PERKIN 2

Photodecarboxylation of phenylglyoxylic acid: influence of *para*-substituents on the triplet state properties

Helmut Görner * and Hans Jochen Kuhn

Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim an der Ruhr, Germany.
E-mail: goerner@mpi-muelheim.mpg.de, kuhn@mpi-muelheim.mpg.de

Received (in Cambridge, UK) 12th August 1999, Accepted 27th September 1999

The photochemistry of several *para*-substituted derivatives of phenylglyoxylic acid (R–PA, R = OCH_3, CH_3, F, Cl, Br and CN) was studied in polar solvents. The triplet state was detected by laser flash photolysis and phosphorescence in acetonitrile, acetone or acetic acid at room temperature and by phosphorescence in polar glasses at −196 °C. In fluid media the phosphorescence intensity and the triplet lifetime are both reduced on addition of propan-2-ol or water. The rate constant for H-atom abstraction by the triplet of the R–PA from propan-2-ol, $2 \times 10^4 - 8 \times 10^7$ $dm^3\ mol^{-1}\ s^{-1}$ in acetonitrile, increases with the electron-accepting power of the substituent. The intermediate is the corresponding α-carboxy-α-hydroxybenzyl radical. The main transient in neat aqueous solution is the triplet state of the corresponding benzaldehyde as secondary intermediate. Based on results of triplet quenching by water in mixtures with acetonitrile and of time-resolved conductivity measurements, heterolytic α-splitting of the triplet anion involving the benzoyl anion is suggested. Photodecarboxylation occurs in substantial yield for R = CH_3, F, Cl, Br and CN in acetonitrile and $\Phi(-CO_2)$ is enhanced in the presence of water, $\Phi(-CO_2) = 0.4–0.8$ at 5–20% H_2O. The values are larger than in neat aqueous solution, where a decreasing dependence *vs.* pH was generally found. A reaction scheme is presented accounting for the observed intermediates and the dependence of $\Phi(-CO_2)$ on the water content and the pH.

Introduction

The role of water in the photodecarboxylation of phenylglyoxylic acid (PA) has been a long-standing puzzle.[1,2] Of the α-keto carboxylic acids mainly pyruvic acid, the simple aliphatic analogue of PA, has been investigated by photochemical methods.[2–10] The photochemistry of PA, however, differs significantly from that of pyruvic acid. PA undergoes photoreduction in the presence of H-donating solvents and photodecarboxylation in mixtures of water with inert polar solvents, such as acetonitrile, acetone or acetic acid.[11–15]

$$PA \xrightarrow{h\nu} BA + CO_2 \qquad (1)$$

The quantum yield for decarboxylation of PA in acetonitrile in the presence of 10–20 mol dm^{-3} water is $\Phi(-CO_2) \approx 0.8$ and the reaction is suitable as a chemical actinometer.[12,13] Under these conditions PA is present as anion and benzaldehyde (BA) and CO_2 are virtually the only photoproducts. On the basis of phosphorescence and T-T absorption measurements at room temperature we have recently concluded that the triplet anion of PA is deactivated by a reaction with water.[14] Moreover, transient conductivity studies in neat aqueous solution and mixtures with acetonitrile revealed that the formation of BA is faster than (or as fast as) the neutralization reaction. Thus we have suggested that reaction (1) occurs *via* heterolytic α-splitting resulting in the benzoyl anion, $C_6H_5CO^-$, or its protonated congruent. Free radicals play no role in the decarboxylation mechanism of PA in the presence of water.[14,15]

Photolysis of 1- and 2-naphthylglyoxylic acid in mixtures of acetonitrile with water yields CO_2 and the corresponding naphthaldehydes.[16] A heterolytic C–C bond cleavage involving carbanions has been demonstrated for other aromatic systems.[17,18] Photolysis of alkyl phenylglyoxylates involves radicals.[19,20] The homolytic and heterolytic mechanisms for decarboxylation have been reviewed by Budac and Wan.[21] The role of water in the mixtures with inert polar solvents is fourfold: the presence of water favours the heterolytic *vs.* a homolytic mechanism and determines the acid–anion ground state. Water interacts with the triplet state of the anion (thereby forming the BA or naphthaldehyde precursor) and interacts with the excited singlet state of the anion (thereby bypassing the latter reaction towards the aromatic aldehydes).[14–16]

This work provides a deeper insight into the mechanistic details of the decarboxylation of R–PA. For this purpose we have introduced several substituents (R = OCH_3, CH_3, F, Cl, Br and CN) in the *para* position. The results in mixtures of water with inert polar organic solvents and as a function of the pH are presented. They support the proposed heterolytic splitting reaction. Despite a large variation of the reactivity of water with the triplet state of the anion, the *para* substituent (R = CH_3, F, Cl, Br and CN) has no significant effect on the $\Phi(-CO_2)$ values with respect to the pH dependence in neat aqueous solution and in the mixtures of water (>5 mol dm^{-3}) with acetone or acetonitrile.

Results

Ground state and excited singlet state

The absorption spectra of the R–PA in acetonitrile have maxima at 250–300 nm (see Experimental section) and, with the exception of OCH_3–PA, a pronounced shoulder around 340–380 nm with an ε value of 50–90 $dm^3\ mol^{-1}\ cm^{-1}$. Addition of water to acetonitrile leads to a blue-shift of the spectrum at λ >280 nm. The absorption spectrum in neat water shows a significant pH dependence, *e.g.* for CN–PA the absorbance at 250 nm increases with increasing pH between 0 and 2 and remains almost constant thereafter (not shown). Similar curves were found for other R–PA, *e.g.* for A_{290} of OCH_3–PA and an opposite dependence at longer wavelengths (A_{340}). Three

Table 1 Phosphorescence maxima (in nm) in glassy and fluid media[a]

Compound	Room temperature Acetonitrile	 Acetone	−196 °C Ethanol
OCH_3–PA	470,505,550sh		463,501,544
CH_3–PA	465,500	472,513,554sh	466,506,550
PA[b]	470,505,550sh	472,511,555sh	466,505,545
F–PA	472,520,555sh	475,515,557sh	465,505,550
Cl–PA	470,508,550sh	477,515,560sh	470,510,558
Br–PA	470,508,555sh	472,514,560sh	468,508,555
CN–PA	486,524,560sh		480,520,566

[a] In air- and argon-saturated solutions at −196 and 25 °C, respectively, $\lambda_{exc} = 340$ nm for acetone and 250–280 nm for the other media (sh: shoulder). [b] Values taken from ref. 14.

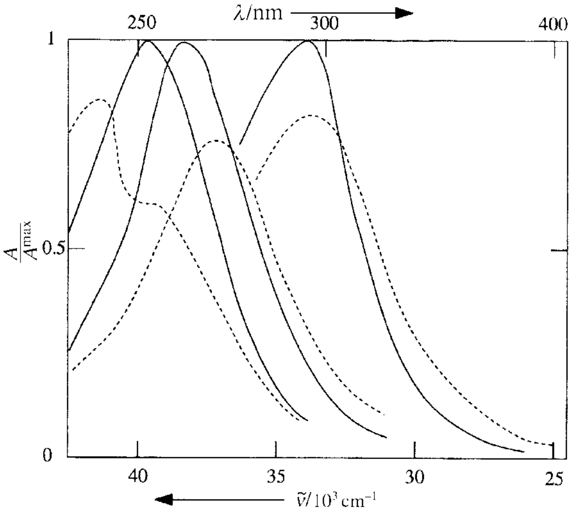


Fig. 1 Absorption spectra of CN-, CH_3- and OCH_3–PA (from left to right) in aqueous solution at pH 3.3 (——) and pH 0 (– – –).

examples below and above the pK_a value are shown in Fig. 1. The pH for 50% change at the appropriate wavelengths is taken as a measure of the pK_a value. For PA itself[14] and the R–PA p$K_a = 1.1$; only for CN–PA the pK_a value is slightly larger (≈1.2).

