

behavior has been observed for the flat-surface case due to the interference between the reflected field at the dipole site with the dipole oscillator itself.<sup>8</sup> Moreover, it has also been acknowledged by GN that their results cannot yield the correct asymptotic results for a flat surface in the limit  $a \rightarrow \infty$  with a fixed value of  $d$ ,<sup>6</sup> whereas it has been noted that eq 7 and 8 can indeed lead back to the correct flat-surface limit.<sup>2</sup> We have further shown that these discrepancies do not arise from the dipole approximation alone. In Figure 3 we show similar calculations as in Figure 2 for the range  $0 < a/d < 4$  with  $d$  fixed at 50 Å, which implies that  $a/\lambda \leq 0.048$ . Discrepancies are obvious in spite of the fact that the dipole approximation should hold for such a small ratio of  $a/\lambda$ . Hence, we conclude that one must be very careful about the limitations of the GN model when it is applied to the di-

pole-sphere system. In addition to the conditions  $a \ll \lambda$  and  $d \ll \lambda$  as noted before, the value of  $a$  cannot be too large for a fixed  $d$ . Since some of the previous calculations do not exhibit an awareness of this condition,<sup>9</sup> it would be of interest to reexamine all the problems on surface-enhanced Raman scattering and other photochemical processes as previously treated by GN adopting their model for the molecular decay rates.<sup>4</sup>

**Acknowledgment.** This research was supported by the Air Force Office of Scientific Research, United States Air Force (AFSC), under Contract F49620-86-C-0009, the National Science Foundation under Grant CHE-8620274, and the Office of Naval Research.

**Registry No.** Ag, 7440-22-4.

(8) Chance, R. R.; Prock, A.; Silbey, R. *Adv. Chem. Phys.* **1978**, *37*, 1.

(9) See, e.g., Figure 1 of ref 4.

## Triplet State and Photodecarboxylation of Phenylglyoxylic Acid in the Presence of Water

Hans Jochen Kuhn and Helmut Görner\*

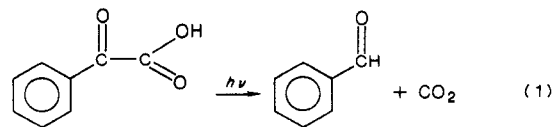
Max-Planck-Institut für Strahlenchemie, D-4330 Mülheim a. d. Ruhr, West Germany  
(Received: October 21, 1987; In Final Form: March 28, 1988)

The photodecarboxylation of phenylglyoxylic acid (PA) was studied by quantum yield ( $\Phi_d$ ) and time-resolved conductivity measurements in polar solvents at room temperature.  $\Phi_d$  is substantial ( $\geq 0.3$ ) in the presence of 3–30 M water in acetonitrile and at  $\text{pH} \leq \text{p}K_a = 1.1$  in neat water. The triplet states of PA, of its ethyl ester, and of 4-carboxybenzaldehyde were observed by nanosecond laser flash photolysis and emission spectroscopy. The initial transient obtained from PA (e.g., in acetonitrile  $\lambda_{\text{max}} = 322$  nm; lifetime  $\geq 3$   $\mu\text{s}$ ) is assigned to the  $n, \pi^*$  triplet state, and a second transient (in 2-propanol;  $\lambda_{\text{max}} = 313$  nm;  $t_{1/2} > 100$   $\mu\text{s}$ ) is assigned to the Ph-COH-COOH radical. Phosphorescence was observed in glassy matrices at  $-196$  °C and in acetonitrile, acetone, and acetic acid at 25 °C. In the latter ("inert") solvents the phosphorescence intensity and the triplet lifetime (up to 20  $\mu\text{s}$ ) are reduced by addition of alcohols or water. The rate constant of H-atom abstraction by triplet PA from 2-propanol is  $1.5 \times 10^6$   $\text{M}^{-1} \text{s}^{-1}$  in acetonitrile. Addition of water to PA in the "inert" solvents results in a non-Stern-Volmer behavior for triplet quenching. Excitation of PA in neat aqueous solution yields the triplet of benzaldehyde, the excited photoproduct, as main transient whereas triplet PA could not be detected. A mechanism accounting for the dependences of  $\Phi_d$  on the pH and on the  $\text{H}_2\text{O}$  concentration in mixtures with acetonitrile is proposed. Water governs the photochemistry of PA in three respects, via the acid-base equilibrium, as triplet quencher, and by reducing the quantum yield of intersystem crossing to the anion triplet.

### Introduction

The photochemistry of  $\alpha$ -keto acids has been studied for more than 100 years.<sup>1-14</sup> Phenylglyoxylic acid (PA, benzoylformic

acid), like its aliphatic analogue, pyruvic acid, undergoes both photoreduction and photodecarboxylation.<sup>2-7</sup> The latter reaction is particularly efficient in aqueous solution yielding benzaldehyde (BA) as the major photoproduct.<sup>2,11-13</sup> Photodecarboxylation of PA (eq 1) occurs in water with a quantum yield ( $\Phi_d$ ) of about



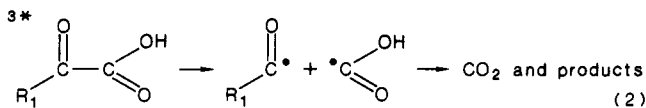
0.3 at  $\text{pH} \leq 1.3$  (where PA is mainly present as acid), but  $\Phi_d$  is small in dry acetonitrile solution.<sup>11</sup> In mixtures of these solvents  $\Phi_d$  increases with  $[\text{H}_2\text{O}]$ , reaches a maximum ( $\Phi_d \approx 0.8$ ) at 5–15 M water, and decreases at higher  $[\text{H}_2\text{O}]$ . In  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution (3:1 vol) PA has been proposed as a convenient chemical actinometer for the 250–400-nm region.<sup>11,12</sup> For the photo-

- (1) (a) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 844. (b) Givens, R. S.; Levi, N. In *The Chemistry of Acid Derivatives, Chemistry of Functional Groups*; Patai, S., Ed.; Wiley: New York, 1979; Part 1, Suppl. B, p 641.  
(2) Leermakers, P. A.; Vesley, G. F. *J. Am. Chem. Soc.* **1963**, *85*, 3776.  
(3) (a) Leermakers, P. A.; Vesley, G. F. *J. Org. Chem.* **1963**, *28*, 1160. (b) Kendall, D. S.; Leermakers, P. A. *J. Am. Chem. Soc.* **1966**, *88*, 2766.  
(4) (a) Fujisawa, T.; Monroe, B. M.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 542. (b) Fujisawa, T.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 4175.  
(5) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 6455.  
(6) (a) Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 77. (b) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3483.  
(7) Emori, S.; Colpa, J. P.; Wan, J. K. S. *Chem. Phys. Lett.* **1983**, *98*, 142.  
(8) Mittal, L. J.; Mittal, J. P.; Hayon, E. *J. Phys. Chem.* **1973**, *77*, 1482.  
(9) Davidson, R. S.; Goodwin, D.; Fournier de Violet, P. *Chem. Phys. Lett.* **1981**, *78*, 471.  
(10) (a) Rosenfeld, R. N.; Weiner, B. *J. Am. Chem. Soc.* **1983**, *105*, 3485. (b) Back, R. A.; Yamamoto, S. *Can. J. Chem.* **1985**, *63*, 542.  
(11) Defoin, A.; Defoin-Straatmann, R.; Hildenbrand, K.; Bittersmann, E.; Kreft, D.; Kuhn, H. J. *J. Photochem.* **1986**, *33*, 237.  
(12) Kuhn, H. J.; Defoin, A. *EPA Newslett.* **1986**, No. 26, 23.

(13) Görner, H.; Kuhn, H. J. *Abstracts, International Conference on Photochemistry, 13th, 1987, Budapest*; pp 116–117.

(14) Defoin, A.; Defoin-Straatmann, R.; Kuhn, H. J. *J. Labelled Compd. Radiopharm.* **1982**, *19*, 891.

decarboxylation of pyruvic acid ( $R_1 = \text{CH}_3$ ) in polar solvents a radical pair mechanism, involving the scission of the C-C bond after population of the lowest triplet state, has been proposed.<sup>6</sup>



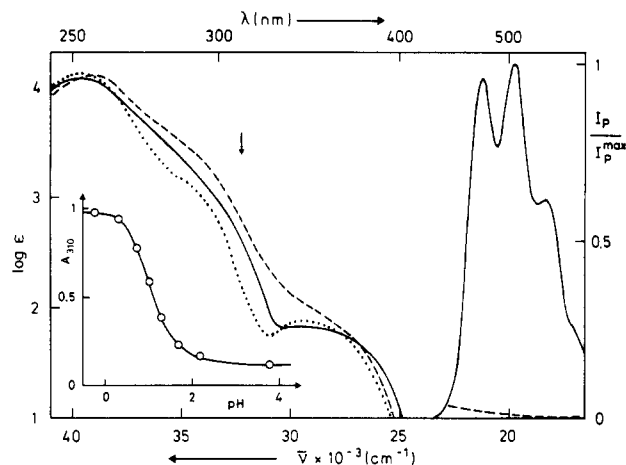
Similar mechanisms have been claimed for PA ( $R_1 = \text{Ph}$ ) in a single crystal<sup>7</sup> as well as in acetonitrile and aqueous solution.<sup>5,8</sup> However, on the basis of photo-CIDNP measurements in acetonitrile/water mixtures it has been suggested that free-radical primary products, including  $\cdot\text{COOH}$  and benzoyl, play only a minor role and H-atom abstraction seems to be unimportant in this "relatively inert" medium.<sup>11</sup> Photodecarboxylation of PA in  $\text{D}_2\text{O}$  yields formyl-deuteriated benzaldehyde.<sup>11,14</sup> Irradiation of BA and several other aromatic aldehydes in  $\text{D}_2\text{O}$  leads to formyl H/D exchange, too.<sup>15</sup> Both photodecarboxylation of PA and H/D exchange of BAs strongly depend on the concentration of (heavy) water.<sup>11-16</sup> Although some knowledge of these phenomena has been compiled, the role of water is still not yet well understood, as has already been pointed out by Leermakers and Vesley.<sup>2</sup>

In the present paper we aim at a better understanding of the mechanism of photodecarboxylation of PA. For this purpose we studied the photochemical properties of PA by means of emission spectroscopy and laser flash photolysis including transient conductivity measurements. Several transients of PA in solution were identified and their properties were compared with results obtained from phosphorescence and continuous irradiation. In addition, the corresponding ethyl ester (ethyl phenylglyoxylate, EPG)<sup>17,18</sup> and 4-carboxybenzaldehyde (CBA)<sup>16</sup> were studied. With these derivatives similar, but also distinctly different features compared to PA were expected and have indeed been found.

### Experimental Section

The 248-nm line of an excimer laser was used for excitation unless otherwise indicated. For a few measurements the 308-nm excimer line or the third harmonic of a Nd laser (353 nm) was used. The laser flash photolysis apparatus and the detection system (transient digitizer R7912) were the same as in previous work.<sup>16</sup> The samples were purged by argon unless otherwise indicated. In some cases (e.g., where photolysis of a photoproduct is involved) and for conductivity measurements a flow-through cell was used (area  $1 \times 1 \text{ cm}^2$ ) for optical measurements whereas in the other cases the irradiated volume (ca.  $1 \times 1 \times 10 \text{ mm}^3$ ) was exchanged by bubbling with argon. The conductivity cell (path length 5 mm) contained three cylindrical glassy carbon electrodes with a gap distance of 8 mm; only one of the two identical sections was excited. The slow conductivity signals (5  $\mu\text{s}$ –10 s) were measured by a 0.2-MHz ac bridge (40 V) and a transient digitizer (Tektronix 390). A dc bridge (200 V), shielded by a metal housing to reduce the electromagnetic noise from the laser discharge, and one or two 150-MHz amplifiers (10 times; Comlinear) were used for shorter time intervals (resolution 20 ns). Typically, the amplitude is 100 times larger with the ac than with the dc bridge.

The emission spectra were recorded on a spectrofluorometer (Perkin-Elmer LS-5) for quenching measurements or a Spex-Fluorolog for corrected spectra. The quantum yields were obtained by use of benzophenone in butyronitrile at  $-196^\circ\text{C}$  as reference assuming  $\Phi_p = 1$ . Phosphorescence quenching was carried out with small amounts of additives (up to 5 vol %) during continuous bubbling with argon. Deviations from linear Stern-Volmer dependences in the range  $I_p^\circ/I_p = 2$ –4 are indicated; due to some emission other than the weak phosphorescence,  $I_p$  could typically not be reduced to values below 10–20%. The samples were purged



**Figure 1.** Absorption and emission spectra of PA in argon-saturated acetonitrile (—) and water (pH 0.5 (---) and pH 12 (···)) at  $25^\circ\text{C}$ . (Inset)  $A_{310}$  as a function of pH.

with argon and studied at  $25 \pm 1^\circ\text{C}$  unless indicated otherwise (e.g., quenching by oxygen and phosphorescence at  $-196^\circ\text{C}$ , respectively). The pH was adjusted by addition of  $\text{HClO}_4$  or  $\text{NaOH}$  and measured directly in the solution (electrode: Radiometer, Type 2321).

