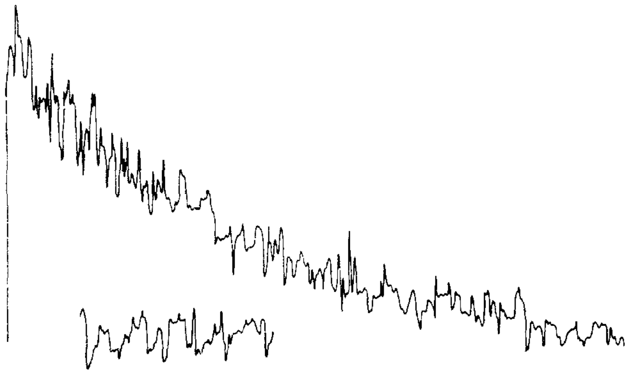

Figure 2. A typical CO_2 4.3-μm fluorescence decay curve obtained from 60 mtorr of pyruvic acid when an ArF* laser fluence of 4.65 mJ/cm^2 is used. The time scale funs from 0 to 200 μs. The cold gas filter cell was evacuated.

averager. The overall detection system time constant is $\lesssim 1$ μs. Gas pressures were measured with calibrated thermocouple gauges.

Results

Irradiation of 0.05 to 1.5 torr pyruvic acid at 193 nm (ArF* laser; fluence ca. 4 mJ/cm^2) results in intense IR emission near 4.3 μm. A typical fluorescence decay curve is shown in Figure 2. In all cases, the rise time of the observed emission is detector limited. The amplitude and decay time of the IR fluorescence are essentially identical whether or not it is viewed through the 4.3-μm band-pass filter. If the CGF cell is filled with pyruvic acid to ca. 1 torr, with acetaldehyde to ca. 20 torr, or with carbon monoxide to 15 torr, no significant change in fluorescence amplitude or decay time is found. Bandpass filters studies explicitly indicate no emission near 3.3 μm (C–H stretching regime). These results suggest that the observed emission arises from CO_2, where fluorescence at 4.3 μm corresponds to $\Delta v = -1$ transitions in the asymmetric stretch (ν_3) mode. As the ArF* laser fluence is varied over the range 0.8–10.7 mJ/cm^2, we find the photofragment fluorescence intensity varies linearly with UV laser intensity. This suggests that in these experiments, decarboxylation is induced by single-photon absorption. If CO_2 is introduced into the CGF cell, the transmitted (integrated) fluorescence intensity is attenuated relative to that observed through an evacuated CGF cell; the attenuation varies from 23% to 47% as the CO_2 pressure in the CGF cell is increased from 15 to 500 torr. Comparable results are obtained both at low pressures, e.g., with 0.05 torr pyruvic acid in a sample cell, and at high pressures (30 torr of 0.05% pyruvic acid in argon). This suggests that any rotational excitation in the nascent CO_2 product is relaxed within the time required for a few hard-sphere collisions. With less than ca. 5 torr of CO_2 in the CGF cell, our signal-to-noise ratio was not sufficient to resolve any attenuation near the peak of the fluorescence decay curve. Irradiation of pyruvic acid at 249 nm (KrF* laser; fluence ca. 16 mJ/cm^2) also results in CO_2 fluorescence near 4.3 μm, although with substantially lower intensity than observed at 193 nm. This fluorescence is attenuated by ca. 72% when the CGF cell is filled with 500 torr of CO_2. The observed attenuation is essentially independent of pyruvic acid pressure. Irradiation of pyruvic acid at 308 nm (XeCl* laser; fluence ca. 7 to $\gtrsim$ 1000 mJ/cm^2) results in no observable IR fluorescence for sample pressures up to 1 torr. Similarly, irradiation of pyruvic acid at 351 nm (XeF* laser; fluence ca. 2.5–250 mJ/cm^2) results in no observable IR fluorescence. These findings indicate only that the ν_3 mode of the CO_2 product is not excited following photolysis at 308 or 351 nm. Appreciable excitation in the ν_2 mode is possible but would not be observed due to the 7 μm cutoff of our detector. The results reported here are summarized in Table I.