Apparently, the lifetime of the excited singlet state of R–PA is extremely short since only weak fluorescence could be detected, either in fluid or in glassy media. The largest quantum yield of fluorescence, ≈0.01 in ethanol at −196 °C, was found for OCH_3–PA.

Phosphorescence in glassy media

The emission spectrum of Br–PA in butyronitrile at −196 °C has maxima at 464 and 502 nm and progressions at 545 and 595 nm. Very similar spectra with changes in λ_{max} of less than 20 nm were recorded for all R–PA in ethanol (Table 1). By comparison with the parent molecule we conclude that the emission in the case of the R–PA has to be attributed to phosphorescence.[2,14] For several R–PA (*e.g.*, Br–PA) it was shown that the shape of the spectrum and the maximum are independent of λ_{exc} (230–380 nm for concentrations of 10^{-4} and 10^{-2} mol dm^{-3}, respectively). Similar phosphorescence spectra were recorded in glassy ethylene glycol and water mixtures (2:1, v/v), where the phosphorescence spectrum is less structured and the maximum is slightly blue-shifted. Replacement of neutral by acid water (pH ≤ 1, R = CH_3, Br) has no marked effect on the spectrum. This indicates that in glasses the emission from both, acid and anion, is similar.

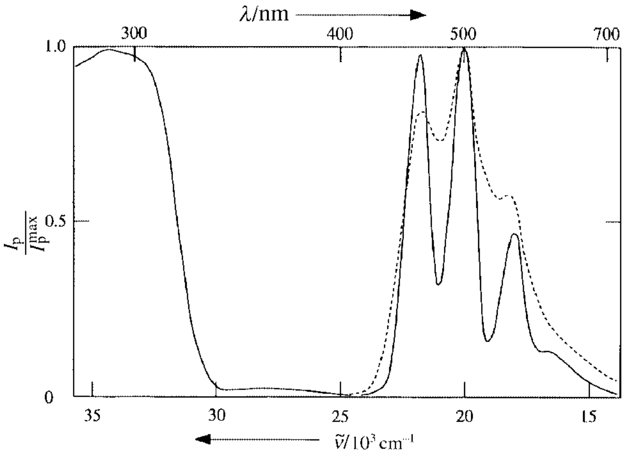


Fig. 2 (a) Phosphorescence spectra of OCH_3–PA in ethanol at −196 °C (——) and in argon-saturated acetonitrile at 25 °C (– – –); $\lambda_{exc} = 340$ nm and $\lambda_p = 500$ nm.

The phosphorescence quantum yield (Φ_p) and the corresponding lifetime (τ_p) were determined in ethanol and/or butyronitrile at −196 °C. The Φ_p values are in all cases between 0.5 and 0.95, indicating that deactivating processes other than those leading to the lowest triplet play only a minor role. The phosphorescence lifetime is typically $\tau_p = 3$ ms in both media and shows only minor changes (smaller than ±0.6 ms) with substitution. It should be emphasized that oxygen virtually does not quench Φ_p nor τ_p in these glassy solvents. The first maximum of the phosphorescence band of the R–PA in glassy butyronitrile corresponds to a triplet energy of approximately 259 kJ mol^{-1}. Slightly smaller values were found at room temperature, the smallest with 242 kJ mol^{-1} for CN–PA.

Phosphorescence in fluid media

Phosphorescence was also observed for the R–PA in argon-saturated acetonitrile and acetone solutions at 24 °C (Table 1). The spectra are less structured but the maximum is nearly the same as in glassy ethanol or butyronitrile. The two major peaks depend only little on the substituent and the medium. Examples of the phosphorescence spectra in glassy and fluid media are shown in Fig. 2. The quantum yield is reduced at least 100-fold on going from −196 to 24 °C. This corresponds with the change in lifetimes. We therefore suggest that the quantum yield of intersystem crossing (Φ_{isc}) is also close to unity for all of the R–PA in organic solvents at room temperature. The longest phosphorescence lifetimes in the 10–30 μs range and first-order decay were obtained with $\lambda_{exc} = 308$ nm at the lowest possible pulse intensity (Table 2).

The intensity at the maximum (I_p) and τ_p are both quenched by alcohols (Figs. 3a and 3b, respectively). Plots of I_p°/I_p and τ_p°/τ_p *vs.* the propan-2-ol concentration are linear, the Stern–Volmer constants ($K_{2\text{-p}}$) were obtained from the slopes. $K_{2\text{-p}}$ and the rate constant for phosphorescence quenching ($k_{2\text{-p}}$) increase both in the order CH_3–, F–, Cl–, Br– and CN–PA (Table 3). For a given R–PA one would expect the same result from the two methods, *i.e.* $\tau_p \times k_{2\text{-p}} = K_{2\text{-p}}$. Indeed, this is fulfilled (within the experimental error) in several cases, *e.g.*, when τ_p was obtained by using a low concentration and a small laser intensity.

From the linear part of I_p^{-1} *vs.* [H_2O] (Figs. 3a and 3b) a Stern–Volmer constant was estimated; K_{H_2O} ranges from 0.1 to ≥70 dm^3 mol^{-1} (Table 4). As a second measure for the phosphorescence quenching by water the slope (k_{H_2O}) of the linear part of τ_p^{-1} *vs.* [H_2O] was taken. The reactivity against water, as measured by K_{H_2O} and k_{H_2O}, increases for the substituent in the above order and is slightly larger for a given R–PA in acetone than in acetonitrile and markedly smaller in acetic acid. A further more accurate measure for the reactivity of the triplet is obtained from T-T absorption (see below).

Table 2 Phosphorescence and triplet lifetimes, absorption maximum and rate constants for quenching by oxygen and cyclohexa-1,3-diene[a]

Compound	Solvent	λ_{exc}/nm	τ_p[b]/μs	τ_T/μs	λ_{TT}[c]/nm	$10^{-9}k_{ox}$/dm^3 mol^{-1} s^{-1}
OCH_3–PA	Acetonitrile	248	0.8	1	445	5 [9][d]
CH_3–PA				4	328,(410)	3 [6]
		308	35	5		
PA[e]		248		3	322,(410)	2 [6]
		308	20	8		
F–PA			16	3		1.5
Cl–PA		248		3	320,(450)	2 [6]
		308	17			
Br–PA		248		3	332,(440)	1.5
		308	14			
CN–PA		248	<2	2	320,(500)	2 [8]
OCH_3–PA	Acetic Acid	308		2	440	
CH_3–PA			20 (>10)	8	320,(410)	
PA[e]		248			318,(420)	6
		308	22 (7)	8		[3]
F–PA			30 (>8)			
Cl–PA			20	10		
Br–PA			20 (>5)	8	325,(400)	
CN–PA				1		

[a] In argon-saturated solution at 25 °C; typical concentration: 0.2, 1.0 and 10 mmol dm^{-3} for $\lambda_{exc} = 248$, 308 and 354 nm, respectively. [b] For the phosphorescence lifetime the concentration was reduced by a factor of 2–10; in parentheses: values in acetone, $\lambda_{exc} = 354$ nm. [c] Weak, second maximum in parentheses. [d] In square brackets: rate constant k_q for quenching by cyclohexa-1,3-diene. [e] Taken from ref. 14.

