glycol polymers were also examined as H_2-evolving catalysts. With Pt polyacrylic acid sodium salt at pH 9.2, H_2 evolution was observed, $\phi \simeq 0.5 \times 10^{-3}$. In turn, with Pt polyethylene glycol no hydrogen could be detected under these conditions. These results are attributed to the tendency of the neutral polymer, polyethylene glycol, to wrap itself around the colloidal SiO_2 particle.[30] Consequently, no catalytic site for H_2 formation by the reduced photoproduct $DQS^{-}\cdot$ that is ejected from the SiO_2 colloid is available. In turn, the Pt polyacrylate supported catalyst is repelled from the SiO_2 interface, and thus the utilization of $DQS^{-}\cdot$ in H_2 production is feasible. The lower yield of hydrogen obtained with the Pt polyacrylate catalyst as compared with that observed with the Pt citrate catalyst, is mainly attributed to the higher ionic strength of the colloid medium originating from the ionized groups of the polymeric support. The increased ionic strength of the system affects the charge separation yield of $DQS^{-}\cdot$ and accelerates its degradative recombination process and hence the subsequent H_2 evolution yield is decreased.

Conclusions

We have demonstrated that the photosensitized H_2 evolution from a basic SiO_2 colloid is mediated by DQS^0 as electron acceptor. No hydrogen formation could be detected from a homogeneous aqueous phase under similar conditions. Similarly, while in the SiO_2 colloid the intermediate photoproducts could be followed, no photoproducts were observed in the homogeneous phase. The charged colloidal interface controls the separation of the ions composing the initial cage complex and stabilizes the ionic products against the recombination reaction. These functions are due to the high surface potential of the colloidal particles that results in electrostatic interactions with the reduced product $DQS^{-}\cdot$. The achievement of H_2 evolution from basic solutions seems to be of interest in designing a system for cyclic photocleavage of water.

Acknowledgment. The assistance of Dr. A. Bino and Dr. S. Cohen (Hebrew University) in the X-ray structure determination is gratefully acknowledged. This research was supported in part by the Sheinborn Foundation (Hebrew Unversity). This research was carried out under the auspices of the Fritz Haber Molecular Dynamics Research Center and the Center of Energy, The Hebrew University of Jerusalem.

Registry No. 1, 86690-04-2; SiO_2, 7631-86-9; Pt, 7440-06-4; $Ru(bpy)_3^{2+}$, 15158-62-0; $Ru(bpy)_3^{3+}$, 18955-01-6; $DQS^{-}\cdot$, 86690-05-3; H_2O, 7732-18-5; TEOA, 102-71-6; H_2, 1333-74-0.

Supplementary Material Available: Tables of structure factors, thermal parameters, and calculated positional parameters of the hydrogen atoms (13 pages). Ordering information is given in any current masthead page.

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[30] Reference 18 pp 295–296.

Photofragmentation of Acrylic Acid and Methacrylic Acid in the Gas Phase

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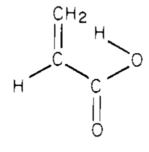
Received March 16, 1983

Abstract: Irradiation of acrylic and methacrylic acids at 193 or 249 nm results in decarboxylation. Energy disposal to the CO_2 product is monitored by photofragment infrared fluorescence and is consistent with a dissociation mechanism whereby CO_2 is formed in concert with a carbene. Our results provide some insight regarding the photophysical processes which obtain prior to chemical reaction.

Introduction

We report here an investigation of the photochemical dynamics of acrylic acid and methacrylic acid in the gas phase. The data obtained provide evidence regarding fragmentation channels available to these species and photophysical processes which ensue following the electronic excitation of α,β-unsaturated carboxylic acids.

The photochemistry of acrylic acid and its derivatives has been extensively studied.[1] Irradiation is commonly found to result in polymerization and, in fact, constitutes a useful route for the preparation of acrylate-type polymers. Little data on the gas phase photochemistry of these compounds have been reported. The pyrolysis of acrylic acid (**1**) or methacrylic acid (**2**) vapor was found to yield a complex mixture of products; decarboxylation is apparently competitive with other processes, such as decarbonylation.[2] Data on the photochemistry of acrylic acids in the gas phase, in conjunction with results from solution-phase photochemical studies, can be useful in characterizing the electronic states responsible for the observed chemistry in each case.



