

Photochemistry of 1- and 2-naphthylglyoxylic acid

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Abstract

The photophysical deactivation properties of excited 1- and 2-naphthylglyoxylic acid (1- and 2-NGA) in polar solvents and their photodecarboxylation were studied by steady-state and pulsed methods. The naphthylglyoxylic acids exhibit fluorescence in low quantum yield (≤ 0.02) and, in glassy media, also phosphorescence in substantial quantum yield (0.2–0.6). The triplet lifetime at -196°C , measured by phosphorescence and laser flash photolysis, lies in the 0.2–0.7 s range. In fluid solution the T–T absorption was observed ($\lambda_{\text{max}} \approx 410\text{--}540$ nm); the triplet lifetime at room temperature lies in the 2–10 μs range and is reduced in the presence of oxygen. Emission from singlet molecular oxygen was observed for 1- and 2-NGA in acetonitrile with quantum yields of 0.7 and 0.6, respectively. Both triplet lifetime and yield are reduced on addition of water to acetonitrile solution. Photochemical conversion of 1- and 2-NGA into the corresponding naphthaldehydes occurs in acetonitrile, water and mixtures thereof, but only in aqueous acetonitrile (1–25% water) is the photoreaction selective and the quantum yield substantial ($\Phi = 0.2\text{--}0.4$). A reaction scheme is presented which accounts for the observed deactivation processes of the excited molecules and the photodecarboxylation via an ionic mechanism in aqueous acetonitrile. © 1998 Elsevier Science S.A.

Keywords: Photodecarboxylation; Fluorescence; Triplet; Quantum yields

1. Introduction

Phenylglyoxylic acid exhibits photodecarboxylation and formation of benzaldehyde in acetone or acetonitrile solution in the presence of water [1–8,10,12]. Since the quantum yield of decarboxylation is high and the reaction is clean, phenylglyoxylic acid can be used as a chemical actinometer [8,10,11]. Recently, the photochemistry of phenylglyoxylic acid and several derivatives has been studied [10,12,14]. The proposed mechanism for photodecarboxylation implies a heterolytic α -splitting involving the anion triplet. This has been confirmed for five 4-substituted derivatives (R: CN, Br, Cl, F, and CH_3); only in the case of $\text{R} = \text{CH}_3\text{O}$ the reactivity of the anion triplet against water and the quantum yield of decarboxylation are small [13]. 4-Nitrophenylglyoxylic acid has quite different photochemical properties [14], as is often found for nitro derivatives of aromatic compounds.

In the present paper we report on the features of excited singlet and triplet states of 1- and 2-naphthylglyoxylic acid (1- or 2-NGA, respectively). The reactivity of the triplet state of the naphthylglyoxylic acids towards water is markedly smaller than that of phenylglyoxylic acid. An open question with phenylglyoxylic acid was the behaviour of its excited singlet state. Obviously, its lifetime is extremely short since

the quantum yield of fluorescence is very low ($\Phi_f < 10^{-3}$). With the naphthyl instead of the phenyl group this difficulty should not arise. Indeed, 1- and 2-NGA show fluorescence, but no indication was found for a new reaction pathway involving excited singlet states of the two naphthylglyoxylic acids. The observed triplet is the main intermediate in the naphthylglyoxylic acid \rightarrow naphthaldehyde (NA) photodecarboxylation.

2. Experimental

The naphthylglyoxylic acids (1-NGA: mp. $110\text{--}112^\circ\text{C}$; 2-NGA: mp. $91\text{--}92^\circ\text{C}$), the naphthils (NTs) and naphthoins were prepared by conventional procedures [15–21]. The naphthaldehydes (NAs) and naphthoic acids (NSs) were distilled or recrystallized commercial quality (Aldrich, Merck). The molar coefficients at the absorption maxima (in units of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) of the naphthylglyoxylic acids in the three solvents, (a) dry acetonitrile, (b) water (pH 3.7) and (c) acetonitrile/water 3:1 mixture are as follows. 1-NGA: (a) 212 nm, 5.97; 244 nm (inflection), 2.27; 316 nm, 0.92. (b) 212 nm, 5.04; 240 nm, 1.76; 324 nm, 0.91. (c) 212 nm, 4.56; 238 nm, 1.96; 312 nm, 0.88. 2-NGA: (a) 214 nm, 3.02; 244 nm (infl.), 2.55; 252 nm, 2.99; 284 nm, 0.75; 296

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nm, 0.94. (b) 208 nm, 3.12; 246 nm (infl.), 3.70; 252 nm, 4.23; 286 nm, 1.11; 296 nm, 1.22; 346 nm, 0.30. (c) 214 nm, 0.96; 244 nm (infl.), 3.35; 250 nm, 3.84; 286 nm, 0.79; 344 nm, 0.11.