Table I. Attenuation of CO_2 Fluorescence at 4.3 μm by a CO_2 Cold Gas Filter (CGF)

excitation wavelength, nm	% attenuation[a] at CGF pressure (torr) of 15	60	500
193	23	31	47
249	25	38	72
308	*b*	*b*	*b*
351	*b*	*b*	*b*

[a] Defined as the ratio of integrated fluorescence intensities observed through filled and evacuated filter cells. [b] No fluorescence observed.

The sensitivity of our detection system can be estimated so as to better interpret the null results obtained upon photolysis at 351 and 308 nm. By analogy with typical ketones and carboxylic acids, the absorption cross section of pyruvic acid near 193 nm should be roughly 10^{-18} cm^2 so an ArF* laser fluence of 5 mJ/cm^2 will result in ca. 1% dissociation when a quantum yield of unity is assumed.[14] Infrared emission from 50 mtorr of pyruvic acid can be observed with a signal-to-noise ratio of 3 which must correspond to fluorescence from ca. 5×10^{-4} torr of CO_2. The absorption cross section at 308 nm is approximately one-tenth[15] that at 193 nm, so a XeCl* laser fluence of ca. 50 mJ/cm^2 should yield about 10 mtorr of CO_2 from 1 torr of pyruvic acid. On the basis of our signal-to-noise ratio in the ArF* experiments, we can determine that the failure to observe any fluorescence in the 308-nm experiments indicates that for photodissociation at this wavelength $\lesssim 5\%$ of the CO_2 molecules emit at 4.3 μm. The absorption coefficient of pyruvic acid at 351 nm is ca. three times larger[15] than it is at 308 nm. Thus, in the 351-nm experiments, $\lesssim 5\%$ of the CO_2 product fluoresces at 4.3 μm.

Discussion

The observation of fluorescence at 4.3 μm on irradiating pyruvic acid at 193 or 249 nm demonstrates the formation of a population of CO_2 molecules, some component of which is vibrationally excited. The CGF studies provide an indication of the extent of this vibrational excitation. A CGF cell containing CO_2 at 300 K functions[13] by absorbing radiation from any ro-vibrational transition which terminates on thermally populated CO_2 states. $(00^0 0)$ and $(01^1 0)$ are appreciably populated at 300 K (the latter to the extent of 40% of the former) so that CGF results nominally indicate the extent to which the 4.3-μm emission originates from states more highly excited than the $(01^1 1)$ state. When the CGF contains relatively low pressures of CO_2, it primarily attenuates $(00^0 1) \rightarrow (00^0 0)$ and $(01^1 1) \rightarrow (01^1 0)$ emission,[16,17] but with increasing CO_2 pressure, emission from hot bands is absorbed to some extent. Since virtually no fluorescence attenuation can be observed with less than ca. 5 torr of CO_2 in the CGF cell, we conclude that essentially all of the emission observed within a few

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(14) Leermakers and Vesley[6,7] report that the quantum yield for CO_2 formation is unity over the wavelength range they investigated (ca. 370–300 nm). We assume the quantum yield remains constant down to 193 nm.

(15) This estimate is based on the UV absorption spectrum of pyruvic acid in hexane. The vapor pressure of the acid was not sufficient for a gas-phase absorption spectrum to be determined with spectrometers available to us. Also see ref 18 for published spectral data.

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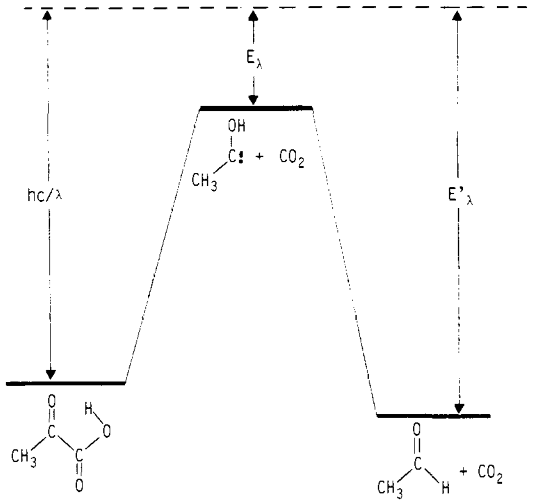

Figure 3. Energy-level diagram for the decarboxylation of pyruvic acid. Fragmentation via a carbene intermediate results in an available energy of E_λ. In the case of a single-step mechanism, the available energy is E'_λ.