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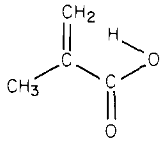

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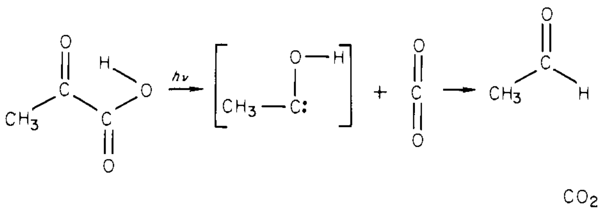
We have recently reported a study of the gas-phase photofragmentation dynamics of pyruvic acid.[3] Evidence was obtained indicating that the dissociation mechanism involves two discrete steps: (eq 1) i.e., CO_2 and an hydroxycarbene are formed in concert followed by subsequent isomerization of the carbene to acetaldehyde. This suggests the possibility that species, such as



(1)

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[1] See, for example: Bamford, C. H.; Jenkins, A. D.; Ward, J. C. *J. Polym. Sci.* **1960**, *48*, 37–51. Bamford, C. H.; Dewar, M. J. S. *Proc. R. Soc. London, Ser. A* **1949**, *197*, 356–363.

[2] Forman, R. L.; MacKinnon, H. M.; Ritchie, P. D. *J. Chem. Soc. C* **1968**, 2013–2016.

[3] Rosenfeld, R. N.; Weiner, B. *J. Am. Chem. Soc.* **1983**, *105*, 3485–3488.

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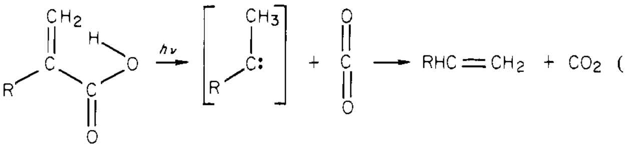
acrylic acid, or methacrylic acid, can undergo fragmentation by an analogous mechanism (eq 2), where R = H or CH_3. Here we



(2)

explore the possibility that α,β-unsaturated carboxylic acids undergo photodecarboxylation following UV irradiation. Time-resolved infrared (IR) fluorescence is used as a probe for decomposition products. This method can provide information on the identity of any fluorescing fragments, thier mode of formation (e.g., photochemical vs. collision induced), and their ro-vibrational energy distribution.[4-6] Our results suggest that, following UV photoexcitation, acrylic acid and methacrylic acid undergo decarboxylation in the gas phase via a two-step mechanism, e.g., eq 2. In each case, vibrational energy disposal to the CO_2 product appears to be consistent with a simple statistical model for energy partitioning in unimolecular fragmentations. These findings provide some basis for addressing the role of nonradiative processes in the photochemistry of α,β-unsaturated carboxylic acids.

Experimental Section

The experimental methods employed in our photofragment IR fluorescence work have been described previously[3,4] and so wil be outline only briefly here. Acrylic acid or methacrylic acid is flowed through a fluorescence cell diluted in argon. Experiments conducted at 193 nm generally employed 0.02 torr of carboxylic acid in a selected amount of argon buffer, while for experiments at 249 nm, ca. 0.80 torr of carboxylic acid in a selected amount of argon was used.[7] The sample is photolyzed with ca. 15-ns pulses from a Lambda Physik EMG 101 excimer laser at 193 nm (ArF*), 249 nm (KrF*), or 308 nm (XeCl*). Infrared fluorescence is observed at 90° relative to the excimer laser beam through an evacuable cold gas filter (CGF) cell[8] of 1-cm pathlength and a 4.3-μm bandpass filter (0.67-μm fwhm). A 50-mm^2 InSb detector (7-μm cutoff) is used to monitor IR emission. Following two amplification stages, the detector output is processed by a PARC 162/164 boxcar averager. The risetime of our detection system is $\lesssim 1$ μs. Laser pulse energies are measured with a Scientech 36-0001 power/energy meter. Sample pressures are measured using calibrated thermocouple gauges.