Table 3 Stern–Volmer constant and rate constants for quenching of phosphorescence and T-T absorption by propan-2-ol[a]

Compound	$K_{2\text{-}p}$[b]/dm^3 mol^{-1}	$10^{-6}k_{2\text{-}p}$[c]/dm^3 mol^{-1} s^{-1}	$10^{-6}k_{2\text{-}p}$[d]/dm^3 mol^{-1} s^{-1}
OCH_3–PA		⩽0.03	⩽0.02
CH_3–PA	10	0.82	0.8 (1.4)[e]
PA[f]	24	1.5	1.5 (1.7)
F–PA	40	2	1.6 (1.8)
Cl–PA	⩾40	2.6	2.5 (3.0)
Br–PA	>20	>3	3 (2.8)
CN–PA	⩾100	>30	

[a] In argon-saturated acetonitrile at 25 °C using $\lambda_{exc} = 248$ nm, unless specified otherwise. [b] Stern–Volmer constant, $\lambda_{exc} = 250$–280 nm in acetonitrile, 330–350 nm in acetone. [c] Rate constant for phosphorescence quenching. [d] Rate constant for quenching of T-T absorption; $\lambda_{exc} = 354$ nm in acetone. [e] Values in parentheses refer to acetone. [f] Taken from ref. 14.

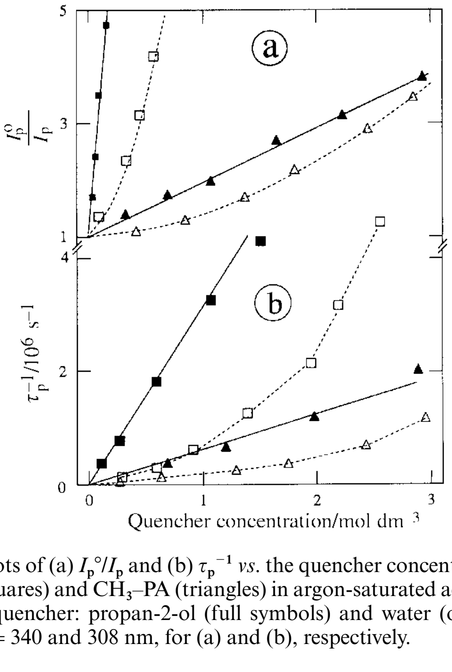


Fig. 3 Plots of (a) I_p^0/I_p and (b) τ_p^{-1} *vs.* the quencher concentration for Br–PA (squares) and CH_3–PA (triangles) in argon-saturated acetonitrile at 25 °C; quencher: propan-2-ol (full symbols) and water (open symbols); $\lambda_{exc} = 340$ and 308 nm, for (a) and (b), respectively.

Absorption of the triplet state of phenylglyoxylic acid

For most R–PA (0.1–0.5 mmol dm^{-3}) in acetonitrile solution at room temperature two transients, a major short-lived (T_{PA}) and a minor longer-lived ($T_{K'}$) were observed by laser flash photolysis ($\lambda_{exc} = 248$ nm). Examples are shown in Figs. 4a and 4c for CN- and OCH_3–PA, respectively. T_{PA} is formed concomitantly with the pulse and decays by first-order kinetics ($k_{obs} = 1/\tau_T$). The triplet lifetime is in the 1–10 μs range (Table 2). T_{PA} is quenched by oxygen, a typical value of the rate constant is $k_{ox} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}. T_{PA} is also quenched by cyclohexa-1,3-diene and rate constants (k_q) close to the diffusion-controlled limit were obtained from linear dependences of τ_T^{-1} on [quencher].

Transient T_{PA}, observed with the R–PA in the three inert polar solvents at room temperature, is assigned to the lowest triplet state, in analogy to the parent molecule.[14] The absorption maximum (λ_{TT}) changes only little on variation of the substituent, *e.g.* from 320 nm (CN–PA) to 332 nm (CH_3–PA) and a second weak band emerges in the visible range (Table 2). The only exception is OCH_3–PA; here λ_{TT} is around 450 nm and the spectrum extends to the red spectral range (Fig. 4c).

Absorption of the triplet state of benzaldehyde

In aqueous solution at pH = 1 the R–PA (0.1–0.5 mmol dm^{-3}, $\lambda_{exc} = 248$ nm) exhibit essentially a short-lived transient (T_{BA}) in the UV which decays by first-order kinetics and a longer-lived one with a low ΔA. The lifetime of the major transient T_{BA} ranges from 30 ns (F–PA) to 1 μs (OCH_3–PA) and λ_{TT} is red-shifted in the order PA (342 nm), Cl–PA and Br–PA (403 nm). For CH_3–PA it was verified that T_{BA} is quenched by oxygen (rate constant: ⩾10^9 dm^3 mol^{-1} s^{-1}). The ratio of absorbances of the longer- and shorter-lived transients is substantial only for OCH_3–, CH_3– and CN–PA with no transient at pH ⩾ 4 for the latter case. $\Delta A(T_{BA})$ increased on repeated flashing when the excited volume (*ca.* 0.01 cm^{-3}) was not exchanged, indicating that T_{BA} originates from an excited photoproduct rather than from the given R–PA. This transient of PA itself has already been assigned to the triplet state of BA.[14]

On increasing the pH (up to pH = 5), ΔA (measured at λ_{TT} of T_{BA}) is approximately constant for OCH_3–PA, but decreases in the other cases. For PA and CN–PA the change in ΔA is so large that practically no transient could be detected at pH > 4

Table 4 Stern–Volmer constant and rate constants for phosphorescence and triplet quenching by water[a]

Compound	Solvent	K_{H_2O}[b]/dm^3 mol^{-1}	$10^{-6}k_{H_2O}$[c]/dm^3 mol^{-1} s^{-1}	$10^{-6}k_{H_2O}$[d]/dm^3 mol^{-1} s^{-1}
OCH_3–PA	Acetonitrile	0.1[e]	0.2	≤0.05
CH_3–PA		0.8[e]	0.8	0.9
PA[f]		2[e]	>4	6
F–PA		1[e]	>4	3.5
Cl–PA		7	>3	8.5
Br–PA		6[e]	>4	11
CN–PA		>70	≥40	≈100
OCH_3–PA	Acetone			0.01
CH_3–PA		1.5	2	1.8
PA[f]		18	≥5	7
Cl–PA		10		14
Br–PA		6[e]	10	15
CH_3–PA	Acetic Acid	0.2[e]	0.4	0.2
PA[f]		1.6	<0.3	0.6
F–PA			0.5	
Cl–PA		0.5[e]	0.6	0.5
Br–PA		0.6[e]	>0.5	0.8
CN–PA				8

[a] In argon-saturated solution at 25 °C using $\lambda_{exc} = 308$ nm, unless specified otherwise. [b] Stern–Volmer constant, $\lambda_{exc} = 250$–280 nm for acetonitrile, 330–350 nm in the other solvents. [c] Rate constant for phosphorescence quenching, taken from plots of $1/\tau_p$ *vs.* the H_2O concentration. [d] Rate constant for quenching of T-T absorption, data from Table 5. [e] I_p^{-1} *vs.* $[H_2O]$ is upward curved, K_{H_2O} taken as $1/[H_2O]_{1/2}$. [f] Taken from ref. 14.