The naphthaldehydes and other photoproducts were detected by HPLC using a N-3C18 column and gradient elution with methanol — KH_2PO_4 buffer (10 mM), 2:3 and 4:1; detection wavelengths 290 nm (1-NGA) and 240 nm (2-NGA); 5–10 μl samples. Carbon dioxide was analyzed by GC after catalytic hydrogenation to methane (cf. [12]). Solvents (Merck, Darmstadt) were p.A. (ethanol, 2-propanol), Uvasol quality (acetone, acetonitrile) or distilled (*n*-butyronitrile, ethylene glycol); water was purified by a Millipore system or triply distilled. Acetonitrile BAKER 'low water' for DNA synthesis (0.002–0.003% H_2O) was used for irradiations at '0% water' in acetonitrile; unless otherwise indicated the amount of water is given in vol. %.

The quantum yields of decarboxylation and product formation for $\lambda_{\text{irr}} = 280$ or 336 nm were determined (samples of 3.0 ml solution of 2.5×10^{-4} M naphthylglyoxylic acid at $25 \pm 0.1^\circ\text{C}$) by means of an Electronically Integrating Actinometer [9,10], $\approx 6.5 \times 10^{-11}$ Einstein/count or $\approx 1.12 \times 10^{-8}$ Einstein s^{-1} at 336 nm, $\approx 5.3 \times 10^{-11}$ Einstein/count or $\approx 0.87 \times 10^{-8}$ Einstein s^{-1} at 280 nm, calibrated by ferrioxalate actinometry [11], 1000 W Hg–Xe lamp, Spectral Energy GM 252 High Intensity Grating Monochromator, 2365 grooves/mm, dispersion 1.6 nm/mm, slit width 3 mm; the conversion was 5–10%. Since quantum yields were calculated at low initial conversions only, no corrections were necessary for light absorption by photoproducts in spite of their spectral overlap. 6–9 single irradiation experiments at different doses form the basis for each Φ_{Δ} determination.

The corrected emission spectra were recorded on a Spex-Fluorolog and the quantum yields of fluorescence and phosphorescence were obtained using optically matched solutions ($A_{265} = 0.3$, 1 cm pathlength and $A_{313} = 0.2$, 0.4 cm tube at 25 and -196°C , respectively) and 9,10-diphenylanthracene in ethanol ($\Phi_{\text{f}} = 1.0$ at -196°C) as standard. The phosphorescence could be selectively detected on a spectrofluorimeter (Perkin Elmer LS-5) by applying an appropriate time delay in the ms range, while its lifetime was determined in the laser set-up. The fluorescence lifetimes were measured by a single-photon counting apparatus.

Two excimer lasers emitting at 248 or 308 nm (Lambda Physik, EMG 201 MSC or EMG 200) were used for most spectroscopic and kinetic measurements, unless otherwise indicated. For a few measurements also the third harmonic of a Nd-laser (354 nm) was used. For the conductivity measurements a flow-through cell was used (pathlength 5 mm) which contains three cylindrical glassy carbon electrodes in distances of 5 mm, only one of the two identical sections was excited. The conductivity signals (5 μs –10 s) were measured by a 1 MHz AC bridge (40 V) and a transient digitizer (Tektronix 390AD). The laser flash photolysis apparatus and

the procedure used for the emission measurements were the same as in previous work [12].

Phosphorescence of singlet molecular oxygen at 1269 nm [22–27] was detected by using a cooled Ge detector (North Coast, EO 817FP), a silicon and an interference filter and an amplifier (Comlinear, CLC-103). The lifetimes of $\text{O}_2(^1\Delta_{\text{g}})$ in benzene, butyronitrile, acetonitrile and ethanol are typically 30, 50, 65 and 10 μs , respectively. The signal extrapolated to ca. 1 μs after the pulse (I_{Δ}) was found to show linear dependences either for a given incident laser intensity (I_{L}) on the absorbed energy ($1-10^{-\text{A}}$) or for a fixed concentration on I_{L} (the latter slope is denoted as S_{Δ}). The quantum yield of $\text{O}_2(^1\Delta_{\text{g}})$ formation (Φ_{Δ}) was obtained from S_{Δ} values using either acridine or 2-acetonaphthone as references with $\Phi_{\Delta}^{\text{ref}} = 0.71$ and 0.84, respectively [22–24]. A correction was carried out in each solvent using the relative rate constant for radiative deactivation of $\text{O}_2(^1\Delta_{\text{g}})$.