Results

Irradiation of acrylic acid or methacrylic acid at 193 nm results in intense IR fluorescence at 4.3 μm, corresponding to $\Delta v = -1$ transitions in the asymmetric stretch, ν_3, mode of CO_2. In all cases the IR emission is found to have a detector limited risetime independent of sample pressure, indicating that decarboxylation is the result of a unimolecular process. Similar results are obtained following irradiation at 249 nm, but no fluorescence is observed following the 308-nm excitation of either carboxylic acid. No indication of any emitting species, aside from CO_2, is found at any of the excitation wavelengths used. In particular, bandpass filter studies indicate that none of the emission is due to carbon monoxide or to C–H stretching-type vibrations near 3.3 μm (e.g., those of ethylene or propylene). Additionally, in the case of acrylic acid, filling the CGF cell with acrylic acid vapor or with several torr of ethylene results in no change in the observed IR fluorescence amplitude or decay time. Thus, none of the emission detected in our experiments can be due to these species. Because of the 7-μm cutoff of our detector, any emission from the CO_2 bending mode, ν_2, or from the low-frequency modes of other dissociation products cannot be observed. For photofragmentation at 193 or 249 nm, the extent of vibrational excitation in the CO_2 product can be qualitatively gauged[8-10] by comparing the IR fluorescence intensity transmitted through an evacuated CGF cell, I_0, with that transmitted through a CGF cell containing CO_2, I_{CGF}. A filled CGF cell absorbs radiation due to transitions which terminate on CO_2 vibrational states that are populated at 300 K, i.e., the ($0\ 0^0\ 0$) and ($0\ 1^1\ 0$) states. Thus CGF studies allow us to estimate the extent to which emission originates from CO_2 states of higher energy than the ($0\ 1^1\ 1$) state. When the CGF cell is filled with CO_2, the fluorescence observed following the photodissociation of acrylic or methacrylic acid at 193 or 249 nm is attenuated relative to that observed through an evacuated CGF cell (see Figure 1). The results are summarized in Table I. Attenuation is defined as $1 - (I_{CGF}/I_0)$, and the absolute uncertainties of these measurements are on the order of ±10%. The CGF attenuations are, to a good approximation, independent of total sample pressure over the range 0.28 to 10 torr. For both carboxylic acids, photofragment IR fluorescence intensity is found to vary linearly with UV laser intensity over the range 0.5 to 7.7 mJ/cm^2 (193-nm excitation) and 3.3 to 29.6 mJ/cm^2 (249-nm excitation). For 308-nm photolyses, no CO_2 fluorescence was observed for laser intensities between 3.1 and $\gtrsim 1000$ mJ/cm^2 at carboxylic acid pressures $\lesssim 1$ torr.

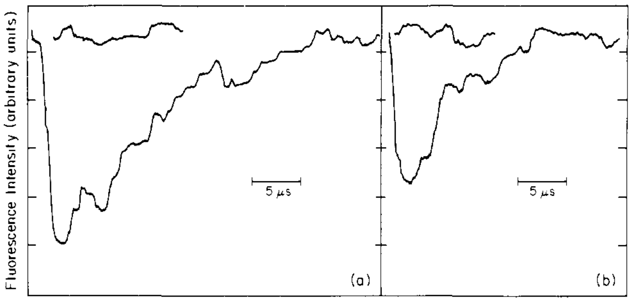


Figure 1. Typical 4.3-μm fluorescence decay curves obtained by photolyzing acrylic acid at 249 nm (12.5 mJ/cm^2). In (a) emission was viewed through an evacuated CGF cell, while in (b) emission was viewed through a CGF cell containing 500 torr of CO_2.

Table I. Attenuation of Integrated Fluorescence Intensity at 4.3 μm by a Cold Gas Filter (CGF) Cell Containing CO_2 at 300 K

	CGF pressure, torr	% attenuation at excitation wavelength 193 nm	249 nm	308 nm
acrylic acid	5	15	17	*a*
	50	17.5	31	*a*
	500	42	60	*a*
methacrylic acid	5	22.5	31	*a*
	50	34	32	*a*
	500	52	56	*a*

[a] No fluorescence observed.