The  $\Phi_d$  values were determined by means of an electronic actinometer as described.<sup>11,12</sup> Carbon dioxide was determined by GC after catalytic hydrogenation: Gaseous products in the irradiation cuvette were purged into a specially designed evacuated gas bulb. By means of a gas sampling valve an aliquot volume was then transferred on a 2-m Porapak N column.<sup>19</sup> After separation  $\text{CO}$  and  $\text{CO}_2$  were catalytically hydrogenated to  $\text{CH}_4$  which can be detected by a sensitive flame ionization detector. A similar system is now commercially available (Chrompak Methaniser).

PA (EGA) was recrystallized from benzene and carbon tetrachloride,<sup>11</sup> CBA (EGA) was used as received, and EPG (Aldrich) was purified by fractional distillation. Vaporimetric molecular weight of PA (15–25 mM), Anal. Calcd: 150. Found: 293 in benzene, 205 in chloroform, 207 in dichloromethane, 155 in acetone, 183 in acetonitrile, 150 in methanol, 126–147, respectively, for 23–53 mM in water. For example, molecular weights in chloroform and dichloromethane are 1.37-fold the monomeric value. Molar absorption coefficient (in  $\text{M}^{-1} \text{cm}^{-1} \times 10^4$ ) of CBA (EPG): acetonitrile,  $\epsilon_{250}$  1.93 ( $\epsilon_{254}$  1.22); acetonitrile/water 3:1 (vol),  $\epsilon_{252}$  1.89. 1,3-Cyclohexadiene and xanthone (EGA) were used as received; benzophenone (EGA) was zone refined. Solvents (Merck, Darmstadt) were p.A. (glacial acetic acid, ethylene glycol, ethanol, 2-propanol, and the other alcohols), Uvasol quality (acetone, acetonitrile, heavy water) or distilled (acetonitrile for  $\Phi_d$  measurements, butyronitrile, Fluka). Water was triply distilled ( $\Phi_d$  measurements) or purified by a Millipore system (all other measurements); all solvent compositions are meant by volume.

### Results

**Absorption Spectra.** The absorption spectrum of PA in acetonitrile (Figure 1) exhibits a maximum at 254 nm ( $\epsilon$   $1.1 \times 10^4 \text{ M}^{-1} \text{cm}^{-1}$ ) and a pronounced shoulder around 345 nm ( $\epsilon$   $69 \text{ M}^{-1} \text{cm}^{-1}$ ).<sup>11</sup> Addition of water causes a blue shift of the spectrum at wavelengths longer than 220 nm. In neat water a significant pH dependence was recorded in the 270–330-nm range; the absorbance at 310 nm ( $A_{310}$ ) decreases with pH on going from 0 to 2 and remains almost constant above (inset of Figure 1); a corresponding increase was measured at 220 nm. The pH for 50% change of  $A_{310}$  is taken as a measure of the  $\text{pK}_a$  value which is  $1.1 \pm 0.1$ . No spectral change was found for EPG in the pH range 0–7, but for CBA an increase of  $A_{230}$  and a corresponding decrease

(15) Defoin, A.; Defoin-Straatmann, R.; Kuhn, H. J. *Tetrahedron* **1984**, *40*, 2651.

(16) Görner, H.; Kuhn, H. J. *J. Phys. Chem.* **1986**, *90*, 5946.

(17) Tominaga, T.; Odaira, Y.; Tsutsumi, S. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1824.

(18) Encinas, M. V.; Lissi, E. A.; Zanocco, A.; Stewart, L. C.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 386.

(19) Weeke, F.; Bastian, E.; Schomburg, G. *Chromatographia* **1974**, *7*, 163.

**TABLE I: Phosphorescence Maxima in Glassy and Fluid Media<sup>a</sup>**

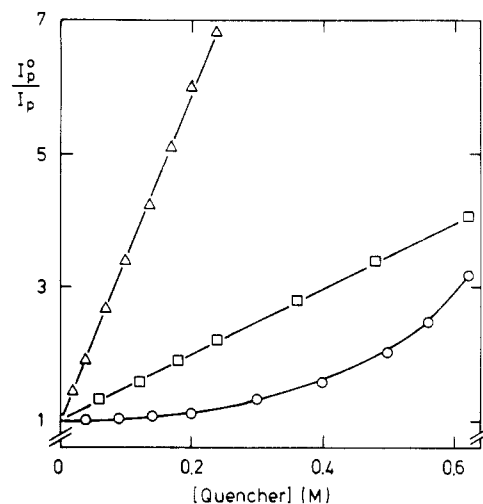
compd	solvent	temp, °C	$\lambda_{\max}$ , nm
PA	butyronitrile	-196	465, 502, 540 sh
PA	ethanol	-196	466, 505, 545, 590 sh
PA	ethylene glycol/EtOH <sup>b</sup>	-196	450
PA	ethylene glycol/H <sub>2</sub> O <sup>b</sup>	-196	443, 472, 510 sh
EPG	butyronitrile	-196	455, 490, 529 sh
EPG	ethanol	-196	465, 502, 550 sh
EPG	ethylene glycol/H <sub>2</sub> O	-196	450, 490 sh
CBA	butyronitrile	-196	412, 444, 480
CBA	ethanol	-196	414, 444, 478, 515
CBA	ethylene glycol/H <sub>2</sub> O	-196	414, 440, 470, 510 sh
BA <sup>c</sup>	butyronitrile	-196	397, 425, 457, 490, 530
BA <sup>c</sup>	ethylene glycol/H <sub>2</sub> O	-196	399, 426, 456, 487
PA	acetonitrile	25	470, 505, 550 sh
PA	acetone	25	472, 511, 555 sh
PA	acetic acid	25	474, 514, 555 sh
EPG	acetonitrile	25	470, 509
EPG	acetone	25	470, 510, 550 sh
CBA	acetonitrile	25	434, 456, 485 <sup>d</sup>
BA <sup>c</sup>	acetonitrile	25	402, 431, 462, 502

<sup>a</sup> In argon-saturated solutions;  $\lambda_{\text{exc}} = 340$  nm for acetone and acetic acid and 250–280 nm for the other media. <sup>b</sup> In 2:1 mixtures (vol). <sup>c</sup> Taken from ref 16. <sup>d</sup> Steady-state phosphorescence at the detection limit under our conditions.

of  $A_{275}$  was found, corresponding to a  $pK_a$  value of 3.6.

**Phosphorescence Spectra.** The emission spectrum of PA in butyronitrile at -196 °C exhibits two maxima at 465, 502 nm and a shoulder at 540 nm (Table I); it is independent of  $\lambda_{\text{exc}}$  (260–380 nm for [PA] = 0.1 and 10 mM, respectively). Similar spectra were recorded in glassy ethanol and in ethylene glycol/water (2:1 vol); in the latter medium  $\lambda_{\text{max}}$  is markedly blue shifted and the emission spectrum is less structured (Table I). Replacement of water by ethanol (in the 2:1 mixture) has no marked effect on the shape and the maximum. From a comparison with the literature<sup>2,11</sup> and the known phosphorescence spectra of BA and CBA<sup>16</sup> the emission of PA has to be attributed to phosphorescence. For PA in ethanol at -196 °C a phosphorescence lifetime of 3 ms and a yield  $\Phi_p \geq 0.6$  were estimated.

Phosphorescence was also detected in argon-saturated acetonitrile, acetone ( $\lambda_{\text{exc}} = 350$  nm), and acetic acid ( $\lambda_{\text{exc}} = 280$ –350 nm) solutions at 25 °C (Figure 1 and Table I). The spectra are nearly the same as in glassy ethanol or butyronitrile. In acetonitrile the spectrum is independent of  $\lambda_{\text{exc}}$  (260–330 nm). The two major peaks are only weakly dependent on the medium. Phosphorescence in substantial yield ( $\geq 0.3$ ) was also observed for CBA and EPG in glassy media (Table I). Similar but less resolved spectra than for PA were recorded for the ester in acetonitrile. Some difficulties in obtaining "good" phosphorescence spectra are not surprising



**Figure 2.** Dependences of the reciprocal phosphorescence intensity vs quencher concentration for PA (0.1 mM) in argon-saturated acetonitrile at 25 °C obtained with 2-propanol ( $\Delta$ ), methanol ( $\square$ ), and H<sub>2</sub>O ( $\circ$ );  $\lambda_{\text{exc}} = 260$  nm.

since the quantum yield of phosphorescence of PA is small ( $\leq 10^{-3}$  in acetonitrile at 25 °C) and smaller for CBA and EPG.

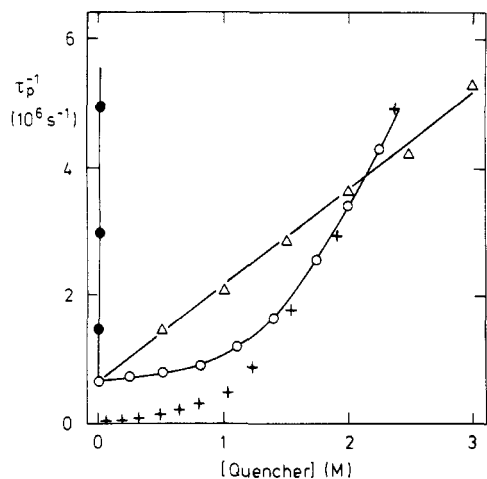
**Phosphorescence Quenching.** The phosphorescence intensity at  $\lambda_{\text{max}}$  of PA in argon-saturated acetonitrile at room temperature is quenched by alcohols and 1,3-cyclohexadiene. Plots of  $I_p^0/I_p$  vs quencher concentration are linear in the cases examined (Figure 2). The Stern-Volmer constants ( $K_q$ ) increase in the order 2-methyl-2-propanol, methanol, ethanol, and 2-propanol and are 3 orders of magnitude larger for 1,3-cyclohexadiene (Table II).

The phosphorescence decay of PA, observed around 500 nm after laser excitation, depends somewhat on the experimental conditions. At the lowest possible intensity (at which no transient absorption could be observed with  $\lambda_{\text{exc}} = 308$  nm) the decay in the range of 100 ns (after the disappearance of the scattered light signal) and several microseconds is essentially first order, corresponding to phosphorescence lifetimes ( $\tau_p$ ) of up to 20 and 22  $\mu$ s for PA in acetonitrile and acetic acid (Table II). The observed half-life decreases with increasing laser intensity due to contribution of T-T annihilation. With  $\lambda_{\text{exc}} = 248$  nm the half-life is markedly shorter because of higher laser intensities required for the signal, and the decay follows mixed first- and second-order kinetics. In acetone or acetonitrile with  $\lambda_{\text{exc}} = 353$  nm  $\tau_p$  is about 8  $\mu$ s; the smaller values are partly due to self-quenching since the required PA concentration is much larger (see Table II). For EPG and CBA  $\tau_p$  is 0.6–3  $\mu$ s, i.e., shorter than for PA under comparable conditions.