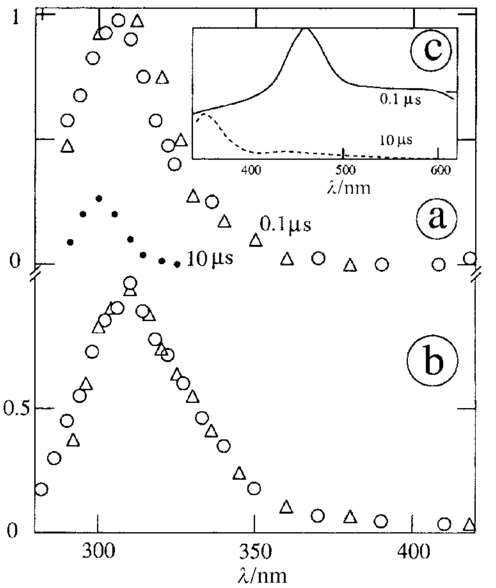


Fig. 4 Transient absorption spectra (a) of CN–PA (circles) and CH_3–PA (triangles) in argon-saturated acetonitrile, 100 ns (open symbols) and 10 µs (●) after the pulse; (b) of CN–PA in argon-saturated propan-2-ol in the absence and presence (9 : 1) of water, pH 10 (circles and triangles, respectively) and (c) of OCH_3–PA in argon-saturated acetonitrile, 0.1 µs (——) and 10 µs (– – –) after the pulse; $\lambda_{exc} = 248$ nm.

(ΔA(pH = 4)/ΔA(pH = 1) <30). In other cases (OCH_3–, CH_3– and Cl–PA) the absorption spectrum is similar to that of T_{BA} at pH = 1. We therefore propose that it is the same major T_{BA} transient observed in the accessible pH range. The reason for its disappearance in the more basic range is the reduced yield since the lifetime increases only slightly on increasing the pH.

H-atom abstraction

In propan-2-ol a long-lived transient (T_K) was observed for the R–PA throughout (Fig. 4b). For R = OCH_3, CH_3, Cl, Br and CN the λ_{max} values are 330, 320, 318, 324 and 320 nm, respectively. In contrast to the triplet, T_K decays by second-order kinetics; half-lives ($t_{1/2}$) range from 100 µs (Br–PA) to about 1 ms (OCH_3– and CH_3–PA) under our conditions. T_K is quenched by oxygen; the rate constant is typically 2×10^9 dm^3 mol^{-1} s^{-1}. This transient, observed with the parent molecule in several alcohols[14] and with the R–PA in propan-2-ol, is assigned to the corresponding α-carboxy-α-hydroxybenzyl (ketyl) radical. For OCH_3–PA and CH_3–PA in 100% propan-2-ol the triplet appeared concomitantly to the laser pulse since the rate constant ($k_{2\text{-p}}$) for quenching by propan-2-ol is smaller than 10^5 dm^3 mol^{-1} s^{-1}. The $k_{2\text{-p}}$ values were obtained from the linear dependence of k_{obs} (of T-T absorption in acetonitrile solution) *vs.* the propan-2-ol concentration (0–1 mol dm^{-3}). They are a direct measure for the reactivity of the triplet against H-atom abstraction.

The remaining transient ($T_{K'}$) after triplet decay in acetonitrile is tentatively also assigned to the ketyl radical since the spectrum and the dependence of λ_{max} on the substituent are similar to those of T_K. The ratio of absorbances of $T_{K'}$ and T_{PA} (ΔA(K′)/ΔA(PA)), measured at both maxima, ranges from 0.2 to 0.5. Although ΔA(K′) is small the rather short triplet lifetime in acetonitrile indicates a reaction competing with phosphorescence and non-radiative intersystem crossing. This reaction may be either H-atom abstraction from acetonitrile or from the carboxyl group in the R–PA.

Decay of the triplet in water–acetonitrile mixtures

As pointed out above, the triplet lifetime of most R–PA becomes shorter on addition of water to acetonitrile. The plot of k_{obs} *vs.* the H_2O concentration (Fig. 5b), in analogy to that of τ_p^{-1} *vs.* $[H_2O]$ (Fig. 3b), does not simply show initially a linear dependence on the H_2O concentration; k_{obs} increases only slightly in the 0–2% range and shows a more or less linear dependence between 2 and 10% of water. Upon 248 nm excitation and detection at ≈330 nm, the curve reaches a maximum and decreases on going to neat water (results not shown). From the above described behaviour in neat acetonitrile together with that in neat aqueous solution it is clear that the maximum originates from a change in formation of two different transients, the triplet states of the R–PA and the corresponding photoproducts, T_{PA} and T_{BA}, respectively.

In order to reduce the probability for excitation of R–BA sufficiently, we used R–PA at 10–100 times higher concentrations, $\lambda_{exc} = 308$ nm. Then the initial dependence of k_{obs} *vs.* $[H_2O]$ is the same as for $\lambda_{exc} = 248$ nm (Table 5), but no maximum was found for the R–PA (Fig. 5b); k_{obs} increases

Table 5 Triplet decay kinetics ($10^{-6}\,k_{obs}/s^{-1}$) in the presence of water[a]

Compound	Solvent	λ_{exc}/nm	Vol. H_2O (%) 1	5	10	15
OCH_3–PA	Acetonitrile	248		0.4	<0.8	
CH_3–PA			0.3	1.3	3.5	5
		308	0.3	1.1	3.8	6.6
PA[b]			0.08	5.5	16	⩾30
F–PA			0.2	3.4	9	20
Cl–PA		248	0.6	12	40	>50
Br–PA			0.6	22	>30	
CN–PA			50	>60		
OCH_3–PA	Acetone	354	0.3	0.3	0.4	
CH_3–PA			0.3	3.8	8	13
PA[b]			1.5	10	24	39
Cl–PA			0.8	30	>50	
Br–PA			2	30	>50	
CH_3–PA	Acetic Acid	308	0.12	0.2	0.5	1
PA[b]		248	0.01	0.2	0.7	1.5
Cl–PA		308	0.4	0.9	1.2	3.3
Br–PA			0.12	0.4	1.2	2.5
CN–PA			4		>50	

[a] In argon-saturated solution at 25 °C. [b] Taken from ref. 14.

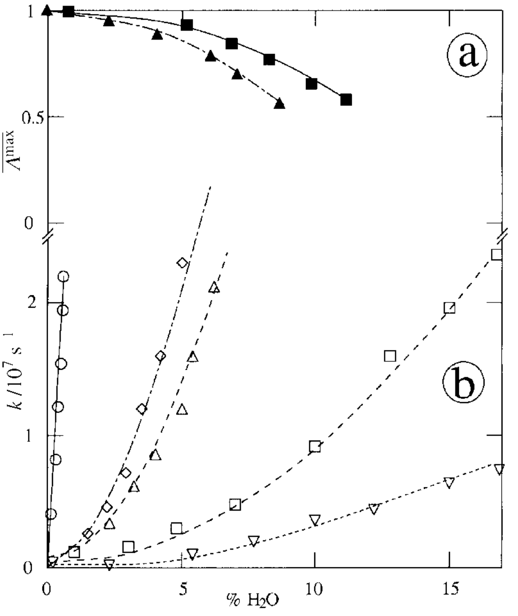


Fig. 5 Plots *vs.* the H_2O concentration (pH = 7) of (a) $\Delta A(\lambda_{max})$ for F–PA (■) and Cl–PA (▲) and (b) $k_{obs}(T_{PA})$ for CN– (○), Br– (◇), Cl– (△), F– (□) and CH_3–PA (▽) in argon-saturated acetonitrile; λ_{exc} = 308 nm.

monotonically up to the detection limit of about $5 \times 10^7\ s^{-1}$. The triplet yield of the R–PA, which is proportional to ΔA(PA), depends also on the amount of water. It decreases with increasing water content in acetonitrile as has been reported for the parent molecule[14] and shown in Fig. 5a for two cases.

Transient conductivity

A conductivity change concomitant with the laser pulse was observed for the R–PA in argon-saturated aqueous solutions in a broad pH range. At pH = 2 the signal ($\Delta\kappa$: positive for increasing conductivity) decreases within 30 ns and remains constant for seconds. The rate constant for the fast decrease becomes measurable at pH = 3 and increases further to 0.2–1 µs on going to pH = 4. The signal remains constant on a prolonged time scale (up to seconds). However, at pH = 6 the conductivity signal increases within 1 µs and decreases, thereby approaching the initial value within seconds.