Discussion

Our results indicate that acrylic acid and methacrylic acid undergo photodecarboxylation following irradiation at either 193 or 249 nm. CGF studies demonstrate that the observed fluorescence corresponds primarily to hot band transitions. At low CGF pressures, e.g., 5 torr of CO_2, CO_2 emission due to the transitions ($0\ 0^0\ 1$) → ($0\ 0^0\ 0$) and ($0\ 1^1\ 1$) → ($0\ 1\ ^1\ 0$) is attenuated, but with increasing CGF pressure, emission originating

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(4) Rosenfeld, R. N.; Sonobe, B. I. *J. Am. Chem. Soc.* **1983**, *105*, 1661-1662.

(5) Hermann, H. W.; Leone, S. R. *J. Chem. Phys.* **1982**, *76*, 4795-4765.

(6) Moss, M. G.; Ensminger, M. D. McDonald, J. D. *J. Chem. Phys.* **1981**, *74*, 6631-6635.

(7) If pressures $\gtrsim 1$ torr of carboxylic acid are employed, the fluorescence cell windows become coated with polymeric material after a few laser pulses. Thus, static fills could not be analyzed for photoproducts by conventional means, preventing us from estimating decarboxylation quantum yields. Since a single laser pulse decomposes only ca. 1% of the irradiated carboxylic acid, it was not practical to generate and trap sufficient products for analysis under flowing gas conditions.

(8) (a) McNair, R. E.; Fulghum, S. F.; Flynn, G. W.; Feld, M. S.; Feldman, B. J. *Chem. Phys. Lett.* **1977**, *48*, 241-244. (b) Chu, J. O.; Flynn, G. W.; Weston, R. E., Jr. *J. Chem. Phys.* **1983**, *78*, 2990-2997.

(9) Huddleston, R. K.; Fujimoto, G. T.; Weitz, E. *J. Chem. Phys.* **1982**, *76*, 3839-3841.

(10) Caledonia, G. E.; Green, B. D.; Murphy, R. E. *J. Chem. Phys.* **1982**, *77*, 5247-5248.

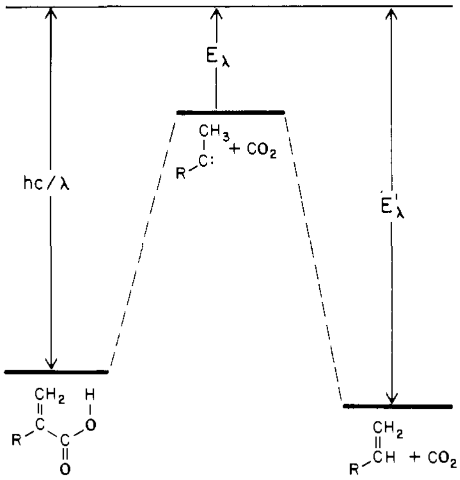

Figure 2. Schematic energy level diagram for the fragmentation of acrylic acid (R = H) and methacrylic acid (R = CH_3). See text for explanation of notation.

Table II. Energy Available to the Products of the Decarboxylation of Acrylic Acid[a] (See Figure 2)

excitation wavelength, nm	E_λ, kcal/mol	E_λ', kcal/mol
193	81	151
249	48	118
308	26	96

[a] In the case of methacrylic acid, the corresponding available energies are 1.5 kcal/mol less than those indicated for acrylic acid.

from other CO_2 vibrational states can be partially quenched owing to pressure broadening[9,10] (see Table I). Since the observed CGF attenuations are found to be independent of carboxylic acid pressure, we conclude that CO_2 rotational relaxation is rapid relative to our detection system risetime for the experimental conditions employed here.