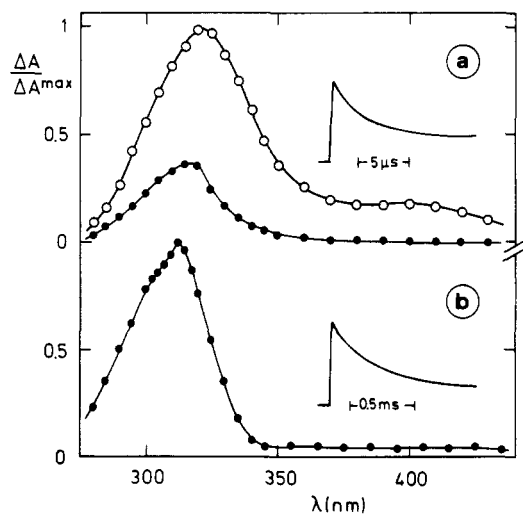
**TABLE II: Phosphorescence Lifetime and Data Obtained from Phosphorescence Quenching<sup>a</sup>**

compd	solvent	$\lambda_{\text{exc}}$ , nm	$\tau_p$ , <sup>b</sup> $\mu$ s	additive	$K_q$ , <sup>c</sup> M <sup>-1</sup>	$k_q$ , M <sup>-1</sup> s <sup>-1</sup>
PA	acetonitrile	248	3.6	1,3-cyclohexadiene	$2 \times 10^4$	$6 \times 10^9$
PA	acetonitrile	248		2-propanol	24	$1.5 \times 10^6$
PA	acetonitrile	248		ethanol	19	$1 \times 10^6$
PA	acetonitrile	248		methanol	5	
PA	acetonitrile	248		2-methyl-2-propanol	<4	
PA	acetonitrile	248		H <sub>2</sub> O <sup>d</sup>	15	$\geq 3.5 \times 10^6$
PA	acetonitrile	308	20			
PA	acetonitrile	353	8			
PA	acetone	353	7	2-propanol	10	$1.7 \times 10^6$
PA	acetone	353		H <sub>2</sub> O <sup>d</sup>	18	$\geq 5 \times 10^6$
PA	acetic acid	248	>1	H <sub>2</sub> O <sup>d</sup>	1.6	$>3 \times 10^5$
PA	acetic acid	308	22			
EPG	acetonitrile	248	0.6	1,3-cyclohexadiene		$1 \times 10^{10}$
EPG	acetonitrile	248		H <sub>2</sub> O	<0.5	$<1 \times 10^5$
EPG	acetonitrile	248		2-propanol		$1.5 \times 10^6$
CBA	acetonitrile	248	1	1,3-cyclohexadiene	$\geq 2 \times 10^4$	$1 \times 10^{10}$
CBA	acetonitrile	248		2-propanol	100	$\geq 3 \times 10^7$
CBA	acetonitrile	308	3			

<sup>a</sup> In argon-saturated solution at 25 °C. <sup>b</sup> Using the lowest possible pulse intensity, [PA]  $\approx 0.3$ ,  $\leq 1$ , and  $\approx 5$  mM for  $\lambda_{\text{exc}} = 248$ , 308, and 353 nm, resp. <sup>c</sup> Steady-state measurements,  $\lambda_{\text{exc}} = 250$ –280 nm (340–350 nm) for acetonitrile (acetone, acetic acid). <sup>d</sup>  $I_p^{-1}$  and  $\tau_p^{-1}$  vs [H<sub>2</sub>O] are upward curved; the slopes were obtained from the quasi-linear part; see text.



**Figure 3.** Dependences of the reciprocal phosphorescence lifetime vs quencher concentration for PA (3 mM) in argon-saturated acetonitrile at 25 °C obtained with 1,3-cyclohexadiene (●), 2-propanol (Δ), and H<sub>2</sub>O (○);  $\lambda_{\text{exc}} = 248$  nm. (+) [PA] = 1 mM, H<sub>2</sub>O, reduced laser intensity;  $\lambda_{\text{exc}} = 308$  nm.

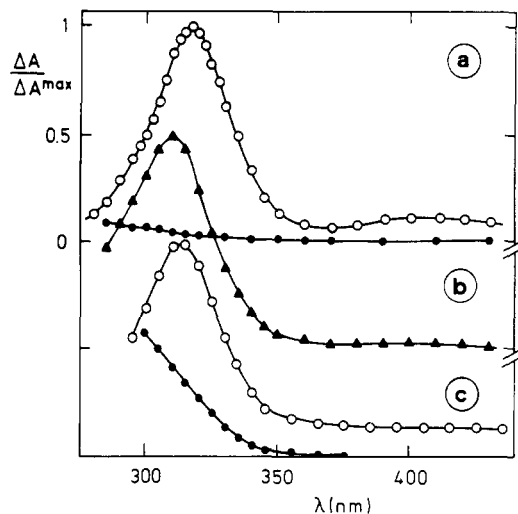


**Figure 4.** Transient absorption spectra of PA (0.3 mM) (a) in acetonitrile 20 ns (○) and 2  $\mu$ s (●) after the pulse and (b) in 2-propanol 50 ns after the pulse (argon-saturated,  $\lambda_{\text{exc}} = 248$  nm, 25 °C). (Inset) Decay kinetics at  $\lambda_{\text{max}}$ .

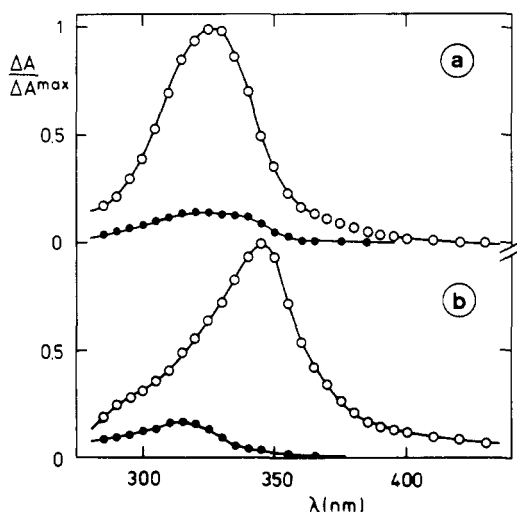
Both  $I_p$  and  $\tau_p$  are markedly reduced by oxygen (e.g., down to  $<1/10$  in air-saturated acetonitrile solutions). Also  $\tau_p$  is quenched by alcohols and 1,3-cyclohexadiene; linear dependences of  $\tau_p^{-1}$  on quencher concentration were obtained (Figure 3; slope,  $k_q$ ). The slopes from both methods show a similar trend (Table II), and the Stern-Volmer constants are equal (within experimental error) to the product  $\tau_p k_q$ . A discrepancy in some cases arises from the longer phosphorescence lifetime under steady-state conditions compared to laser excitation.

On addition of small amounts of (neutral) water to PA in acetonitrile the emission spectrum remains unchanged but  $I_p$  and  $\tau_p$  are reduced. Plots of  $I_p^0/I_p$  and  $\tau_p^{-1}$  do not show linear dependences on [H<sub>2</sub>O] below 1 M (Figures 2 and 3). Nevertheless, estimates for the quenching rate constant could be obtained from the slope of the linear part of  $I_p^{-1}$  (or  $\tau_p^{-1}$ ) vs [H<sub>2</sub>O], typically in the 1–3 M range. These values (Table II) may be compared with the  $k_q$  values obtained from T–T absorption (see below). Phosphorescence quenching by the organic additives was also found for EPG and CBA (Table II). For the ester, however, the rate constant for quenching by water is much smaller than for PA.

**Transients in "Inert" Solvents.** On excitation of PA (0.1–0.5 mM,  $\lambda_{\text{exc}} = 248$  nm) in argon-saturated acetonitrile at room temperature two transients, a major short-lived (T, denoting triplet,  $\lambda_{\text{max}} = 322$  nm) and a minor longer-lived (K', denoting ketyl radical,  $\lambda_{\text{max}} \approx 320$  nm) were observed (Figure 4a). The ratio



**Figure 5.** Transient absorption spectra of EPG (0.3 mM) (a) in acetonitrile 20 ns (○) and 2  $\mu$ s (●) after the pulse, (b) in 2-propanol 2  $\mu$ s after the pulse, and (c) in water 20 ns (○) and 2  $\mu$ s (●) after the pulse (argon saturated,  $\lambda_{\text{exc}} = 248$  nm, 25 °C).



**Figure 6.** Transient absorption spectra of CBA (0.3 mM) (a) in acetonitrile 20 ns (○) and 2  $\mu$ s (●) after the pulse and (b) in water 20 ns (○) and 2  $\mu$ s (●) after the pulse (argon saturated,  $\lambda_{\text{exc}} = 248$  nm, 25 °C).

of absorbances of the two species ( $\Delta A(K')/\Delta A(T)$ ), measured at both  $\lambda_{\text{max}}$ , is  $\leq 0.4$ . At low laser intensity and when  $\Delta A$  of the remaining transient K' was subtracted, the decay kinetics of T follow mainly a first-order law ( $k_{\text{obsd}} = \tau_T^{-1}$ ). Nevertheless, the decay in the absence of additives is limited either by T–T annihilation ( $\lambda_{\text{exc}} = 248$  nm) or by self-quenching (353 nm). Only with  $\lambda_{\text{exc}} = 308$  nm both processes can be considered to be negligible under our conditions.

T is quenched by oxygen (rate constant  $k_{\text{ox}} = 2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>), alcohols (see below), and 1,3-cyclohexadiene; from the linear dependence of  $k_{\text{obsd}}$  on [1,3-cyclohexadiene] a rate constant close to the diffusion-controlled limit was obtained (Table III). In acetic acid, although this is not completely transparent at 248 nm, similar effects were found with PA in larger concentrations ( $>0.5$  mM; see Table III).

Essentially the same results were observed for the major transient T in the accessible range ( $\lambda > 330$  nm) when  $\lambda_{\text{exc}} = 353$  nm was used (Table III). From a linear plot of  $k_{\text{obsd}}$  vs [PA] (up to 0.2 M) a rate constant for self-quenching of  $k_{\text{PA}} = 2 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup> and an intercept of  $\tau_T^{-1} = 4.9 \times 10^4$  s<sup>-1</sup> were obtained in acetonitrile. This indicates that (i) static quenching plays no discernible role and that (ii) the highest  $\tau_T$  and  $\tau_p$  values coincide (ca. 20  $\mu$ s). On xanthone-sensitized excitation ( $\lambda_{\text{exc}} = 353$  nm) of PA in acetonitrile the xanthone triplet ( $\lambda_{\text{max}} = 620$  nm) is quenched with the rate constant of approximately  $5 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. At [PA] = 2 mM (corresponding to a lifetime of about 100

TABLE III: Data Obtained from T-T Absorption Measurements<sup>a</sup>

compd	solvent	$\lambda_{\text{exc}}$ , nm	$\lambda_{\text{max}}$ , nm	$\tau_T$ , <sup>b</sup> $\mu\text{s}$	$10^{-9}k_{\text{ox}}$ , $\text{M}^{-1} \text{s}^{-1}$	$10^{-9}k_q$ , <sup>c</sup> $\text{M}^{-1} \text{s}^{-1}$
PA	acetonitrile	248	322, 410 sh	3	2	6
PA	acetonitrile	308		8		
PA	acetonitrile <sup>d</sup>	353	<380, 400 sh	1		
PA	acetone	353	<330, 400 sh	1	1	
PA	acetic acid	248	318, 420 sh	6		
PA	acetic acid	308		8		3
EPG	acetonitrile	248	318, 405 sh	0.8	2	10
EPG	acetone	353		0.5		
EPG	acetic acid	248	316, 410 sh	1		
CBA	acetonitrile	248	325	1.8	2	12
CBA	acetonitrile	308		2.5		10
CBA	acetone	353		$\leq 1$		
CBA	acetic acid	248	322	0.7		

<sup>a</sup>In argon-saturated solution at 25 °C. <sup>b</sup>Using concentrations of typically 0.2,  $\leq 1$ , and 5 mM for  $\lambda_{\text{exc}} = 248, 308$ , and 353 nm, respectively. <sup>c</sup>Rate constant for quenching by 1,3-cyclohexadiene. <sup>d</sup>On xanthone-sensitized excitation.

TABLE IV: Properties of the Hydroxybenzyl Radical K in Solution<sup>a</sup>

compd	solvent	$\lambda_{\text{max}}$ , nm	$t_{1/2}$ , ms	$10^{-6}k_q$ , <sup>b</sup> $\text{M}^{-1} \text{s}^{-1}$
PA	2-propanol	313	>0.2 <sup>c</sup>	1.5 (1.7) <sup>d</sup>
PA	ethanol	312	>0.1 <sup>c</sup>	0.8
PA	methanol	315	>0.05	0.6
PA	2-methyl-2-propanol	<sup>e</sup>		$\leq 0.2$
PA	acetonitrile	320	>0.01	
PA	butyronitrile	315	>0.05	
EPG	2-propanol	310	>0.2 <sup>c</sup>	1.5
EPG	acetonitrile	300	>0.2	
CBA	2-propanol	320	>0.05	60

<sup>a</sup>In argon-saturated solution at 25 °C,  $\lambda_{\text{exc}} = 248$  nm unless indicated otherwise. <sup>b</sup>Rate constant for triplet quenching by alcohols in acetonitrile. <sup>c</sup>Detection of T in 100% alcohol, lifetime  $\leq 0.4 \mu\text{s}$ . <sup>d</sup>In acetone,  $\lambda_{\text{exc}} = 353$  nm. <sup>e</sup>K not observed.

ns for the xanthone triplet) the remaining transient is assigned to T since it shows  $\lambda_{\text{max}} < 380$  nm and  $\tau_T = 1 \mu\text{s}$  (Table III).

For EPG and CBA in acetonitrile (Figures 5a and 6a) the  $\Delta A(K')/\Delta A(T)$  ratio is considerably smaller ( $\leq 0.1$ ) than for PA whereas  $\lambda_{\text{max}}$ ,  $\tau_T$ , and the effects of quenchers (oxygen, 1,3-cyclohexadiene) are rather similar (Table III).