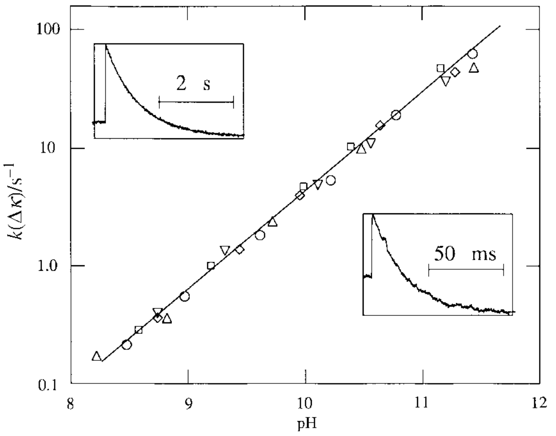


Fig. 6 Effect of pH on the rate constant for decay of $\Delta\kappa$ for CN– (○), Br– (◇), Cl– (△), CH_3– (▽) and OCH_3–PA (□) in argon-saturated aqueous solution; insets: conductivity change of OCH_3–PA at pH 9.1 (lower) and pH 11.1 (upper); λ_{exc} = 248 nm.

When the OH^- concentration is further increased (up to pH = 10) the short-time dependence remains virtually unchanged, *i.e.* $\Delta\kappa$ becomes positive and remains constant between 1 and >100 µs. A small decrease of $\Delta\kappa$ within a few 100 ns (in some cases, λ_{exc} = 248 nm) is ascribed to photoionization and subsequent neutralization.[14] This is supported by the result that the relative contribution of this side reaction decreases with decreasing laser intensity. On a long time scale $\Delta\kappa$ decreases below the initial value prior to the pulse (Fig. 6, insets) and the decay becomes significantly pH dependent. The rate constant of this slow decay (k_7, see Discussion section) increases linearly with the logarithm of the OH^- concentration (Fig. 6).

A positive $\Delta\kappa$ signal concomitant with the laser pulse was observed for the R–PA in neat argon-saturated acetonitrile solutions. The decay to the initial value ($\Delta\kappa = 0$) within 2–20 µs indicates that no longer-lived charged species is formed. On addition of water in amounts of 2–20%, the half-life of $\Delta\kappa$ is reduced and the amplitude then becomes negative, *i.e.* smaller than prior to the pulse. On a prolonged time scale the conductivity remains constant between a few µs and about 1 s. The rate constant for the decay of $\Delta\kappa$ shows also a non-linear dependence on the H_2O concentration (Fig. 7) but the absolute values are smaller than the k_{obs} values for triplet decay (Fig. 5b).

Table 6 Quantum yields of decarboxylation in mixtures with water[a]

			Vol. H_2O (%)				
Compound	Solvent	Method[b]	0[c]	1	5	10	25
OCH_3–PA	Acetonitrile	A			0.34	0.31	0.25
CH_3–PA		A	0.17			0.86	0.79
PA[d]		A				0.66	0.6
		B		0.1	0.4	0.6	0.8
F–PA		A				0.54	0.50
		B		<0.1	0.3		0.69
Cl–PA		A	0.2		0.6		
		B			0.6		
Br–PA		A	0.11	0.70	0.67	0.65	0.53
		B			0.4		0.71
CN–PA		A			0.53	0.47	0.25
CH_3–PA	Acetone	A	0.05		0.65	0.75	0.78
		B			0.6		0.7
F–PA		B	<0.05	0.5	0.65	0.65	
Cl–PA		B		0.5	0.4		0.4
Br–PA		B	<0.05		0.8	0.8	0.75

[a] In argon-saturated solution. [b] A: $\lambda_{irr} = 313$ nm, GC analysis, B: $\lambda_{irr} = 366$ nm, HPLC analysis, typical concentration: 2.5 and 50 mmol dm^{-3}, respectively. [c] Vol % $H_2O = 0.02 \pm 0.01$. [d] Taken from ref. 14.

Table 7 Quantum yields of decarboxylation in aqueous solution at different pH[a]

		pH				
Compound	Method[b]	0	1	2	Nat.[c]	5
OCH_3–PA	C		0.13		0.25	0.15
CH_3–PA	C	0.2	0.2	0.15	0.15	<0.07
PA	A	0.3	0.38	0.21	0.09	0.03
	A[d]	0.4	0.57	0.46	0.36	0.3
F–PA	C	0.4	0.3	0.1	0.1	
Cl–PA	A	0.35	0.28	0.10	0.1	0.04
	A[d]	0.31	0.29	0.26		0.24
	C	0.35	0.3	0.12		<0.05
Br–PA	C	0.3	0.3	0.13	0.08	0.04
CN–PA	C	0.18	0.12	0.05	0.02	

[a] In argon-saturated solution. [b] A: $\lambda_{irr} = 313$ nm (GC analysis), C: $\lambda_{irr} = 254$ nm (UV absorption), typical concentration: 2.5 and 0.1 mmol dm^{-3}, respectively, unless indicated otherwise. [c] $\lambda_{irr} = 366$ nm for PA (concentration = 50 mmol dm^{-3}) at natural pH ≈2.6–2.8. [d] Acetone (2 mol dm^{-3}) sensitized.

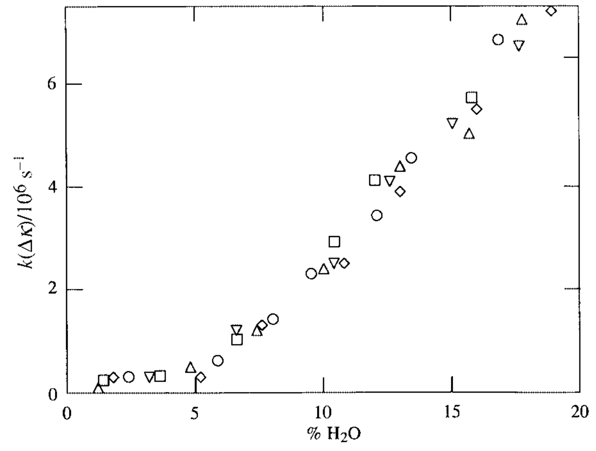


Fig. 7 Rate constant for decay of $\Delta\kappa$ *vs.* the H_2O concentration for CN– (○), Br– (◇), Cl– (△), CH_3– (▽) and OCH_3–PA (□) in argon-saturated acetonitrile; $\lambda_{exc} = 308$ nm.

Continuous irradiation

Several R–PA (CH_3, Cl, F, Br and CN) readily undergo photodecarboxylation in acetonitrile–water yielding the corresponding BA with high $\Phi(-CO_2)$ (Table 6). The concentration of both products increases as a function of the irradiation time, corresponding to the decomposition of the R–PA. The R–PA exhibit a characteristic dependence of $\Phi(-CO_2)$ on the water concentration. Typically, $\Phi(-CO_2)$ is low in neat acetonitrile, reaches a maximum at 5–20% water and decreases further.

The photoreaction of OCH_3–PA forms a very special case. Here, in neat acetonitrile or with low water content the products are mainly anisic acid ($\lambda_{irr} = 313$ nm), some 4,4′-dimethoxybenzil, but only traces of anisaldehyde, as shown by HPLC analysis. The quantum yield of disappearance (0.09 and 0.38 in acetonitrile and water, respectively) and that of anisaldehyde formation (0.002 and 0.35) increase considerably with increasing water content, while those of anisic acid (0.08 and 0.03) and benzil (0.02 and <0.01) formation decrease. Actually, only at >50% water, the aldehyde is the main product besides some anisic acid (no benzil formed). The course of the reaction at low water content is still not known. It was established that in mixtures with D_2O, naturally, the formyl-deuteriated aldehyde $(BA)_D$–OCH_3 is formed which, however, cannot be obtained by direct photodeuteriation[22] of anisaldehyde.