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{ref}} \frac{S_{\Delta} \times k_{\text{r}}^{\text{ref}}}{S_{\Delta}^{\text{ref}} \times k_{\text{r}}} \quad (1)$$

This ratio ($k_{\text{r}}/k_{\text{r}}^{\text{ref}}$) with respect to benzene is known to be 1.2, 0.30 and 0.23 in butyronitrile, acetonitrile and ethanol, respectively [25–27].

3. Results

3.1. Continuous irradiation

The absorption spectra of the two naphthylglyoxylic acids in aqueous solution at room temperature are shown in Fig. 1 for pH 0 and 4. The maxima of 1-NGA are around 212, 240 and 324 nm and 2-NGA has four maxima at 208, 246, 296 and 346 nm. The pH effect is similar as for phenylglyoxylic

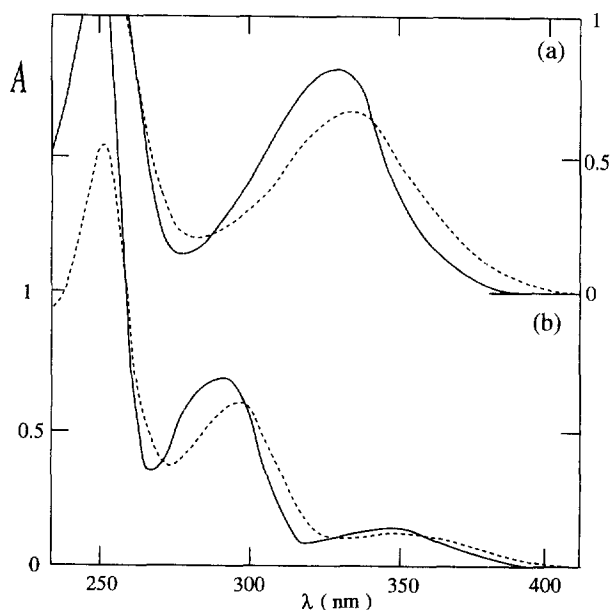


Fig. 1. Absorption spectra of (a) 1-NGA (90 μM) and (b) 2-NGA (60 μM) in aqueous solution at pH 0 (---) and pH 4(—).

acids [12], i.e., protonation shifts the maxima slightly to the red spectral range. From the changes in absorbance at an appropriate wavelength (e.g., 370 nm for 1-NGA) pK_a values of 1.1–1.3 were obtained for both naphthylglyoxylic acids. Addition of acetonitrile leads to a red-shift of the maximum in the UV range.

Upon steady-state photolysis of the naphthylglyoxylic acids in acetonitrile, water and mixtures thereof, we identified (by HPLC) the corresponding naphthaldehydes and carbon dioxide as the major photoproducts besides the naphthoic acids, small amounts of the naphthils and, in the absence of water, a trace of an unknown compound. As an example the photodecomposition of 1-NGA and the formation of 1-NA, 1-NS, and 1-NT at $\lambda_{irr} = 336$ nm are shown in Fig. 2 for neat argon-saturated acetonitrile. Neither 1- or 2-naphthoin nor carbon monoxide could be detected as products.

Both the position and height of bands in the UV spectra of the naphthylglyoxylic acids and their photoproducts change with water content of the solvent acetonitrile. This effect renders the reaction spectra of irradiated solutions very much different, depending on water content. Examples prior to and after irradiation ($\lambda_{irr} = 280$ nm) are shown for 2-NGA in argon-saturated (Fig. 3a) neat acetonitrile and (Fig. 3b) in the presence of 1% H_2O .

Accordingly, the product pattern and yields vary, as does the quantum yield of photodecomposition (Φ_d) of 1- and 2-NGA. The latter yield is low at $\leq 0.003\%$ H_2O , shows a steep increase with increasing water content toward a broad maximum at ≈ 5 – 10% H_2O , then a slight decrease at higher water content (Table 1).