**Transients in Alcohols.** A long-lived transient (K, denoting ketyl) was observed for PA in argon-saturated 2-propanol. The absorption spectrum of K is identical (within experimental error) with that of K' (compare parts a and b of Figure 4). K decays by second-order kinetics; the half-life ( $t_{1/2}$ ) under our conditions is longer than 200  $\mu\text{s}$ . In the presence of oxygen the decay kinetics follow a pseudo-first-order rate law ( $k_{\text{ox}} = 2 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ ). A second short-lived transient in 2-propanol and mixtures with acetonitrile is identified as T. Also, EPG (Figure 5b) and CBA exhibit a transient K with properties similar to that of PA (Table IV).

Whether or not T in 100% 2-propanol can be observed depends on the rate constant for quenching by 2-propanol. From the linear dependence of  $k_{\text{obsd}}$  (for T in acetonitrile solution) vs [2-propanol] (up to 1 M) a rate constant for quenching of  $k_q = 1.5 \times 10^6 \text{M}^{-1} \text{s}^{-1}$  was obtained for PA. With ethanol, methanol, and 2-methyl-2-propanol the  $k_q$  values are  $0.8 \times 10^6$ ,  $0.6 \times 10^6$ , and  $\leq 0.2 \times 10^6 \text{M}^{-1} \text{s}^{-1}$ , respectively. The formation of K is in agreement with the lack of phosphorescence for PA in butyronitrile at 25 °C. Addition of water to PA in alcohols reduces  $\Delta A(K)$ . A similar rate constant for quenching by 2-propanol was obtained for EPG in acetonitrile whereas for CBA it is significantly larger than for PA (Table IV).

**Transients in Aqueous Solution.** Essentially two transients were observed by laser flash photolysis of PA (0.1–0.5 mM) in acidic aqueous solution (pH 1.5), a short-lived transient ( $T_{\text{BA}}$ ) and a longer-lived one (probably K) with a low  $\Delta A$  ( $\Delta A(K)/\Delta A(T_{\text{BA}}) \leq 0.1$ ).  $T_{\text{BA}}$  has  $\lambda_{\text{max}} = 342$  nm, decays by first-order kinetics (lifetime 30 ns), and is quenched by oxygen, maleic acid, and 1,3-cyclohexadiene (rate constants  $\geq 1 \times 10^9 \text{M}^{-1} \text{s}^{-1}$ ). If the excited volume ( $0.1 \times 0.1 \times 1 \text{cm}^3$ ) was not exchanged,  $\Delta A(T_{\text{BA}})$  increased on repeated flashing. This indicates that  $T_{\text{BA}}$  originates

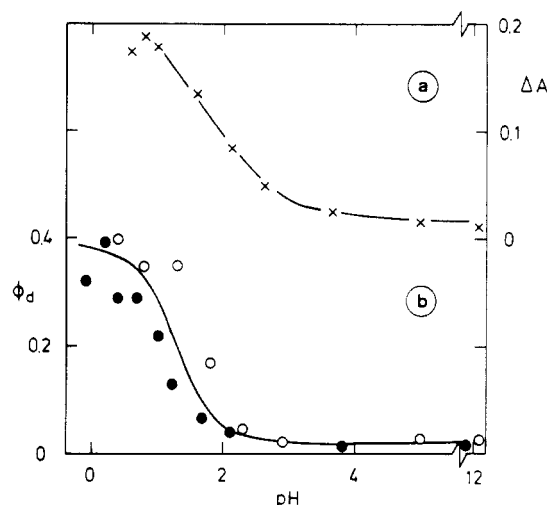


Figure 7. Effect of pH for PA in argon-saturated aqueous solution at 25 °C (a) on the yield of formation of triplet BA ([PA] = 0.3 mM,  $\lambda_{\text{exc}} = 248$  nm) and (b) on  $\Phi_d$  (● and ○ refer to [PA] = 0.1 mM,  $\lambda_{\text{irr}} = 254$  nm and 50 mM, 365 nm, respectively).

from an excited photoproduct rather than from PA itself. On decreasing the pH from 3 to 0.8,  $\Delta A$  (measured at  $\lambda_{\text{max}}$  of  $T_{\text{BA}}$ ) increases (Figure 7); below pH 0.8  $\Delta A$  becomes smaller due to our limited time resolution (20 ns). Practically no transient could be detected at pH 4–10 even at high laser intensity ( $\Delta A(\text{pH } 4)/\Delta A(\text{pH } 1) < 0.1$ ). The reason for its disappearance in the pH range 1–3 is a reduced yield of formation of  $T_{\text{BA}}$  since the lifetime is virtually unchanged.

For CBA in water (pH 4–6) two short-lived transients ( $\lambda_{\text{max}} = 345$  and 700 nm, respectively) and a long-lived transient were detected (Figure 6b). The species with  $\lambda_{\text{max}} \approx 700$  nm is assigned to the hydrated electron; it was identified by the characteristic absorption spectrum and by quenching with  $\text{N}_2\text{O}$  and  $\text{O}_2$ . The formation of the hydrated electron is not surprising since it also appears with BA and several derivatives under comparable conditions.<sup>16</sup> The weak long-lived transient with  $\lambda_{\text{max}} < 310$  nm may be the radical cation of CBA or a radical formed by water addition. The second short-lived transient has already been assigned to a triplet state of CBA.<sup>16</sup>

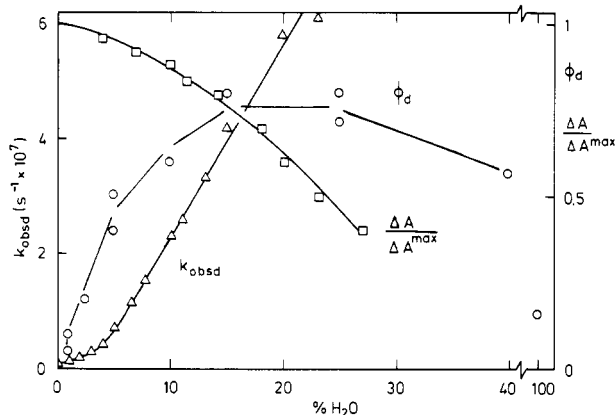
EPG shows a major transient with  $\lambda_{\text{max}} = 320$  nm (Figure 5c) and  $\tau = 300$  ns at pH 1–5 (probably a triplet state<sup>18</sup>) and a long-lived transient ( $\lambda_{\text{max}} < 300$  nm, not identified). At pH 7 and high laser intensities the hydrated electron could be observed, too. The other experiments, especially the conductivity measurements (see below), were carried out at reduced laser intensity where photoionization of the three compounds was negligible.

**Transients in Mixtures with Water.** In view of the recent steady-state decarboxylation measurements,<sup>11</sup> flash photolysis studies were also carried out in acetonitrile/water mixtures. On addition of (neutral) water to PA in acetonitrile the lifetime of T is reduced. However, the ratio  $\tau_T^0/\tau_T$  does not simply show

TABLE V: Triplet Decay Kinetics in the Presence of Water<sup>a</sup>

compd	solvent	$10^{-6}k_{\text{obsd}}, \text{ s}^{-1}, \text{ for } \% \text{ H}_2\text{O}$						$10^{-6}k_{\text{H}_2\text{O}}, \text{ M}^{-1} \text{ s}^{-1}$
		1	2	5	10	15	20	
PA	acetonitrile	0.8	1.2	6	23	42	$\geq 50$	6
PA	acetone <sup>c</sup>	1.5	2.5	10	24	39	$\geq 50$	7
PA	acetic acid	0.05	0.1	0.3	0.9	1.8	3.0	0.6
PA	acetic acid <sup>c</sup>	0.01		0.2	0.7	1.5	2.1	0.6
EPG	acetonitrile	1.7			2		2	<0.1
EPG	acetone <sup>c</sup>	2.2			2.4		2.5	<0.02
CBA	acetonitrile	18	40	<50				50
CBA	acetone <sup>c</sup>	25	60					200
CBA	acetic acid	5	11	34	>50			14

<sup>a</sup> In argon-saturated solution at 25 °C,  $\lambda_{\text{exc}} = 248 \text{ nm}$  and  $[\text{PA}] = 0.3\text{--}0.6 \text{ mM}$  unless indicated otherwise. <sup>b</sup> Obtained from the linear part of  $k_{\text{obsd}}$  vs  $[\text{H}_2\text{O}]$ ; see text. <sup>c</sup>  $\lambda_{\text{exc}} = 353 \text{ nm}$ ;  $[\text{PA}] = 5\text{--}20 \text{ mM}$ .



**Figure 8.** Plots of  $k_{\text{obsd}}$  for triplet decay of PA ( $\Delta$ ),  $\Delta A_{330}$  for triplet formation ( $\square$ , both  $0.3 \text{ mM}$ ,  $\lambda_{\text{exc}} = 248 \text{ nm}$ ), and  $\Phi_d$  ( $\circ$ ,  $[\text{PA}] = 60 \text{ mM}$ , from UV absorption,  $\lambda_{\text{irr}} = 365 \text{ nm}$ ) vs  $[\text{H}_2\text{O}]$  for PA in argon-saturated acetonitrile solution at 25 °C.

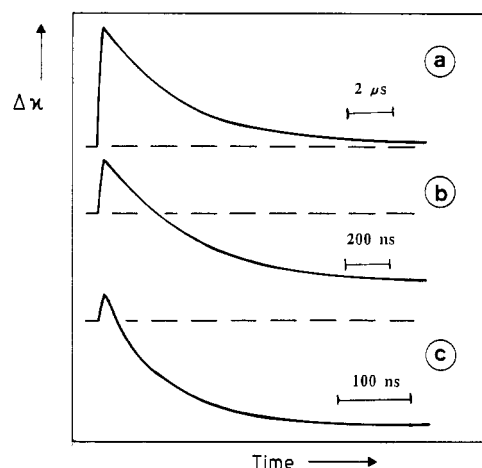
a linear dependence on  $[\text{H}_2\text{O}]$ ;  $k_{\text{obsd}}$  increases only slightly in the 0–2% range, shows a more or less linear dependence on  $[\text{H}_2\text{O}]$  between approximately 4 and 20%, and approaches a maximum (corresponding to a lifetime of about 20 ns) at approximately 30%  $\text{H}_2\text{O}$  (Figure 8 and Table V). (A final decrease of  $k_{\text{obsd}}$  on going to 100%  $\text{H}_2\text{O}$  is due to formation of  $\text{T}_{\text{BA}}$ . However, this transient is difficult to measure since  $\Delta A(\lambda_{\text{max}})$  decreases with increasing  $[\text{H}_2\text{O}]$ .) The rate constant for quenching T by water ( $k_{\text{H}_2\text{O}}$ ), estimated from the linear part (4–20%  $\text{H}_2\text{O}$ ), is  $6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and slightly smaller with  $\text{D}_2\text{O}$  ( $5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ). The corresponding dependence on  $[\text{H}_2\text{O}]$  in acetic acid shows much smaller  $k_{\text{obsd}}$  values and  $k_{\text{H}_2\text{O}} = 0.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (5–30%  $\text{H}_2\text{O}$ ).

With  $\lambda_{\text{exc}} = 353 \text{ nm}$  the initial dependence of  $k_{\text{obsd}}$  vs  $[\text{H}_2\text{O}]$  for PA in acetonitrile is the same as for  $\lambda_{\text{exc}} = 248 \text{ nm}$ , but no maximum could be found;  $k_{\text{obsd}}$  increases monotonously up to the detection limit of about  $5 \times 10^7 \text{ s}^{-1}$ , indicating that  $\text{T}_{\text{BA}}$  is not formed under these conditions. (The reason is the ca. 100-fold larger PA concentration for the longer  $\lambda_{\text{exc}}$  so that the photoproduct is formed only in negligible amount in contrast to  $\lambda_{\text{exc}} = 248 \text{ nm}$ .) The data in acetone (Table V) are similar to those in acetonitrile.

Addition of water to PA in acetonitrile leads not only to the significant kinetic changes but also to a decrease of  $\Delta A(\lambda_{\text{max}})$  (Figure 8). This decrease is due to a reduced yield of formation of T since the measurement was carried out with sufficient time resolution. It was ensured that different water/acetonitrile mixtures did not change the initial population of the excited singlet state of PA (same laser intensity and  $A_{248}$ ). We thus conclude that the precursor of T interacts with water, thereby reducing the yield of T.