Table II. Available Energy for Vibrational Excitation of CO_2 [a]

excitation wavelength (λ), nm	E_λ, kcal/mol	E'_λ, kcal/mol
193	93	153
249	60	120
308	38	98
351	26	86

[a] E_λ and E'_λ correspond to mechanisms 1 and 2, respectively. See Figure 3.

microseconds of the UV laser pulse (corresponding to the nascent photoproduct) must arise from CO_2 hot-band transitions. With CGF pressures greater than 100 torr, emission due to transitions from, e.g., combination or isotopic bands may also be attenuated as a result of pressure broadening.[16,17] The conclusion that CO_2 formed by the photodissociation of pyruvic acid at 193 or 249 nm emits primarily on hot-band transitions is consistent with the time dependence of fluorescence decay signals observed with and without a CGF. We find that for photolysis at 193 nm, a CGF attenuates the peak of the fluorescence decay (i.e., within 5 μs of the UV laser pulse) only to the extent of 10% or less at all CGF pressures. For photolysis at 249 nm, the corresponding attenuation 21–48% (CGF pressure = 15–500 torr). This result indicates that for both irradiation wavelengths most of the fluorescing CO_2 photoproduct is vibrationally hot and suggests that CO_2 formed via 193-nm photolyses is more highly excited than that formed via 249-nm photolyses. Although it is possible that an intermediate species, such as an hydroxycarbene, may contribute to the observed emission, this is not likely a major component since no fundamental bands near 4.3 μm are anticipated for such a species. CGF studies using the appropriate vapors indicate that the observed emission does not originate from acetaldehyde or from pyruvic acid.

The observation that vibrationally hot CO_2 is formed upon the photolysis of pyruvic acid at 193 and 249 but *not* 308 nm (or 351 nm) is a consequence of the dynamics of photodissociation. The different laser transitions employed in our experiments populate different excited electronic states of pyruvic acid. Arnett et al.[18] assign absorptions near 351–308 and 249 nm to two (different) (n,π*) transitions while absorption near 193 nm is assigned to a (π,π*) transition. In the photochemistry of small molecules in the gas phase, it is not unusual to find that different excited states either form different primary products or fragment via different mechanisms, for example, direct vs. predissociation. This is not normally the case for polyatomic organic species[19] where extremely large ro-vibrational state densities can efficiently couple zeroth-order electronic states.[20] This coupling can be particularly pronounced when the molecule in question has several low-frequency torsional degrees of freedom. The result is that, as a general rule, "loose" polyatomic molecules generally undergo photofragmentation either from the ground state or a low-lying excited state populated via rapid nonradiative decay. Thus, although we cannot rigorously exclude the possibility that, e.g., the (π,π*) state of pyruvic acid fragments by a different mechanism than one of the (n,π*) states, such a violation of "Kasha's rule" is not expected. This suggests that pyruvic acid likely undergoes decarboxylation either from it's lowest (n,π*) state or, following internal conversion, from the ground electronic state.

The mechanism of the photochemical decarboxylation of pyruvic acid can be discussed further in terms of the energy diagram shown in Figure 3. The overall reaction is estimated[21] to be exothermic by 5 kcal/mol. The energy difference between acetaldehyde and methylhydroxycarbene can be estimated[22] to be ca. 60 kcal/mol. Photoexcitation of pyruvic acid at wavelength λ results in the formation of CO_2. The *maximum* energy available for vibrational excitation of this fragment is E_λ if the five-center mechanism, reaction 1, is followed (and the two fragments are uncoupled after the carbene is formed), but if the four-center mechanism, reaction 2, is followed so that CO_2 and acetaldehyde are formed directly, the maximum available energy is E'_λ (see Figure 3). Relevant values of E_λ and E'_λ are listed in Table II. If the photofragmentation of pyruvic acid occurs from the same electronic state (populated directly or via internal conversion) for all excitation wavelengths, a demonstration that an available energy of ca. 38 kcal/mol is *insufficient* to produce highly excited CO_2 would provide evidence in favor of (1) as the decarboxylation mechanism, if it could also be shown that an available energy ≥60 kcal/mol is sufficient to do so. No generally valid theoretical model for energy disposal is available so the problem will be analyzed in terms of a simplified statistical model. Such a model allows us to discuss our experimental results in comparison to what would be expected in the limit of statistical energy partitioning although, to the extent that the model fits the data, it cannot be regarded as a unique description of the reaction dynamics.