The effect of pH on $\Phi(-CO_2)$ in aqueous solution is summarized in Table 7. The highest values were found in the strongly acidic pH range. However, they are somewhat lower than in the optimum water–acetonitrile mixtures. For F–, Cl–, Br– and CN–PA $\Phi(-CO_2)$ decreases with increasing pH, showing a steep decrease around pH = 1 (Fig. 8). Photo-

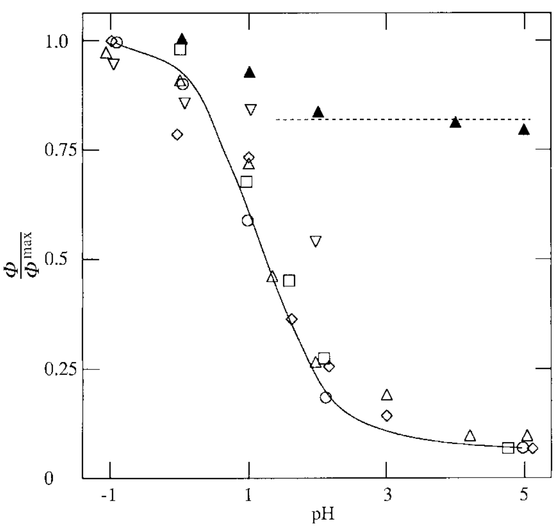


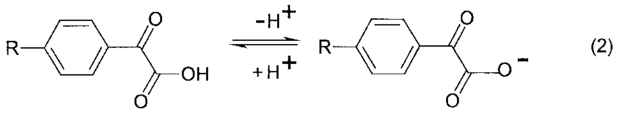
Fig. 8 Relative quantum yield for decarboxylation in argon-saturated aqueous solution as a function of pH for CN– (○), Br– (◇), Cl– (△, ▲), F– (□) and CH_3–PA (▽) (direct: open symbols, acetone sensitized: full); λ_{irr} = 248 nm.

decarboxylation was also studied under sensitized irradiation conditions. Larger $\Phi(-CO_2)$ values were found for R–PA with several sensitizers (*e.g.* acetone, acetophenone, 4,4′-dimethoxybenzophenone) than in their absence in the range pH = 2–6. Here, the results with acetone are presented (full symbols in Fig. 8).

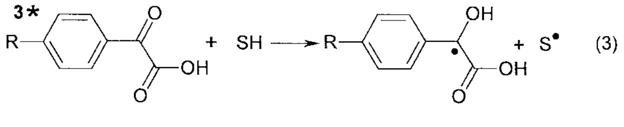
Discussion

Primary photochemical processes

The photochemistry of the R–PA is governed by the equilibrium between the acid and the anion in the ground state.

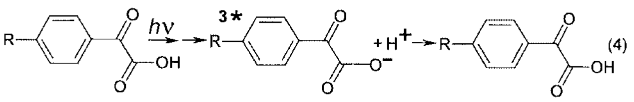


In organic solvents in the absence of water, the R–PA exist in the acid form. Addition of water shifts the equilibrium towards the anion since the pK_a values of all the R–PA in neat aqueous solution are around 1.[14,23] In solvents of low polarity PA is no longer monomeric.[24–26] The triplet state of the R–PA in water-free solutions is well characterized by results from phosphorescence and T-T absorption measurements. The triplet nature of T_{PA} is supported by (i) the absorption spectra (Figs. 4a and 4c), (ii) lifetime measurements from phosphorescence and T-T absorption (Table 2), (iii) the effect of quenching of the decay of T_{PA} by oxygen (Table 2) and (iv) the effects of other quenchers such as propan-2-ol (Figs. 3 and Table 3). H-atom abstraction from propan-2-ol (SH), yielding the α-carboxy-α-hydroxybenzyl (ketyl) radical[27] (transient T_K), occurs according to reaction (3).



The $k_{2\text{-p}}$ values, obtained from the linear dependence of k_{obs} *vs.* the propan-2-ol concentration (Table 3), are a direct measure for the reactivity of the R–PA triplet against H-atom abstraction.

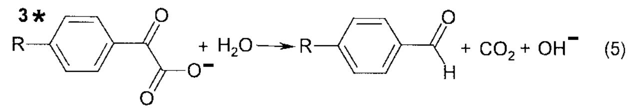
As species involved in the transient conductivity of R–PA in acetonitrile in the presence of small amounts of water (<1 mol dm^{-3}), we propose the strongly conducting H^+ ion and the triplet state of the anion according to reaction (4).



The recovery of the conductivity increase involves the triplet state and is explained by efficient intersystem crossing and fast recombination.

Photodecarboxylation involving the R–PA anion

It has been suggested that the initial increase of $\Phi(-CO_2)$ on increasing the H_2O concentration in acetonitrile (Table 6) is due to formation of the triplet anion.[14] The increasing amount of water shifts equilibrium (2) towards the anion, which on excitation yields the triplet of the anion in high yield. Once this triplet is formed decarboxylation occurs *via* overall reaction (5).



This interpretation holds also for the conductivity results in mixtures with acetonitrile. The initial increase and decrease in $\Delta\kappa$ whose lifetime (<1 μs) and yield decrease with increasing water content (Fig. 7) arises from the release of H^+ according to reaction (4). The gradual increase in $\Delta\kappa$ and the subsequent decrease at pH = 2–5 is ascribed to elimination of OH^-, followed by the neutralization reaction.

$$OH^- + H^+ \rightleftharpoons H_2O \qquad (6)$$

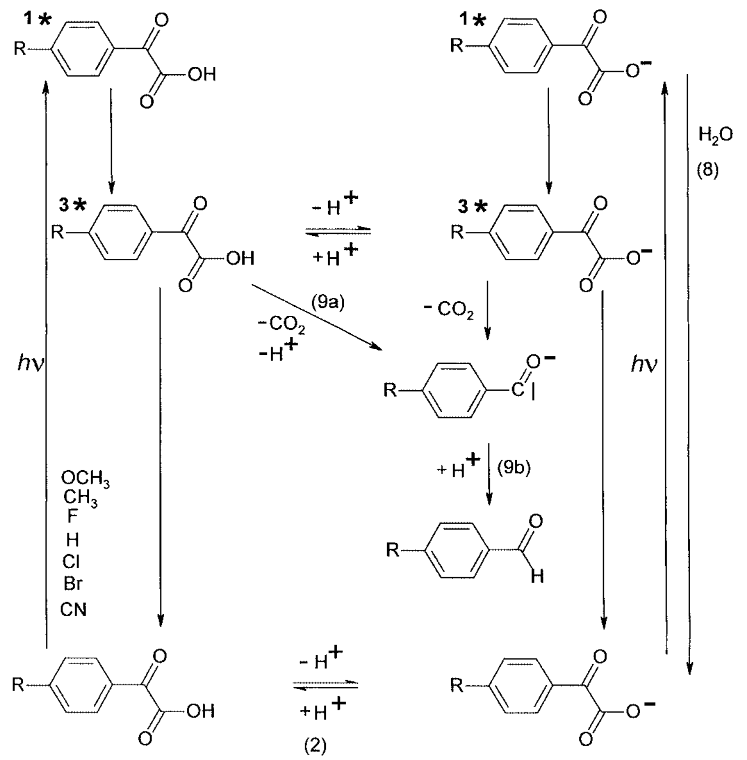
Whether or not deprotonation takes place also from the singlet state or only from the triplet state was previously an open question. For 1- and 2-naphthylglyoxylic acids, where fluorescence appears, in contrast to most R–PA, it has been shown that the singlet state is non-reactive and that the triplet pathway accounts for the $\Phi(-CO_2)$ values of 0.2–0.4 in mixtures of acetonitrile and water.[16]

Reaction (5) can further be specified on the basis of conductivity measurements. The increase in $\Delta\kappa$ in aqueous solution at pH = 8–11 (Fig. 6) is ascribed to OH^- elimination within the pulse width. The reason for the fast pH-dependent decrease of κ in the acidic range is the larger equivalent conductivity of H^+ (Λ = 350 cm^2 Ω^{-1} mol^{-1}) relative to OH^- (Λ = 190 cm^2 Ω^{-1} mol^{-1}). Thus CO_2 and OH^- are suggested to be formed within the laser pulse width throughout and OH^- remains as conducting species in the basic range or is neutralized at lower pH.