For CBA in acetonitrile  $k_{\text{obsd}}$  vs  $[\text{H}_2\text{O}]$  shows some deviation from linearity (at <0.5 M water) and a slope  $k_{\text{H}_2\text{O}} = 5.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , which is much larger than that for PA. A smaller  $k_{\text{H}_2\text{O}}$  value was found in acetic acid, and the largest one was found in acetone (Table V). Addition of water to EPG in acetonitrile has only a small effect on  $k_{\text{obsd}}$ ;  $k_{\text{H}_2\text{O}} < 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

**Transient Conductivity.** For PA (0.1–0.2 mM) in argon-saturated acetonitrile a conductivity increase ( $\Delta\kappa$ ), following the laser



**Figure 9.** Conductivity changes of PA (0.3 mM) in argon-saturated acetonitrile and mixtures with water at 25 °C: (a) 0%, (b) 10%, and (c) 20% water. Note: different scales of  $\Delta\kappa$ .  $\lambda_{\text{exc}} = 248 \text{ nm}$ .

pulse, was observed which approaches the value prior to the pulse within  $10 \mu\text{s}$  (Figure 9a). Addition of water (2–20%) gives rise to four effects: (i) the decay of  $\Delta\kappa$  is accelerated, (ii) the initial increase of the amplitude becomes smaller, (iii)  $\Delta\kappa$  reaches a value which is below that prior to the pulse, i.e., the conductivity after a few 100 ns is reduced, and (iv) this conductivity decrease becomes larger with increasing water concentration (Figure 9b,c). After the initial fast change  $\Delta\kappa$  is constant for more than 1 s. The rate constant for the decay of  $\Delta\kappa$  is  $0.2 \times 10^6$ ,  $0.3 \times 10^6$ ,  $2 \times 10^6$ , and  $10 \times 10^6 \text{ s}^{-1}$  for 0, 5, 10, and 20%  $\text{H}_2\text{O}$ , respectively, i.e., significantly smaller than  $k_{\text{obsd}}$  from the optical measurements (Table V).

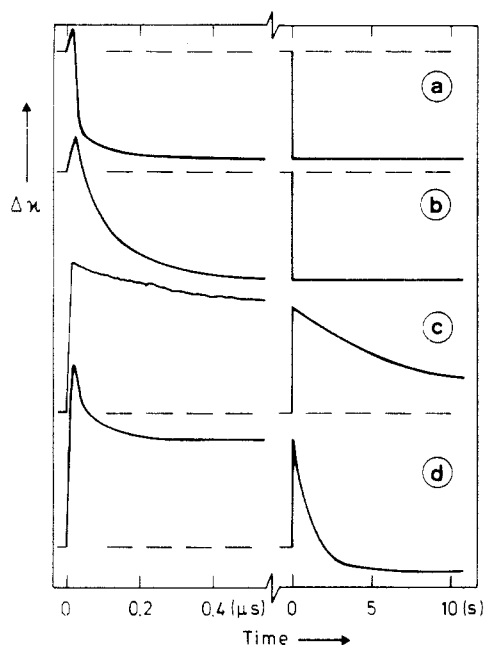
For CBA in acetonitrile we found also a substantial increase in  $\Delta\kappa$  at the end of the laser pulse; its decay occurs within a few microseconds. However, in mixtures with water the signal does not approach a value smaller than the initial one, in contrast to the case of PA. The amplitudes of the conductivity signals of CBA (in the 0.01–1-ms range) and of EPG (even after the pulse) are significantly smaller than those of PA.

For PA in aqueous solution at pH 3  $\Delta\kappa$  at first slightly increases during the laser pulse, then decreases below the initial amplitude within 100 ns ( $t_{1/2} < 50 \text{ ns}$ ), and remains constant for seconds (Figure 10a). On increasing the pH the decrease of  $\Delta\kappa$  becomes slower, corresponding to  $t_{1/2} \approx 100 \text{ ns}$  at pH 4 (Figure 10b) and  $\approx 1 \mu\text{s}$  at pH 5. When the pH was changed from 5 to 6, the conductivity change was converted from a decrease into an increase. At pH 6  $\Delta\kappa$  increases within the pulse width, decreases partly within  $0.5 \mu\text{s}$ , and remains constant in the microsecond and millisecond range; it then decreases very slowly, thereby approaching the initial value within seconds (Figure 10c). In the more basic range the time dependence of  $\Delta\kappa$  remains virtually unchanged between  $0.1 \mu\text{s}$  and 10 ms, but the decay at longer times becomes significantly faster. The rate constant for the decay of  $\Delta\kappa$  is approximately 1, 10, and  $90 \text{ s}^{-1}$  at pH 10, 11, and 12, respectively. In addition,  $\Delta\kappa$  reaches an amplitude value which is smaller than that prior to the pulse (Figure 10d).

TABLE VI: Quantum Yield of Decarboxylation in Mixtures with Water<sup>a</sup>

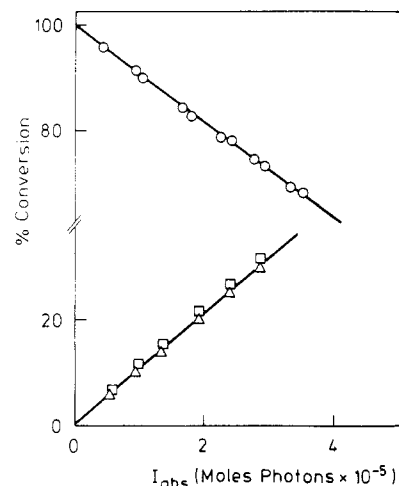
compd	concn, mM	solvent	$\lambda_{\text{irr}}$ , nm	$\Phi_d$ for vol % H <sub>2</sub> O				
				1.0	2.5	5	10	25
PA	50	acetonitrile <sup>b</sup>	365	0.05	0.21	0.51		0.72
PA	50	acetonitrile	365	0.1	0.2	0.4	0.6	0.8 <sup>c</sup>
PA	50	acetonitrile	365					(0.8) <sup>d</sup>
PA	50	acetonitrile	254					0.62 <sup>b</sup>
PA	50	acetonitrile	313					0.81 <sup>b</sup>
PA	1	acetonitrile	313				(0.66)	(0.6)
PA	0.1	acetonitrile	254	0.15	0.25	0.54		
PA	50	acetone	365	0.1	0.15	0.5	0.6	0.70 <sup>b</sup>
PA	50	acetone	365				(0.7)	(0.6)
PA	50	acetic acid	365	0.02	0.04	0.08	0.15	0.5
PA	1	acetic acid	313			(0.3)		(0.5)
EPG	50	acetonitrile	365			(0.01)	(0.03)	
CBA	2	acetonitrile	313					<0.05
CBA	2	acetonitrile	313					(<0.02)

<sup>a</sup>In argon-saturated solution at 25 °C; values obtained from absorption changes unless indicated otherwise. <sup>b</sup>Taken from ref 11. <sup>c</sup>The same value in air-saturated solution. <sup>d</sup>Values in parentheses refer to CO<sub>2</sub> measurements.



**Figure 10.** Conductivity changes of PA (0.3 mM) in argon-saturated aqueous solution at 25 °C,  $\lambda_{\text{exc}} = 248$  nm, using (a) pH 3, (b) pH 4, (c) pH 6, and (d) pH 10. Note: different scales of  $\Delta\kappa$ . Left and right sides refer to the fast (dc) and slow (ac) conductivity setups, respectively.

**Continuous Irradiation.** The simultaneous analytical monitoring of the photochemical decomposition of PA in a CH<sub>3</sub>CN/H<sub>2</sub>O mixture and the formation of CO<sub>2</sub> and BA is shown in Figure 11. BA and CO<sub>2</sub> are formed in equal amounts as PA decomposes. However, in acetonitrile or acetone in the absence of water,  $\Phi_d$ , as obtained from formation of CO<sub>2</sub>, is larger than  $\Phi_d$ , as obtained UV spectroscopically from the decomposition of PA (Table VI). This discrepancy is essentially not a concentration effect and was also found in acetonitrile or acetone in the presence of small amounts of water (up to 5%). It points to the possibility of unknown free-radical products formed by  $\alpha$ -cleavage which may play a minor role. Indeed, in dry acetonitrile benzil is formed besides unidentified trace compounds as established by GC and HPLC analysis. Virtually no solvent isotope effect was found with PA for the yields of either decrease of PA or formation of BA in acetonitrile/(heavy) water, 3:1.<sup>11</sup> Water effects cannot be mimicked by alcohols or acids (*p*-toluenesulfonic acid, acetic acid). The effect of pH on  $\Phi_d$  (Figure 7b) has already been reported for PA.<sup>11</sup>  $\Phi_d$  is approximately 0.3 at pH 0.4–1.3 and it drops to  $\approx 0.02$  at pH >2; i.e., for the acid  $\Phi_d$  is more than 10 times larger than for the anion. Preliminary measurements at pH 3–6 under acetone-sensitized conditions (313 nm, 90% water) indicate a more than 4-fold increase in  $\Phi_d$  (CO<sub>2</sub>, GC).



**Figure 11.** Percentage of conversion of PA (O, 50 mM) into CO<sub>2</sub> (□) and BA (Δ) as a function of the number of absorbed light quanta in argon-saturated CH<sub>3</sub>CN/H<sub>2</sub>O (3:1 vol) at 25 °C,  $\lambda_{\text{irr}} = 365$  nm.

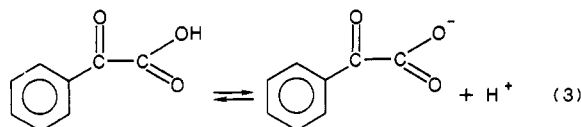
An increase of  $\Phi_d$  vs [H<sub>2</sub>O] (up to ca. 25%) was found for PA in both acetonitrile (Figure 8) and acetone, but a significantly smaller increase was found in acetic acid (Table VI). The slope of this quasi-linear dependence (relative values 0.8, 1.0, and 0.2, respectively) is taken as a measure for the reactivity toward decarboxylation and may be compared with  $k_{\text{H}_2\text{O}}$ , the reactivity of the triplet with water (Table V). Within the range 0.25–0.0125 M in CH<sub>3</sub>CN/H<sub>2</sub>O (3:1)  $\Phi_d$  equals  $0.75 \pm 0.05$  (365 nm; UV analysis).<sup>11</sup> Also, for 5–50% water in acetonitrile  $\Phi_d$  is essentially independent of the PA concentration in the range 0.1–50 mM (Table VI). Similar  $\Phi_d$  values in argon and air-saturated water-containing solution under certain conditions (e.g., 365 nm, UV analysis, 5 mM, 25% water) indicate that reactions with oxygen are not important.

For EPG (50 mM) in neat acetonitrile, ethyl mandelate and BA were identified by GC as major photoproducts (365 nm), besides ethyl benzoate, acetaldehyde, benzil, benzoin, and ethane, but CO<sub>2</sub> (and CO) were not detected in substantial amounts. Ethyl mandelate and BA predominate also in CH<sub>3</sub>CN/H<sub>2</sub>O (3:1; pH  $\approx 7$  as well as pH 1.1). The quantum yield of decomposition of EPG, estimated from UV and GC, is about 0.3 in the presence of 25% water and is also substantial in neat acetonitrile (0.07, GC;  $\Phi_{\text{initial}} \approx 0.25$ , UV). The above product distribution resembles that observed formerly for EPG in benzene;<sup>17</sup> cf. ref 6a.

For CBA (50 mM) in CH<sub>3</sub>CN/H<sub>2</sub>O (3:1) no significant change in the long-wavelength absorption was observed on prolonged irradiation at 365 nm; the CO<sub>2</sub> formation was within the blind range, nor was any product detected by HPLC. This is in agreement with  $\Phi_d$  measurements at smaller concentrations (Table VI).

## Discussion

**Effects of Solvent and pH on the Ground State.** In solvents of moderate polarity, such as dichloromethane, the intramolecularly chelated trans conformer of PA (referring to the carbonyl groups) prevails.<sup>20,21</sup> In polar solvents (e.g., acetonitrile, ethanol) the intramolecular H-bonds are destroyed and 1:1 solvent complexes are present.<sup>21</sup> Vaporimetric molecular weight determinations show that PA forms dimers in benzene but is monomeric in methanol, acetone, or water and probably also in acetonitrile (see Experimental Section). The absorption spectrum of PA in aqueous solution exhibits a decrease of the long-wavelength band near 310 nm with increasing pH (inset of Figure 1). This results from the acid-base equilibrium (eq 3). The thus obtained  $pK_a$



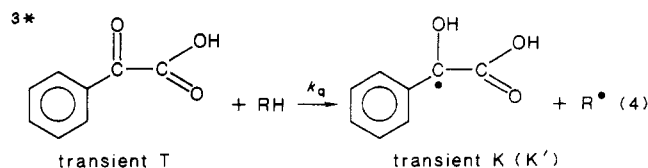
value of 1.1 is comparable with a published one ( $pK_a = 1.39$ ).<sup>22</sup> A hydrate of PA seems to appear only at  $pH \ll 1$ .<sup>23</sup> For comparison, the  $pK_a$  value of CBA is 3.6. In neat acetonitrile (Figure 1), acetone, and acetic acid PA should be present as acid. This is in line with the absorption spectra which indicate the increasing contribution of the anion with increasing water content in mixtures with acetonitrile.