A statistical energy disposal model similar to that suggested by Bogan and Setser[23] can be employed to calculate the probability that fragmentation yields CO_2 with an internal energy ε when the available energy is E. This probability is denoted as $f(\epsilon;E)$ in eq 3, where $N_c(\epsilon)$ is the vibrational density of states for CO_2 at an

$$f(\epsilon;E) = \frac{N_c(\epsilon)\int_{E_t=0}^{E-\epsilon} P_r(E-\epsilon-E_t)\cdot E_t^{1/2}\,dE_t}{\sum_{\epsilon=0}^{E} N_c(\epsilon)\int_{E_t=0}^{E-\epsilon} P_r(E-\epsilon-E_t)\cdot E_t^{1/2}\,dE_t} \qquad (3)$$

internal energy ε, E_t is the translational energy of separation for the two fragments, and $P_r(E-\epsilon-E_t)$ is the degeneracy of ro-vibrational states for the polyatomic fragment at an internal energy $E-\epsilon-E_t$. All relative rotational degrees of freedom are included in $P_r(E-\epsilon-E_t)$. Kinsey[24] has shown that the density of states for a one-dimensional translation is proportional to $E_t^{1/2}$, so the numerator in (3) corresponds to the product of state densities for CO_2 at energy ε and all the remaining degrees of freedom at energy $E-\epsilon$. The denominator normalizes the probability distribution function. We have evaluated this probability distribution function for CO_2 formed by the photodissociation of pyruvic acid at 193, 249, and 308 nm with the Whitten–Rabinovitch approximation[25]

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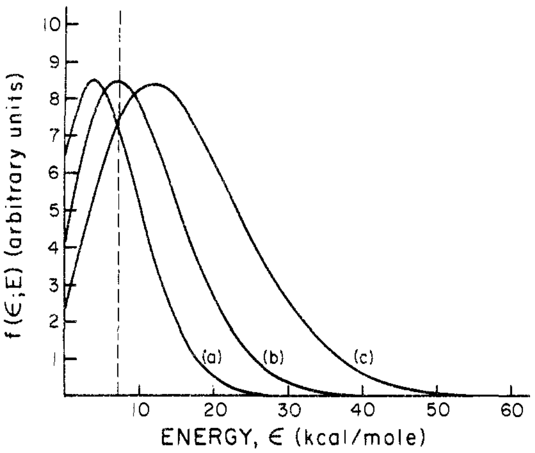

Figure 4. Calculated statistical distribution functions $f(\epsilon;E)$ corresponding to photodissociation experiments at (a) 308, (b) 249, and (c) 193 nm. See text and eq 3. The dashed line is drawn at the minimum energy required for CO_2 fluorescence at 4.3 μm.

to calculate ro-vibrational state densities, using known (CO_2) or estimated (hydroxycarbene) vibrational frequencies and moments of inertia. The results are shown in Figure 4. Inspection of these curves indicates that for photoexcitation of pyruvic acid at 193 or 249 nm, the majority of CO_2 product will have sufficient energy to fluoresce at 4.3 μm. This is not the case for photolysis at 308 nm, where the model indicates that only ca. 40% of the photogenerated CO_2 is formed with internal energy sufficient to fluoresce at 4.3 μm, i.e., greater than 7 kcal/mol. If internal energy in CO_2 is randomly distributed, the fraction of CO_2 molecules with energy ϵ_3 in the ν_3 mode is $f(\epsilon_3;\epsilon)$, where ϵ is the

$$f(\epsilon_3;\epsilon) = \frac{N_3(\epsilon_3)N_{1,2}(\epsilon - \epsilon_3)}{\sum_{\epsilon_3=0}^{\epsilon} N_3(\epsilon_3)N_{1,2}(\epsilon - \epsilon_3)} \quad (4)$$