The failure to observe any CO_2 fluorescence following carboxylic acid excitation at 308 nm suggests either a low quantum yield for decarboxylation and/or that the CO_2 formed at this wavelength has insufficient internal energy to fluoresce at 4.3 μm. Based on our detection sensitivity, we find that if the quantum yield for decarboxylation is unity, the failure to observe any CO_2 fluorescence following 308-nm photolyses indicates that $\lesssim 3\%$ of the CO_2 formed at this wavelength emits at 4.3 μm. Although the fact that CO_2 fluorescence is not observed is consistent (vide infra) with statistical energy disposal among photoproducts in conjunction with mechanism 2, similar results might also be obtained, e.g., if the barrier to decarboxylation were larger than the energy available in our 308-nm experiments.

Some insight regarding the mechanism of decarboxylation can be obtained by comparing experimental results with those anticipated on the basis of an assumed model. An energy level diagram for the mechanism represented in eq 2 is shown in Figure 2. If CO_2 is formed in concert with an unstable intermediate, e.g., a carbene, the maximum energy available for its internal excitation is E_λ when photoactivation is carried out at wavelength λ. If decarboxylation is a single-step process, or if the two fragments are strongly coupled until stable products are formed, the corresponding available energy is E'_λ. These energies can be evaluated using thermochemical estimation methods.[11] The results are indicated in Table II. For a given choice of available energy, the fraction of CO_2 product IR fluorescence arising from hot band transitions can be estimated. This is accomplished using a statistical model for energy partitioning that we have previously described.[3,12] For an available energy, E, the probability that CO_2 will be formed with internal energy, ϵ, is

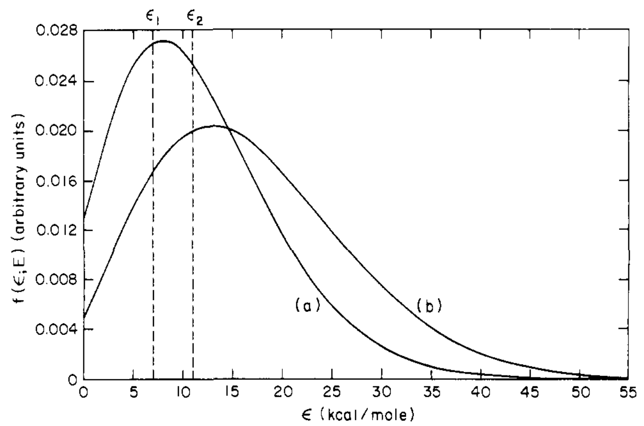

Figure 3. Internal energy distribution for CO_2 formed by the photolysis of (a) methacrylic acid and (b) acrylic acid at 249 nm. The distribution functions were computed using eq 3. Dashed lines are drawn at energies ϵ_1 and ϵ_2; see eq 4.

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

Here, $N_c(\epsilon)$ is the vibrational density of states for CO_2 at an energy ϵ, E_t is the relative translational energy of separation of the two photofragments, and $P_r(E-\epsilon-E_t)$ is the number of remaining rovibrational states (including carbene vibrations and all relative rotations) at an energy, $E-\epsilon-E_t$. We employ the Whitten–Rabinovitch approximation as a means for state counting[13] in computing energy distribution functions for the CO_2 photofragment by use of eq 3 (see Figure 3). Using eq 3, the experimentally derived quantity, I_{CGF}/I_0, can be approximated[14] as

$$I_{CGF}/I_0 \simeq \sum_{\epsilon=\epsilon_2}^{E} f(\epsilon;E) \Big/ \sum_{\epsilon=\epsilon_1}^{E} f(\epsilon;E) \qquad (4)$$

where ϵ_1 is the minimum CO_2 internal energy required for fluorescence on the ν_3 fundamental $[(0\ 0^0\ 1) \rightarrow (0\ 0^0\ 0)]$, i.e., 6.7 kcal mol, and ϵ_2 is the minimum CO_2 internal energy necessary for ν_3 hot band fluorescence from states at least as hot as the $(0\ 2^0\ 1)$ or $(1\ 0^0\ 1)$ states, i.e., 10.5 kcal/mol. For the 249-nm photolysis of acrylic acid, we calculate $I_{CGF}/I_0 = 0.73$ (observe 0.83), while for its 193-nm photolysis, we calculate $I_{CGF}/I_0 = 0.88$ (observe 0.85). For the 249-nm photolysis of methacrylic acid, we calculate $I_{CGF}/I_0 = 0.61$ (observe 0.69), while for its 193-nm photolysis, we calculate $I_{CGF}/I_0 = 0.77$ (observe 0.755). For either carboxylic acid, we calculate that ca. 3–5% of the CO_2 formed upon 308-nm photolysis should fluoresce at 4.3 μm while, based upon our detection sensitivity, we find that $\lesssim 3\%$ of the CO_2 photoproduct fluoresces at this wavelength.