**Phosphorescence.** Leermakers and Vesley have observed the phosphorescence of PA at  $-196^\circ C$  and proposed that the emitting triplet is of  $n, \pi^*$  character.<sup>2</sup> The emission around 450–550 nm (Figure 1 and Table I) which we measured for PA in acetonitrile, acetone, and acetic acid at room temperature is also attributed to phosphorescence on the following basis. First, the spectral range excludes that the emission originates from the first excited singlet state. Also the lifetime ( $\tau_p \geq 10 \mu s$  for PA; Table II) is too long to be compatible with fluorescence. Second, in glasses of ethanol, butyronitrile, and ethylene glycol/water at  $-196^\circ C$ , i.e., under conditions where H-abstraction is strongly retarded, the emission is obviously phosphorescence. Third, the triplet is quenched by oxygen and 1,3-cyclohexadiene. Phosphorescence quenching measurements ( $I_p$  and  $\tau_p$ ) with alcohols correspond with the  $n, \pi^*$  nature of the emitting triplet of PA (Table II). The first maximum of the phosphorescence bands of PA, EPG, and CBA corresponds to energies of approximately 62, 63, and 69 kcal/mol, respectively.

**Assignment of the Transients.** Transient T, observed with PA in acetonitrile at room temperature, is assigned to the lowest triplet state. First, T is quenched by oxygen and 1,3-cyclohexadiene; for the latter the rate constant reaches practically the diffusion-controlled limit (Table III). Second, T can also be generated by xanthone-sensitized excitation although its observation is limited to the wavelength range above 360 nm. Third, similar lifetimes were obtained from the phosphorescence of PA and the absorption of T (compare Tables II and III). Finally,  $\tau_T$  and  $\tau_p$  are reduced by additives in a similar manner (see below). The question, whether T can only be assigned to the triplet of the acid ( $^3Ph-CO-COOH$ ) or also to that of the anion ( $^3Ph-CO-COO^-$ ) is discussed below. The major transients of CBA<sup>16</sup> and EPG<sup>18</sup> have already been assigned to triplet states.

The long-lived transient K, observed with the maximum  $\Delta A$  in several alcohols, is assigned to the  $\alpha$ -carboxy- $\alpha$ -hydroxybenzyl (ketyl) radical. This radical has been observed by ESR,<sup>4</sup> and the detection by flash photolysis is plausible since (i) it is formed during the triplet decay, (ii) it decays by second-order kinetics, showing half-lives up to 0.2 ms under our conditions (Table IV), and (iii) it is quenched by oxygen. In acetonitrile/2-propanol

mixtures the initially formed triplet is quenched according to eq 4. The rate constant (e.g.,  $k_q = 1.5 \times 10^6 M^{-1} s^{-1}$  for quenching



of triplet PA by 2-propanol) is of a size comparable to that for triplet quenching of aromatic ketones and aldehydes.<sup>16,24–26</sup> As expected from the latter cases, the rate constant for H-atom abstraction decreases for PA in the order 2-propanol, ethanol, and methanol in 2-methyl-2-propanol  $k_q$  is smallest but virtually no radical is formed (Table IV). The rate constant for the bimolecular decay of the  $\alpha$ -carboxy- $\alpha$ -hydroxybenzyl radical is  $3.8 \times 10^8 M^{-1} s^{-1}$ , and the main photoproduct is 2,3-diphenyltartaric acid.<sup>4,11</sup> For EPG and CBA<sup>16</sup> K is analogously assigned to the carboxyhydroxybenzyl radical.

The triplet of PA in acetonitrile decays essentially by phosphorescence and possibly also by radiationless intersystem crossing. Quenching by impurities (e.g., traces of oxygen) and self-quenching (which may also lead to K) play probably only a minor role (for  $[PA] < 1$  mM) while T–T annihilation occurs at higher pulse intensities. In a manner similar to the case of benzophenone,<sup>26</sup> H-atom abstraction of triplet PA from  $CH_3CN$  in low yield is indicated by the  $\Delta A(K')$  value. For comparison, the  $Ph-CO-COOH$  radical is the main transient in butyronitrile (Table IV). H-atom abstraction from the carboxyl group, as a further possibility for formation of K, is considered to be unlikely since  $K'$  was also observed for CBA where this reaction cannot occur due to steric reasons. Nevertheless, H-atom abstraction from the carboxyl group of PA cannot be completely excluded.

The deactivation steps of excited PA ( $R_1 = H$ ) and EPG ( $R_1 = C_2H_5$ ) in organic solvents are illustrated in Scheme I. For both compounds the effects of quenching by oxygen and 1,3-cyclohexadiene in "inert" solvents are similar and H-atom abstraction from alcohols is important. A similar behavior has been reported for BA<sup>16</sup> and is proposed for CBA. In the absence of water formation of free radicals via  $\alpha$ -splitting is conceivable<sup>5</sup> for PA but is still an open question. While triplet quenching by water is not significant for EPG, this effect is discussed below in more detail for PA.

**Formation of the Triplet State of Benzaldehyde.** Transient  $T_{BA}$ , observed for PA in aqueous solution at low pH (see Results), is assigned to a triplet state since it is quenched by oxygen, maleic acid, and 1,3-cyclohexadiene (see Results). Three possibilities may be considered: (i)  $T_{BA}$  is the triplet of the acid ( $^3Ph-CO-COOH$ ), (ii)  $T_{BA}$  is the triplet state of benzaldehyde ( $^3BA$ ) formed by monophotonic excitation and decarboxylation of triplet PA, and (iii)  $T_{BA}$  is  $^3BA$  formed by consecutive absorption of two photons. In case (iii) decarboxylation of PA may rapidly lead to ground-state BA (eq 1) and the observed triplet is then formed upon absorption of a second photon by BA.

Possibility (i) is excluded since  $\Delta A(T_{BA})$  increases on repeated flashing of the same solution. Under these conditions the concentration of ground-state BA increases correspondingly. Furthermore, the properties of  $T_{BA}$  (absorption spectrum, lifetime) are similar to those of  $^3BA$ .<sup>16</sup> Possibility (ii) is unlikely for energetic reasons. The triplet energies of BA and PA in nonaqueous solvents are 72 kcal/mol<sup>16</sup> and approximately 62 kcal/mol, respectively. A difference of about 10 kcal/mol is also expected if the levels of the  $^3(n, \pi^*)$  states are shifted in water to higher values. We therefore surmise that the decarboxylation occurs in a time shorter than 10 ns since otherwise the triplet state of PA should have been detected. Possibility (iii), i.e., formation of  $^3BA$

(20) (a) Oehme, G.; Fischer, G.; Schellenberger, A. *Chem. Ber.* **1967**, *100*, 425. (b) Fischer, G.; Oehme, G.; Schellenberger, A. *Tetrahedron* **1971**, *27*, 5683. (c) Rindt, A.; Schellenberger, A.; Oehme, G.; Pinske, R. *Tetrahedron* **1973**, *29*, 3051.

(21) Hirota, M.; Shinozaki, F. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 2614.

(22) Wheatley, M. S. *Experientia* **1956**, *12*, 339.

(23) Shinkai, S.; Hamada, H.; Kusano, Y.; Manabe, O. *Tetrahedron Lett.* **1979**, 3511.

(24) Scaiano, J. C. *J. Photochem.* **1973/74**, *2*, 81.

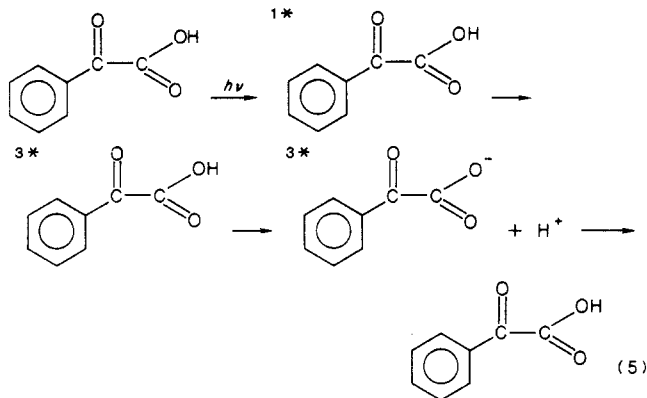
(25) Bensasson, R. V.; Gramain, J.-C. *J. Chem. Soc., Faraday Trans 1* **1980**, *76*, 1801.

(26) Naguib, Y. M. A.; Steel, C.; Cohen, S. G.; Young, M. A. *J. Phys. Chem.* **1987**, *91*, 3033.



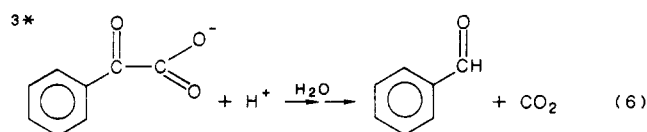
via two consecutive absorption steps, is supported by the similarity of the pH dependences of  $\Phi_d^{11}$  and  $\Delta A(T_{BA})$  (Figure 7).

**Formation and Decay of Conducting Species.** The conductivity results in acetonitrile/water mixtures may be interpreted as follows. For PA in neat acetonitrile the increase of  $\Delta\kappa$ , concomitant with the laser pulse, and the decay to the initial value (Figure 9a) suggest that no longer lived charged species are formed. As intermediate species (lifetime  $\leq 5 \mu\text{s}$ ) we propose the strongly conducting  $\text{H}^+$  ion and the triplet state of the anion which is formed by fast deprotonation of the triplet acid (Scheme I). The conductivity results in the absence of water (assuming  $\Phi_{\text{isc}} = 1$ ) are described by reaction 5 (working hypothesis). The recovery

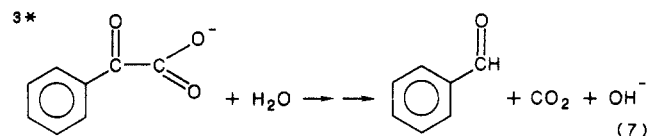


from the conductivity increase in the absence of water is explained by intersystem crossing of  $3^*\text{Ph-COCOO}^-$  into the ground state and fast subsequent protonation. A second possibility which we could not experimentally distinguish from the triplet reaction may be proton formation from the  $1^*\text{Ph-COCOOH}$  state. Photoionization, an alternative explanation for the formation of conducting intermediates, is excluded on the basis of transient absorption measurements (no hydrated electron in water under comparable conditions).

On addition of water the degree of dissociation of ground-state PA increases and the reduction in  $\Delta\kappa$  after decay of the conductivity signal (Figure 6b,c) could be described by the overall reaction 6.



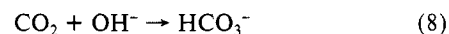
Alternatively, quenching of the triplet anion by water may lead to decarboxylation and  $\text{OH}^-$  formation (eq 7, overall reaction).



In the latter case the decay of  $\Delta\kappa$  represents that of  $\text{OH}^-$  via neutralization. Reaction 7 is suggested to occur in water at  $\text{pH} > 1$  (see below) and should also be favored in mixtures with acetonitrile. In 20% water, for example, the neutralization reaction occurs within 100 ns (Figure 9c). The initial increase in  $\Delta\kappa$ , the amplitude of which decreases with increasing water concentration, may be due to a contribution to  $\Delta\kappa$  by release of  $\text{H}^+$  according to eq 5.

Reaction 7 followed by ion recombination accounts also for the results in water at  $\text{pH} 2-5$  (compare Figure 9c with Figure 10a,b). The decrease in  $\Delta\kappa$  is faster than  $1 \mu\text{s}$  and remains constant for several seconds. At  $\text{pH} 6-10$ , however,  $\Delta\kappa$  increases within the laser pulse, decreases partly, and remains constant for milliseconds or longer, depending on  $\text{pH}$  (Figure 10c,d). This fast increase is, at least in part, due to formation of  $\text{OH}^-$  according to reaction 7. Ion recombination may account for the minor conductivity change during the first 500 ns in the  $\text{pH}$  range 6-10.

The major decrease in  $\Delta\kappa$  within seconds is due to the formation of bicarbonate which has a smaller equivalent conductivity than  $\text{OH}^-$  (reaction 8).<sup>27,28</sup> The rate constant for reaction 8 is 6300



$\text{M}^{-1} \text{s}^{-1}$ .<sup>28</sup> Indeed, the results at  $\text{pH} 10-12$  are in good agreement with this expectation. One could argue that reaction 8 should occur at  $\text{pH} 6-9$  with a lifetime of greater than 1s, i.e., longer than found experimentally (Figure 10c). However, this discrepancy can be explained by the fact that  $\text{OH}^-$  ions are also produced by the laser pulse via reaction 7. (Unfortunately, the strongly acidic range ( $\text{pH} < 2$ ) is not accessible with our conductivity setup).