total internal energy for CO_2, $N_3(\epsilon_3)$ is the density of states for it's ν_3 mode at energy ϵ_3, and $N_{1,2}(\epsilon - \epsilon_3)$ is the density of states for the remaining vibrational modes at an energy $\epsilon - \epsilon_3$. Using (4), we can evaluate the fraction of CO_2 molecules containing at least one quantum of ν_3 excitation for a given internal energy ϵ. If this fraction is denoted as $f'(\epsilon_3;\epsilon)$, the fraction of CO_2 molecules which can emit at 4.3 μm when the total available energy is E is given by $F(E)$, the convolution of the two distribution functions.

$$F(E) = \int_{\epsilon=0}^{E} f(\epsilon;E)\cdot f'(\epsilon_3;\epsilon)\,d\epsilon \quad (5)$$

For an available energy of 38 kcal/mol, corresponding to a 308-nm photolysis, evaluation of (5) yields $F(38) \approx 8\%$, i.e., 8% of the photochemically generated CO_2 should fluoresce, while photolyses at 249 and 193 nm yield $F(60) \approx 61\%$ and $F(93) \approx 82\%$, respectively. In discussing the sensitivity of our detection system (vide supra), we estimate that $\lesssim 5\%$ of the CO_2 produced by the 308-nm photolysis of pyruvic acid fluoresces at 4.3 μm. It is possible that a 308-nm photolysis produces *no* (or $\ll 1\%$) CO_2 product excited in the ν_3 mode. If this is the case, it suggests that pyruvic acid may fragment via a different excited state than in the 249- or 193-nm experiments. However, in view of the approximations involved in estimating our detection sensitivity (e.g., assumed values for UV absorption cross sections) and the assumptions implicit in the statistical energy disposal model, our experimental results appear in qualitative accord with those predicted when the statistical model was used. If, as seems likely, internal conversion to a common electronic state precedes photofragmentation at the various excitation wavelengths used here, then it is clear that a single-step mechanisms, reaction 2, cannot account for our results, i.e., CO_2 fluorescence at 4.3 μm is observed for 193- and 249-nm but *not* 308- or 351-nm excitation of pyruvic acid. This follows since for $\lambda \lesssim 351$ nm, the maximum energy available for CO_2 excitation is $E'_\lambda \geq 86$ kcal/mol if mechanism 2 obtains (see Table II). The statistical-energy partitioning model we have described indicates that for fragmentation via (2), a 351-nm photolysis would generate CO_2 product, ca. 80% of which would emit at 4.3 μm. Thus, the failure to observe any fluorescence in the 351- or 308-nm experiments suggests that the primary dissociative step is the formation of CO_2 in concert with an unstable intermediate such as a hydroxycarbene. This conclusion is consistent with the observation that the photolysis of pyruvic acid in aqueous solution leads to the formation of acetoin.[6]

A five-center mechanism analogous to reaction 1 might be formulated for the decarboxylation of other α,β-unsaturated carboxylic acids, such as acrylic acid. We are presently investigating the photofragment fluorescence behavior of acrylic and substituted acrylic acids in order to ascertain the extent to which mechanistically related processes have similar consequences vis-à-vis their associated energy disposal dynamics. Moreover, the results we have described suggest a useful approach for the generation of hydroxycarbenes that might be applied in studying hydroxymethylene, H–C–OH. We are currently pursuing this possibility.

Summary

CO_2, vibrationally excited in its ν_3 mode, is observed as a product of the photodissociation of pyruvic acid at 193 and 249 nm but not at 308 or 351 nm. A simple statistical model for energy disposal to the products of a unimolecular decomposition was described. Our experimental results, in conjunction with this energy-disposal model, suggest that the photodissociation of pyruvic acid occurs via a five-center mechanism, reaction 1, whereby CO_2 is formed in concert with an unstable intermediate, a hydroxycarbene. Thus, a useful photochemical method for the generation of hydroxycarbenes is indicated.

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Registry No. CO_2, 124-38-9; $CH_3\text{–}\ddot{C}\text{–}OH$, 30967-49-8; pyruvic acid, 127-17-3.