We conclude that the proposed mechanism for decarboxylation, e.g., eq 2, in conjunction with a statistical model for energy partitioning in fragmentation reactions, is in reasonable accord with our experimental results. It appears that model and experiment agree most closely in the limit of large available energy (short excitation wavelength). This is not surprising in view of the semiclassical nature of the state counting approximation used. If decarboxylation were a one-step process, or if it occurred via any mechanism whereby the full exoergicity of the reaction was available for partitioning among the final products, eq 3 and 4

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[11] Benson, S. W. "Thermochemical Kinetics"; 2nd ed., Wiley: New York, 1976.

[12] Also see: Bogan, D. J.; Setser, D. W. *J. Chem. Phys.* **1976**, *64*, 586–602. Kinsey, J. L. *Ibid* **1971**, *54*, 1206–1217.

[13] Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972; p 131.

[14] A somewhat more rigorous approach to simulating I_{CGF}/I_0 would involve convolving each $f(\epsilon;E)$ with the probability that CO_2 containing energy, ϵ, is excited in the ν_3 mode ($v \geq 1$) as was done in ref 3.

Scheme I

$$\mathrm{AA(S_0)} \longrightarrow \mathrm{AA}^* \tag{5}$$

$$\mathrm{AA}^* \rightsquigarrow \mathrm{AA}^3(\mathrm{n},\pi^*) \tag{6}$$

$$\mathrm{AA}^3(\mathrm{n},\pi^*) + \mathrm{AA(S_0)} \xrightarrow{k_7} \text{polymer} \tag{7}$$

$$\mathrm{AA}^3(\mathrm{n},\pi^*) \overset{k_8}{\rightsquigarrow} \mathrm{AA(S_0)}^\dagger \tag{8}$$

$$\mathrm{AA(S_0)}^\dagger + \mathrm{M} \xrightarrow{k_9} \mathrm{AA(S_0)} + \mathrm{M} \tag{9}$$

$$\mathrm{AA(S_0)}^\dagger \xrightarrow{k_{10}} \mathrm{C_2H_4} + \mathrm{CO_2} \tag{10}$$

indicate that $I_{\mathrm{CGF}}/I_0 \gtrsim 0.90$ for both carboxylic acids (249- *or* 193-nm excitation). This is at variance with our experimental results. Thus, the two-step decarboxylation mechanism proposed here, while not a unique explanation, is consistent with the observed energy disposal dynamics.