**Photochemical Reactions in Water/Acetonitrile Mixtures.** The remarkable dependence of  $k_{\text{obsd}}$  (triplet decay),  $\tau_p^{-1}$ , and  $I_p^{-1}$  on  $[\text{H}_2\text{O}]$  for PA in acetonitrile (Figures 2, 3, and 8, Tables II and V) may be interpreted as follows. In the absence of water the observed triplet has probably  $n, \pi^*$  character.<sup>2</sup> Since  $k_{\text{obsd}}$  increases only slightly in the presence of a small amount of water ( $< 0.5 \text{ M}$ ), we propose solvation but virtually no triplet quenching by a single water molecule. The almost linear dependence of  $k_{\text{obsd}}$  vs  $[\text{H}_2\text{O}]$  in the 0.5-10 M range indicates a medium effect.

Supposing that in acetonitrile PA is present as acid, the addition of water should increase the amount of the anion by a shift of the ground-state equilibrium in Scheme II toward the right side. We presume that the T-T absorption spectra of the acid and the anion are similar and undistinguishable with our means. In competition to intersystem crossing a quenching step of  $3^*\text{Ph-COCOO}^-$  by water has to be postulated (Figure 8 and Table V). We consider a water-assisted fission of the C-C bond. This may be induced either by hydrogen bonding to the carbonyl group or by increasing the  $\pi, \pi^*$  character of the reactive triplet in the presence of water, as found for other ketones.<sup>29,30</sup> As short-lived intermediate we consider either the benzoate anion<sup>31</sup> or its protonated mesomer. We are not able to distinguish between these two species and, for simplicity, use  $(\text{Ph-CO})^-$ ; see Scheme II. In both cases the rate-determining step for  $\Delta\kappa$  is the neutralization reaction.

The comparison of the plots of  $k_{\text{obsd}}$  and  $\Phi_d$  vs  $[\text{H}_2\text{O}]$  (Figure 8 and Tables V and VI) indicates a branching leading from  $3^*\text{Ph-COCOO}^-$  into BA and ground-state  $\text{Ph-COCOO}^-$ . In the presence of 5% water, for example, about 90% of the molecules are quenched by water but  $\Phi_d$  has reached only 50% of its maximum value. The branching may occur either directly from  $3^*\text{Ph-COCOO}^-$  or from  $(\text{Ph-CO})^-$  and should favor  $\text{Ph-COCOO}^-$  for small water concentration. At higher water content (25-50%) the lifetime of the initially formed triplet is shorter than 20 ns whereas the time required for ion recombination is still longer than 30 ns (Figure 9c). The only transient observed under these conditions, if photoionization is avoided, is  $3^*\text{BA}$ , the excited photoproduct.

The question remains as to why  $\Phi_d$  decreases on going from 20 to 100% water (Figure 8).<sup>11</sup> According to Scheme II one would expect a maximum in formation of  $1^*\text{Ph-COCOO}^-$  in neat aqueous solution at  $\text{pH} > \text{p}K_a$  and also for  $\Phi_d$ . Obviously, the latter is not the case since  $\Phi_d$  is only about 10% of the value at  $\text{pH} 0-1$  (Figure 7b). Therefore, a further process is involved. One possibility could be a lowering of the reactivity of the reactive triplet due to an enhanced contribution of the  $\pi, \pi^*$  triplet with increasing water content. A second possibility, a deactivation step of  $1^*\text{Ph-COCOO}^-$  (probably into the ground state) competing with intersystem crossing into the reactive triplet, is suggested from an extrapolation of the triplet yield in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  mixtures

(27) Kern, D. M. *J. Chem. Educ.* **1960**, *37*, 14.

(28) Schuchmann, M. N.; Sonntag, C. v. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1184.

(29) Ledger, M. B.; Porter, G. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 539.

(30) Lutz, H.; Br  h  ret, E.; Lindqvist, L. *J. Phys. Chem.* **1973**, *77*, 1758.

(31) Chandrasekhar, J.; Andrade, J. G.; Rague Schleyer, P. v. *J. Am. Chem. Soc.* **1981**, *103*, 5612.

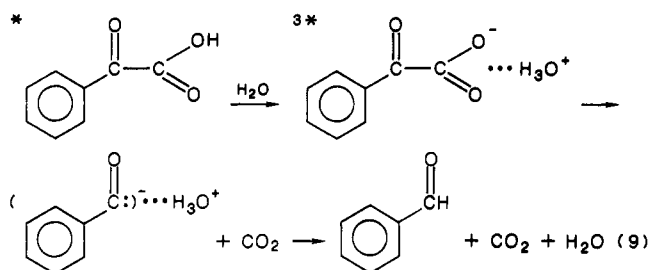
to neat aqueous solution (Figure 8). This indicates that there should be a water-assisted-quenching step which reduces the yield of the observable triplet. Reduction of  $\Phi_{isc}$  of the anion is not unusual,<sup>32</sup> but for PA the reason is not known.

Oxygen has only little effect on  $\Phi_d$  in mixtures of an "inert" solvent with water (Table VI). This is readily explained by the proposed mechanism since triplet quenching by oxygen cannot successfully compete with the reaction involving water. In argon-saturated acetone, acetonitrile, and acetic acid solutions the water content that is necessary to quench the triplet as efficiently as oxygen in air-saturated (water-free) solutions is approximately 1, 2, and 15 M, respectively.

Bearing in mind that the quantum yield of the H/D exchange of BA in acetonitrile shows a similar dependence on  $[H_2O]$  as  $\Phi_d$  for PA (ref 16 and Figure 8 of this work), one could suppose the same reason for the maximum in both cases. However, this is not the case. Water is necessary for formation of an intermediate from  $^3BA$  (carbene or zwitterionic species), and the smaller quantum yield in neat aqueous solution is ascribed to a lower reactivity of triplet BA, whereas the yield remains constant.<sup>16</sup> For PA again water is required for the reaction but the smaller  $\Phi_d$  value in water at pH > 1.1 is due to the reduced  $\Phi_{isc}$  of the anion.

**Photochemical Reactions in Aqueous Solution.** The finding that no triplet of PA could be detected by nanosecond laser flash photolysis in aqueous solution at room temperature agrees with the lack of phosphorescence. Excitation of the acid at pH < 2 yields only the triplet state of BA ( $T_{BA}$ ) but no transient that could be assigned to  $^3Ph-COCOOH$ . Two possibilities arise: either the triplet of PA is not populated under these conditions or its lifetime is so short that it escapes our observation. The latter is indicated by the marked reduction of the triplet lifetime on addition of water in acetonitrile (Figures 3 and 8).

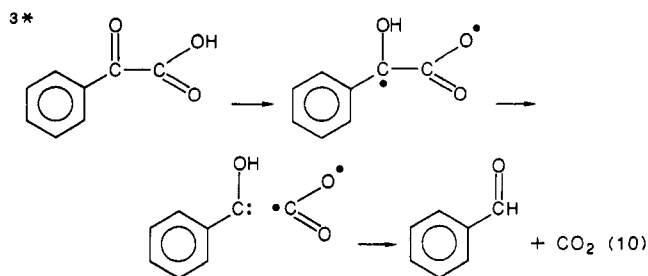
The significant pH effect on  $\Phi_d$  (Figure 7b)<sup>11</sup> originates from the ground-state equilibrium (eq 3). As a decarboxylation mechanism accounting for the results in aqueous solution at pH  $\leq pK_a$  we propose reaction 9, which involves a deprotonation of



excited PA (singlet or triplet) at the carboxyl group. Subsequent decarboxylation goes along with generation of  $(Ph-CO)^{\cdot-}$  which forms BA by reaction with water or by addition of  $H^+$ . For the decarboxylation of the anion at pH >  $pK_a$  we propose an analogous mechanism Scheme II. Together with the proposed reduction of  $\Phi_{isc}$  for the anion, these heterolytic  $\alpha$ -splitting reactions are in line with the observed pH dependence of  $\Phi_d$  (Figure 7b).<sup>11</sup> Scheme II is further supported by the increase in  $\Phi_d$  on acetone-sensitized excitation of the anion. Other possibilities which are excluded or less likely are the following:

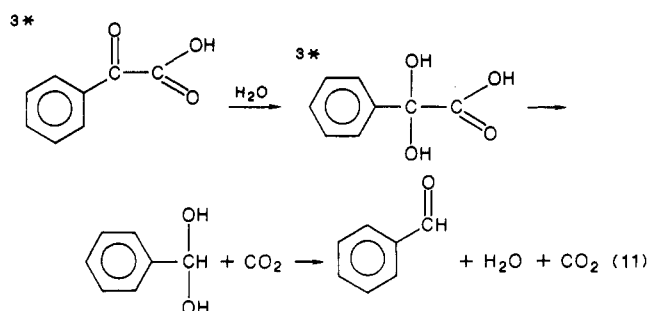
Possibility I is splitting of the C-C bond according to eq 2 as proposed for pyruvic acid<sup>6</sup> and other aliphatic  $\alpha$ -oxocarboxylic acids.<sup>33</sup> It may account for the observations with PA in the absence of water (Scheme I). ESR experiments, however, gave no indication for formation of the free  $Ph-CO^{\cdot}$  radical in the presence of water.<sup>33d</sup>

Possibility II is a fast 1,4-H transfer from carboxyl OH to the carbonyl group followed by a fast splitting of the C-C bond.



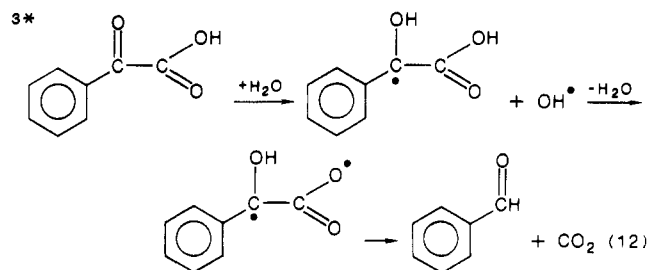
For pyruvic acid this possibility has already been visualized (triplet carbene mechanism).<sup>3a</sup> Then the question arises as to why reaction 10 does not occur in non-aqueous solvents. This may be understandable if the 1,4-H transfer would only occur from a  $\pi, \pi^*$  triplet and if the gap between the lowest  $n, \pi^*$  and  $\pi, \pi^*$  triplets decreases on increasing the solvent polarity. Such a level shift, which should be most pronounced for water, has been reported for excited ketones (e.g., benzophenone, acetophenone).<sup>29,30</sup> The blue shift of the phosphorescence spectrum of PA at  $-196^\circ C$  in the presence of water (Table I) would agree with this expectation but ethanol has an effect similar to that of water.

Possibility III is formation of the hydrate (eq 11) which may



lose  $CO_2$  and form BA by subsequent water elimination. This may be excluded for energetic reasons since the triplet energy of the excited hydrate is probably much larger than the available 62 kcal/mol.

Possibility IV involves H-atom abstraction by triplet PA from water. The remaining OH radical may abstract another H-atom from the carboxyl group, and the intermediate biradical leads to decarboxylation and via a 1,2-H shift finally to BA.



For benzophenone in aqueous solution an analogous formation of the OH radical has been considered<sup>25,29</sup> but has recently been excluded.<sup>34</sup> Equation 12 is difficult to reconcile with the high  $\Phi_d$  values and the pH effect. Possibilities I-IV do not agree with the results from transient conductivity.