The slow decrease of $\Delta\kappa$ in the 10 ms–10 s range at pH = 9–11 (Fig. 6) is ascribed to formation of bicarbonate, reaction (7),[28,29] which has a markedly smaller equivalent conductivity ($\Lambda \leq 50$ cm^2 Ω^{-1} mol^{-1}) than that of OH^-.

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (7)$$

A value of k_7 = 7000 dm^3 mol^{-1} s^{-1} is obtained from the slope in Fig. 6 for several R–PA. A comparable value, k_7 = 6900 dm^3 mol^{-1} s^{-1}, has been reported on the basis of a pulse radiolysis study.[28] The amplitude (at *ca.* 1 ms after the pulse) is a measure of the relative $\Phi(-CO_2)$ value. This latter value is similar for CH_3–, F– or Br–PG at pH 10 and somewhat larger for OCH_3–PG, in agreement with the steady state values at pH = 5 (Table 5). Moreover, the yield was found to be roughly the same



Scheme 1

for F–PG at pH = 3.5 and 10, using the amplitudes and the equivalent conductivities of H^+ and OH^-.

Effect of water

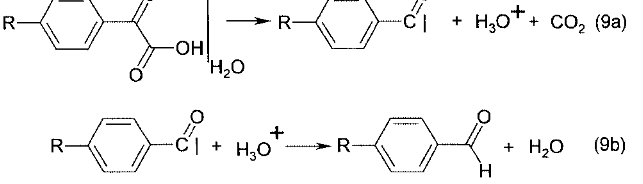
The non-linear dependence of k_{obs} on the H_2O concentration (Fig. 5b) is suggested to result from a water assisted photoprocess. Addition of water increases the amount of anion by shifting the ground state equilibrium (2) to the right hand side. In the absence of water the observed triplet of R–PA (except for OCH_3) in acetonitrile has probably n,π* character and the R–PA are present as acids. Quenching of triplet R–PA by a single water molecule is not efficient since a small amount of water (<0.5 mol dm^{-3}) has only a small effect on the decay kinetics, whereas k_{obs} depends almost linearly on the H_2O concentration in the 0.5–10 mol dm^{-3} range, indicating that the quenching step involves more than one water molecule.

As the two triplet forms are probably not distinguishable by T-T absorption spectroscopy, we cannot exclude that the π,π* character of the triplet state increases on addition of water. Hydrogen bonding to the carboxyl group may also play a role. As quenching step we propose reaction (5) of the triplet state of the anion with water, thereby forming the benzoyl anion or its protonated isomer as short-lived intermediate (Scheme 1). Oxygen has only a small effect on $\Phi(-CO_2)$ in mixtures with water. This is readily explained by the proposed mechanism since the reaction with water competes efficiently with triplet quenching by oxygen.

The decrease of $\Phi(-CO_2)$ on going to 100% water (*cf.* Tables 6 and 7) is suggested to be due to quenching of the singlet state,[14] reaction (8) in Scheme 1. This reaction with water reduces the yield of the observable triplet, as is illustrated in Fig. 5a for two cases. In the presence of more than about 20% water, due to the above effect of water on k_{obs}, the triplet is not accessible with our methods. Involvement of hydrates in the excited singlet state is hypothesized. Photodecarboxylation under acetone-sensitized irradiation supports the proposed mechanism since $\Phi(-CO_2)$ is strongly enhanced compared to otherwise the same conditions. For example, for CH_3– and Br–PA in aqueous solution at pH = 5 $\Phi(-CO_2)$ is about ten times larger in the presence than in the absence of the sensitizer (Table 7). This is in line with the low yield of triplet anion formation due to the competing quenching reaction (8) (Scheme 1) on direct excitation, but its efficient formation when the triplet state of the anion is generated by energy transfer.

Photodecarboxylation involving the R–PA acid

The enhancing effect on $\Phi(-CO_2)$ in neat aqueous solution in the range pH = 0–3 with H^+ concentration can be explained by postulating a decarboxylation step from the triplet of the acid.[14]



For all R–PA examined by nanosecond laser flash photolysis in aqueous solution (*e.g.* at pH = 0) no transient could be detected which may be assigned to the triplet state of the acid. Excitation of the acid yields only the triplet state of the corresponding BA (see Results section). This result, in contrast to the features of the triplet of the acid in non-aqueous solution (Table 2), indicates that reaction (9) is faster than 20 ns.

The effect of pH on $\Phi(-CO_2)$ for the R–PA is similar to that of the parent molecule.[14] The general trend is a decrease of $\Phi(-CO_2)$ with pH, *e.g.* on going from pH −1 to +5 (Table 7), which is suggested to be due to three effects, (i) the shift of the ground state equilibrium (2) with $pK_a = 1.1$, (ii) the reduction of the yield of triplet anion for pH > 1, reaction (8) and (iii) the efficiency of the decarboxylation reaction (9) at $pH \leqslant pK_a$.

Reactivity of the triplet and effects of substitution

Sequence (9) is in line with the observed pH dependence of $\Phi(-CO_2)$ for the R–PA (CH_3, F, Cl, Br, CN) taking into

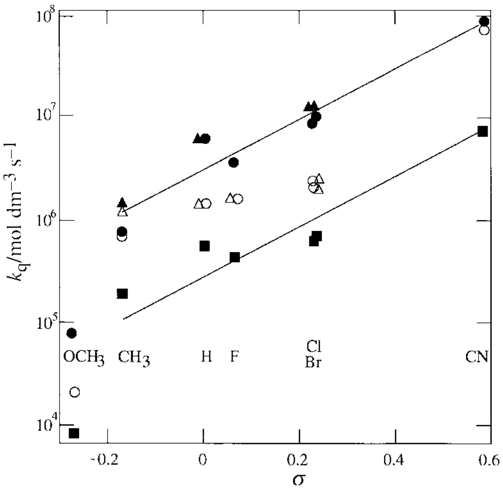


Fig. 9 Semilogarithmic plots of $k_{2\text{-p}}$ (open symbols) for triplet quenching by propan-2-ol and k_{H_2O} (filled symbols) for quenching by water *vs.* the Hammett σ parameter in acetone (triangles), acetonitrile (circles) and acetic acid (squares) using data from Tables 4 and 5.

account that the decarboxylation of the triplet anion is reduced by the efficient quenching step (8). For R = F, Cl and Br $\Phi(-CO_2)$ is 0.3–0.5 at pH = 0.4–1.3, while it drops to approximately 0.02 at pH $\gg$ pK_a (Fig. 8 and Table 7).