A comparison of our findings with observations on the solution-phase photochemistry of acrylic and methacrylic acid may provide some insight regarding the photophysical processes leading to product formation. Since polymerization, rather than decarboxylation, is observed in solution, it is likely that, following irradiation of, e.g., acrylic acid, a relatively long-lived excited state is formed. Studies of the UV-visible absorption spectroscopy of acrylic acid[15] indicate that excitation near 193 nm initially populates a $^1(\pi,\pi^*)$ state while 249-nm excitation initially populates a $^1(\mathrm{n},\pi^*)$ state [absorption at 308 nm corresponds to the low-energy tail of this (n,π^*) transition]. We suggest that regardless of the excited state initially populated, the $^3(\mathrm{n},\pi^*)$ is formed via rapid intersystem crossing. Such nonradiative processes can be particularly efficient in polyatomic molecules with low-frequency, e.g., torsional, degrees of freedom.[16] In solution, this triplet state may encounter ground-state acrylic acid and thereby initiate polymerization. The observation that acrylic acid polymerization can be triplet sensitized[17] is consistent with this hypothesis. If the $^3(\mathrm{n},\pi^*)$ state undergoes nonradiative decay to the ground state prior to encountering any ground-state acid, it can be rapidly relaxed by collisions with the solvent. As a result of this rapid vibrational relaxation, acrylic acid molecules which return to the ground state are left with insufficient internal energy to undergo unimolecular decarboxylation. In the gas phase, at the relatively low pressures characteristic of our experiments, the time between collisions involving two carboxylic acid molecules is $\gtrsim 10^{-5}$ s. Thus a significant fraction of electronically excited acid molecules may return to the ground state prior to such collisions. In this way, vibrationally hot ground-state molecules are formed which can undergo unimolecular decay in competition with collisional relaxation. The observation that the gas-phase pyrolysis of acrylic acids results in decarboxylation[2] appears consistent with this model. However, decarboxylation was found to occur in competition with other fragmentation channels, suggesting that heterogeneous processes may have been significant in the reported study.[2] The scenario suggested here is outlined in Scheme I, where AA represents acrylic acid and S_0, the ground electronic state; an asterisk indicates electronic excitation, a dagger (†) vibrational excitation, and M a collision partner, e.g., solvent or buffer gas molecules. An analogous scheme can be constructed in the case of methacrylic acid. In summary, we suggest that in solution, $k_7 \gtrsim k_8$ and $k_9 >> k_{10}$, whereas in the gas phase, $k_8 > k_7$ and $k_{10} \gtrsim k_9$. This scheme provides a relatively simple explanation for the fact that different photoproducts are observed following the UV irradiation of acrylic and methacrylic acid in gas and solution phases.

Conclusions

We find that both acrylic and methacrylic acid photofragment upon irradiation at 249 or 193 nm, forming CO_2 as a primary product. Vibrational excitation in the CO_2 fragment is monitored by infrared fluorescence and its extent is consistent with a statistical model for energy partitioning in unimolecular decompositions, assuming a fragmentation mechanism where CO_2 is formed in concert with a carbene. This suggests a novel approach for the generation of carbenes in the gas phase. Finally, we suggest a scheme which accounts for the apparently dichotomous reactivity of acrylic acid (and its derivatives) in the gas and solution phases.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. The excimer laser used here was obtained with funds provided by a major instrumentation grant from the National Science Foundation (CHE 81-14966).

Registry No. Acrylic acid, 79-10-7; methacrylic acid, 79-41-4.

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(15) Morita, H.; Fuke, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 922-928.

(16) This constitutes an explanation of "Kasha's rule". See: Jortner, J.; Rice, S. A.; Hochstrasser, R. M. *Adv. Photochem.* **1969**, *7*, 149-309.

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Intramolecular Donor-Acceptor Systems. 10. Multiple Fluorescences from 8-(Phenylamino)-1-naphthalenesulfonates

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Abstract: 8-(Phenylamino)-1-naphthalenesulfonates (**1**) exhibit variations in fluorescence maxima and quantum yields with solvent polarity and substituent change. These facts suggest sequential formation of two excited states, a naphthalene-excited $S_{1,\mathrm{np}}$ state and a charge-transfer state, $S_{1,\mathrm{ct}}$, as in the case of the 6-(phenylamino)-2-naphthalenesulfonates (**2**) (cf. Kosower, E. M. *Acc. Chem. Res.* **1982**, *15*, 259). An inefficient photochemical dissociation of the sulfonate group to form 1-(phenylamino)naphthalene is reported. Previously reported excited-state kinetics are consistent with the two-step mechanism.

Introduction

The sensitivity of the fluorescence maxima and quantum yields of 8-(phenylamino)-1-naphthalenesulfonates (8,1-ANS, **1**) and 6-(phenylamino)-2-naphthalenesulfonates (6,2-ANS, **2**) was first recognized by Weber and Laurence.[2] In water, **1** and **2** are almost nonfluorescent but in nonpolar organic solvents, or when bound to proteins,[3-7] exhibit a strong fluorescence and a blue shift of the

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(1) (a) Tel-Aviv University. (b) State University of New York.

(2) Weber, G.; Laurence, D. J. R. *Biochem. J.* **1954**, *56*, xxxi.

(3) Turner, D. C.; Brand, L. *Biochemistry* **1968**, *7*, 3381.

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