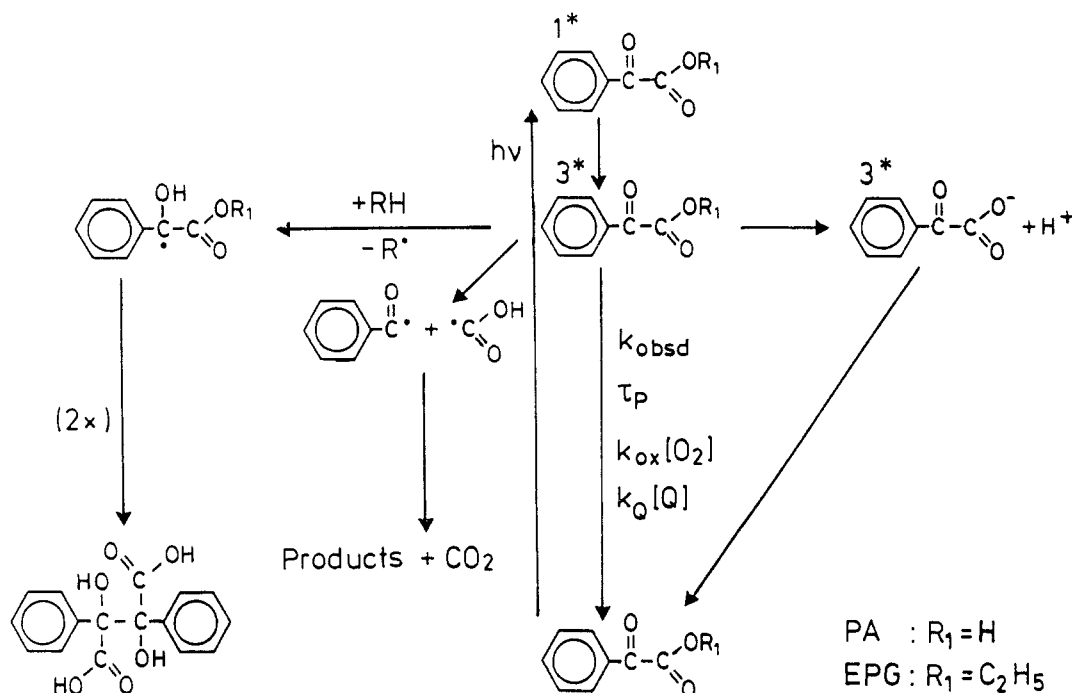
As already mentioned, the effect of water in the photodecarboxylation of PA is reminiscent of that in the photo-deuteriation of BA.<sup>15,16</sup> For this H/D exchange involvement of a zwitterionic intermediate or a 1,2-H shift into a carbene has been proposed.<sup>16</sup> The quenching step of the CBA triplet by water may also be ascribed to this mechanism. With CBA decarboxylation plays practically no role (Table VI). Concerning the

(32) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131. (b) Donckt, E. V.; Porter, G. *Trans. Faraday Soc.* **1968**, *64*, 3218.

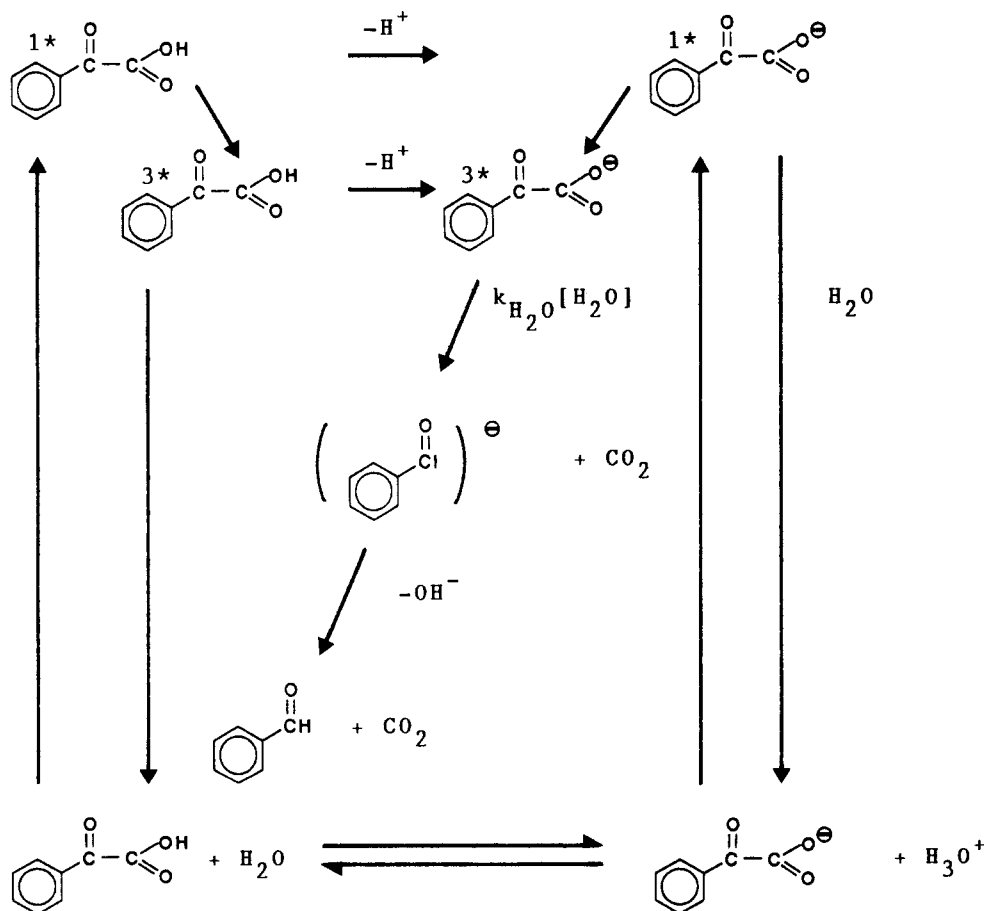
(33) (a) Steenken, S.; Schulte-Frohlinde, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 254. (b) Steenken, S.; Sprague, E. D.; Schulte-Frohlinde, D. *Photochem. Photobiol.* **1975**, *22*, 19. (c) Steenken, S.; Lyda, M. J. *J. Phys. Chem.* **1977**, *81*, 2201. (d) Steenken, S., private communication.

(34) Lougnot, D. J.; Jacques, P.; Fouassier, J. P.; Casal, H. L.; Kim-Thuan, N.; Scaiano, J. C. *Can. J. Chem.* **1985**, *63*, 3001.

SCHEME I: Photoreactions of PA in Organic Solvents (Deprotonation via the Triplet Not Unequivocally Established)



SCHEME II: Photoreactions of PA in Acetonitrile/Water Mixtures (Multiplicity of the Deprotonating State Not Unequivocally Established)



formation of  $\alpha$ -hydroxybenzyl radicals as intermediates in the photoreduction, water has a protecting effect for both PA and CBA but not for EPG.

**Conclusion.** The triplet of PA is characterized by results from time-resolved and steady-state phosphorescence and T-T absorption measurements. It forms the Ph-C(OH)-COOH radical by H-atom abstraction from alcohols and in reduced yield even from "inert" solvents. Water is an environment that strongly

enhances the quantum yield of photodecarboxylation of PA. The increase of  $\Phi_d$  on addition of water to acetonitrile is due to a reaction of triplet PA with water. The maximum in the dependence of  $\Phi_d$  vs  $[H_2O]$  is ascribed to a decreasing efficiency for population of the reactive triplet. In a case like the present where neat aqueous solution proves to be unsuitable for observing transients by ns flash photolysis, the method of mixing with an "inert" solvent, such as acetonitrile, provides a means of extrap-

olation from a well-established to a nonmeasurable case.

**Acknowledgment.** We thank Professors D. Schulte-Frohlinde and K. Schaffner and Dr. G. Koltzenburg for their support and D. Krefit, C. Hüsken, and L. J. Currell for able technical assistance.

**Registry No.** PA, 611-73-4; EPG, 1603-79-8; CBA, 619-66-9; BA, 100-52-7; EtOH, 64-17-5; O<sub>2</sub>, 7782-44-7; H<sub>2</sub>O, 7732-18-5; 2-methyl-2-propanol, 75-65-0; methanol, 67-56-1; 2-propanol, 67-63-0; 1,3-cyclohexadiene, 592-57-4; acetic acid, 64-19-7;  $\alpha$ -carboxy- $\alpha$ -hydroxybenzyl radical, 36877-89-1.

## Properties of Atoms in Molecules: Dipole Moments and Substituent Effects in Ethyl and Carbonyl Compounds

Tom Slee, Annie Larouche, and Richard F. W. Bader\*

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1  
(Received: December 1, 1987)

The theory of atoms in molecules is used to analyze ab initio electron distributions for series of simple ethyl and formyl derivatives. The dipole moments of these molecules are decomposed into their unique charge-transfer and atomic polarization contributions, as defined by the theory. It is shown how atomic charges are related by quantum mechanics to the observable dipole moments of molecules. Substituent effects on atomic charges and hence on dipole moments are described. An analysis of the atomic populations shows that the calculated behavior of substituents on the electron density of the formyl and ethyl groups is in accord with the predictions of qualitative orbital models, employing a separation of  $\sigma$  and  $\pi$  substituent effects. This paper thus gives quantitative expression to those models, by using a theory with a firm quantum mechanical basis. It is suggested that substituent constants can be extracted from the theory of atoms in molecules in an empirical manner. Substituents affect the atomic charges in ethyl and formyl derivatives in contrasting ways, and a perturbation model of changes to the electron density is used to explain this different behavior.

### Introduction

The theory of atoms in molecules defines the average value of every mechanical property for each atom in a molecule and gives the molecular average of each property as a sum of atomic contributions. The definitions of an atom in a molecule, of the average value of its properties, and of their equations of motion are all obtained through a generalization of quantum mechanics to a subsystem of a total system.<sup>1,2</sup> This generalization is unique, as it applies only to regions of real space that satisfy a particular variational constraint, one that is satisfied if the subsystem is bounded by a surface of zero flux in the gradient vector of the charge density:

$$\nabla\rho\cdot\mathbf{n} = 0 \quad \text{for every point on the surface} \quad (1)$$

The quantum boundary condition (eq 1) yields a partitioning of the real space of a molecule into a set of nonoverlapping mononuclear regions, or *atoms*, because of the principal topological property of a many-electron charge distribution—that it generally exhibits local maxima only at the positions of nuclei. A general review of the theory of atoms in molecules has appeared in ref 3.

This paper summarizes the principal characteristics of the charge density of a series of ethyl and formyl derivatives, by studying the net charges and first moments of the atoms in these molecules and by investigating how these atomic moments determine the molecular dipole moment. The interpretation of substituent effects on the electron distribution is also explored.

Figure 1 shows a contour map of the charge density of formyl fluoride and indicates those elements of the theory of atoms in molecules that need to be understood for this paper: the bond paths, the interatomic surfaces, and the bond critical points, or "bond points".

### Atomic Contributions to the Molecular Dipole Moment

The dipole moment of a neutral molecule can be expressed in terms of a sum over the net charges  $q(\Omega)$  and first moments  $\mu(\Omega)$

of every atom  $\Omega$  in the molecule as<sup>4-6</sup>

$$\boldsymbol{\mu} = \sum_{\Omega} Z_{\Omega} \mathbf{R}_{\Omega} - \int \mathbf{r} \rho(\mathbf{r}) \, d\tau = \sum_{\Omega} [q(\Omega) \mathbf{R}_{\Omega} + \boldsymbol{\mu}(\Omega)] \quad (2)$$

where  $\mathbf{R}_{\Omega}$  is the position vector of the nucleus of atom  $\Omega$  measured from some arbitrary origin. The convention has been adopted that  $\boldsymbol{\mu}$  points toward the negative end of the dipole.  $\rho(\mathbf{r})$  is the electron density, which is positive everywhere. The atomic charge is defined as the sum of the nuclear and average electronic charges:

$$q(\Omega) = Z_{\Omega} - \int \rho(\mathbf{r}) \, d\tau = Z_{\Omega} - N(\Omega) \quad (3)$$

and the first moment is the atomic average of the electronic position vector  $\mathbf{r}_{\Omega} = \mathbf{r} - \mathbf{R}_{\Omega}$ :

$$\boldsymbol{\mu} = - \int \mathbf{r}_{\Omega} \rho(\mathbf{r}) \, d\tau \quad (4)$$

The individual contributions  $q(\Omega) \mathbf{R}_{\Omega}$  depend on the choice of origin, but their sum does not, and hence a molecular dipole moment is uniquely determined by a charge-transfer contribution arising from the net charges on the atoms

$$\boldsymbol{\mu}_c = \sum_{\Omega} q(\Omega) \mathbf{R}_{\Omega} \quad (5)$$

and a first moment contribution arising from the polarization of the atomic charge distributions

$$\boldsymbol{\mu}_a = \sum_{\Omega} \boldsymbol{\mu}(\Omega) \quad (6)$$

Both terms are important in the description of a molecular dipole moment.<sup>6</sup> Relating a static molecular dipole moment to only the charge-transfer term through the assignment of a set of atomic charges is unrealistic as it ignores dipolar contributions arising from the atomic polarizations. Use of such a model corresponds to assuming a molecular charge distribution to be composed of a set of spherically symmetric atomic densities, each centered on its own nucleus: a physically unacceptable model even

(1) Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

(2) Bader, R. F. W.; Nguyen-Dang, T. T.; Tal, Y. *Rep. Prog. Phys.* **1981**, *44*, 893.

(3) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9.

(4) Bader, R. F. W.; Bedall, P. M.; Cade, P. E. *J. Am. Chem. Soc.* **1971**, *93*, 3095.

(5) Slee, T. S. *J. Am. Chem. Soc.* **1986**, *108*, 7541.

(6) Bader, R. F. W.; Larouche, A.; Gatti, C.; Carroll, M. T.; MacDougall, P. J.; Wiberg, K. B. *J. Chem. Phys.* **1987**, *87*, 1142.