The dependence of log $k_{2\text{-p}}$ *vs.* the Hammett σ parameter (Fig. 9) reveals an increase of $k_{2\text{-p}}$ on increasing the electron accepting power of the substituent, *i.e.* in the order OCH_3, CH_3, H, F, Cl, Br and CN. This change is quite remarkable since $k_{2\text{-p}}$ increases by more than three orders of magnitude on going from OCH_3–PA to CN–PA. For a given R–PA the $k_{2\text{-p}}$ value in acetone is similar to that in acetonitrile or only slightly larger. Owing to the small $k_{2\text{-p}}$ value for OCH_3 one may expect that T_K should not be formed in acetonitrile, but the possibility of intermolecular or intramolecular H-atom abstraction in this case cannot be excluded.

Generally, the results from triplet quenching by alcohols are in agreement with the assumption that in inert solvents all R–PA are present in the n,π* triplet state of the acid. This is different for OCH_3–PA, where the triplet energy is virtually the same as for other R–PA, but (i) the photoproducts, (ii) the pH dependence of the $\Phi(-CO_2)$ values (Table 7) and (iii) the T-T absorption spectrum (Fig. 4c) are quite different. Thus the $^3\pi,\pi^*$ state is favoured for OCH_3–PA.

Addition of water to an organic solvent gives rise to the non-Stern–Volmer behaviour in the quenching of both T-T absorption and phosphorescence (Figs. 3a and 3b). Nevertheless, the rate constants k_{H_2O}, estimated from the linear part of Fig. 5b, may be used as a measure for the reactivity of triplet quenching by water. These rate constants show a trend to increase in the order R: OCH_3, CH_3, F, H, Cl, Br and CN, covering a range of more than three orders of magnitude (Table 4). The dependence of log k_{H_2O} *vs.* σ (Fig. 9) is essentially linear with the exception of the case OCH_3–PA. A similar dependence on the substituent was found in acetone with slightly larger k_{H_2O} values than in acetonitrile. A corresponding dependence of log k_{H2O} *vs.* σ was also measured in acetic acid, where, however, the k_{H_2O} values are typically tenfold smaller than in acetonitrile.

Concluding remarks

The triplet state of six *para*-substituted PA in acetonitrile, acetone or acetic acid is characterized by results from time-resolved and steady-state phosphorescence and T-T absorption measurements. The corresponding carboxyhydroxybenzyl radical is generated by an H-atom abstraction reaction from propan-2-ol. The increase of $\Phi(-CO_2)$ on addition of water to acetonitrile at room temperature is suggested to be due to a reaction of the triplet anion with water, yielding CO_2 and the corresponding BA. However, a reaction of water with the excited singlet anion reduces $\Phi(-CO_2)$ in neat water. The increase of $\Phi(-CO_2)$ with decreasing pH is ascribed to the decarboxylation reaction involving the triplet state of the acid form of the R–PA.

Experimental

The substituted PA were prepared by conventional procedures.[11–15] Molar absorption coefficients (in $dm^3\ mol^{-1}\ cm^{-1} \times 10^4$) in acetonitrile and (in parentheses) aqueous solution are, R: OCH_3 $\varepsilon_{293} = 1.42$ ($\varepsilon_{288} = 1.65$); CH_3 $\varepsilon_{265} = 1.18$ ($\varepsilon_{263} = 1.40$); F $\varepsilon_{251} = 0.94$ ($\varepsilon_{255} = 1.27$); Cl $\varepsilon_{265} = 1.26$ ($\varepsilon_{263} = 1.25$); Br $\varepsilon_{267} = 1.48$ ($\varepsilon_{267} = 1.78$); CN $\varepsilon_{254} = 1.68$ ($\varepsilon_{255} = 1.92$). Solvents (Merck, Darmstadt): were p.a. (acetic acid, ethylene glycol, ethanol, propan-2-ol and the other alcohols), Uvasol quality (acetone, acetonitrile, heavy water) or distilled (butyronitrile, Fluka). Water was purified by a Millipore (Milli Q) system.

The output at 248 or 308 nm from one of two excimer lasers (Lambda Physik, EMG 201 MSC and EMG 200, respectively) was used for most transient spectroscopic and kinetic measurements. Excitation at 248 nm has the advantage of the extension of the spectra to the shortest wavelength possible, whereas with $\lambda_{exc} = 308$ nm photoionization can be avoided. For a few measurements also the third harmonic of a Nd-laser ($\lambda_{exc} = 354$ nm) was used. The laser flash photolysis apparatus and the procedures used were essentially the same as in previous work.[14,16,30] The fast (0.05–10 μs) and slow (5 μs–10 s) conductivity signals were measured by DC and AC bridges using appropriate transient digitizers (Tektronix 7912AD and 390AD, respectively).[14,31] The hydrated electron could be observed for most R–PA in aqueous solution at pH = 3–10 at high laser intensities ($\lambda_{exc} = 248$ nm). It was identified by the reaction with N_2O or oxygen and its yield decreases in the order OCH_3–, CH_3– and F–PA. The occurrence of photoionization *via* a biphotonic step is not surprising since the hydrated electron was also observed with several substituted BA under comparable conditions.[31] The hydrated electron was not observable using $\lambda_{exc} = 308$ nm, confirming the biphotonic side process with 10 eV excitation energy for $\lambda_{exc} = 248$ nm.

Continuous irradiation was performed with the 366 and 313 nm lines of a 1000 W Xe/Hg-lamp combined with a monochromator[12,13] or at 254 nm using a low-pressure Hg lamp (Gräntzel). The quantum yield $\Phi(-CO_2)$ with $\lambda_{irr} = 313$ or 366 nm was determined by means of an electronic actinometer.[12,13] Actinometry at 254 nm was carried out using uridine in air-saturated aqueous solution at pH = 6, $\Phi = 0.016$.[32] Three methods for detection of photoproducts were used here; $\Phi(-CO_2)$ is derived from CO_2 measurements using GC and HPLC analysis, A and B, respectively and with method C $\Phi(-CO_2)$ is derived from changes in the absorption spectrum at appropriate wavelengths (typically longer than λ_{irr}). The samples were purged by argon and measured at 25 ± 1 °C unless otherwise indicated. GC and HPLC analyses were essentially the same as reported previously.[14,16]

Phosphorescence quenching was carried out on a spectrofluorimeter (Perkin Elmer LS-5) with small amounts of additives (up to 5 vol %) during continuous purging with argon. The quantum yield was determined on a Spex-Fluorolog (corrected spectra) by using benzophenone in butyronitrile at -196 °C as reference and $\Phi_p = 1$. The phosphorescence decay of the R–PA in acetonitrile, observed after laser excitation ($\lambda_{exc} = 248$, 308 and 354 nm), depends somewhat on the experimental conditions. On increasing the laser intensity the half-life decreases. Using 248 nm and a typical concentration of 0.1–0.5 mol dm^{-3}, the phosphorescence lifetime is in the 1–3 μs range. Compared to the intensity-induced effect of T-T annihilation, the effects of inert solvents, λ_{exc} and the concentration are smaller. The latter is demonstrated for several R–PA in acetone

(λ_{exc} = 354 nm); although much larger concentrations had to be used, τ_p is also in the 10–30 μs range (not shown). The intensity at the maximum (I_p) and τ_p are markedly reduced by oxygen (*e.g.* down to <1/10 in air-saturated acetonitrile solutions of most R–PA). When water was added in small amounts to a R–PA in acetonitrile, acetone or acetic acid, the phosphorescence spectrum remained unchanged, but I_p and τ_p were reduced. However, the plots of $I_p{}^o/I_p$ and $\tau_p{}^o/\tau_p$ *vs.* the H_2O concentration are initially non-linear and nearly linear only above a certain water concentration. Deviations from linear Stern–Volmer dependences in the range $I_p{}^o/I_p$ = 2–4 are indicated.

Acknowledgements

We thank Professor K. Schaffner for his support and Mr L. J. Currell and Ch. Laurich for technical assistance.

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Paper 9/06567I