The reaction in aqueous solution under argon is generally clean and effective. Plots of the concentration versus the applied dose of quanta reveal that, in the presence of water, the formation of 1-NA perfectly corresponds to the degradation of 1-NGA (Fig. 4b), while at low water content (1%) there is some 1-NS formed (Fig. 4a) and at 0% the reaction is even more slowed down; in addition, 1-NT and an unknown trace is detected. (Fig. 2).

The naphthaldehydes and the naphthoic acids were shown to be unreactive under the above irradiation conditions, both in the presence and absence of water or air. The same holds for the two naphthils (except for small quantities of naphthaldehyde and naphthoic acid formed), even under prolonged irradiation. Moreover, the naphthaldehydes do not even undergo photodeuteration [28,29] in D_2O containing acetonitrile.

The quantum yield at $\lambda_{irr} = 336$ nm of 1-NA formation (Fig. 5b) follows very closely, partly congruently, that of decomposition of 1-NGA (Fig. 5a). For 2-NGA, as a consequence of a higher yield of 2-NS as accompanying product, Φ_d is slightly smaller (Tables 1 and 2). At $\lambda_{irr} = 280$ nm the situation is similar, with lower quantum yields (Fig. 5a). Quantum yields in neat water are lower than one tenth of those in presence of acetonitrile; upon prolonged irradiation even some naphthoic acid is formed. The influence of pH on

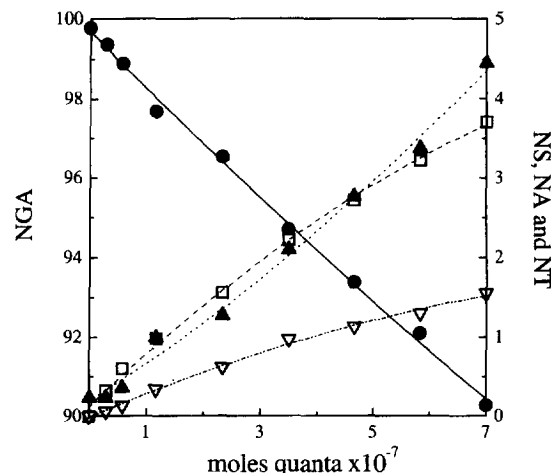


Fig. 2. Photolysis of 1-NGA (250 μ M) in neat argon-saturated acetonitrile at $\lambda_{irr} = 336$ nm, decomposition of 1-NGA (\bullet) and formation of 1-NA (\square), 1-NS (\blacktriangle) and 1-NT (∇).

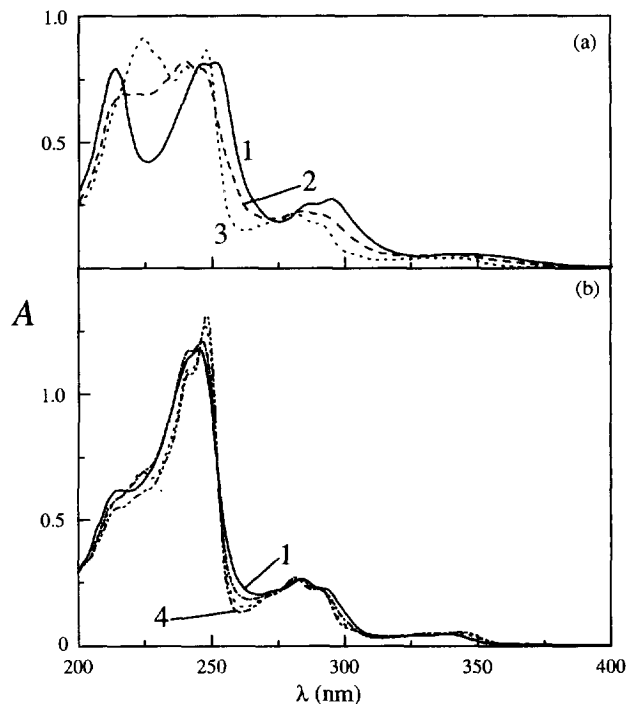


Fig. 3. Absorption spectra of 2-NGA (50 μ M) prior to (1) and after irradiation ($\lambda_{irr} = 280$ nm) in argon-saturated (a) neat acetonitrile and (b) in the presence of 1% H_2O ; 2, 3 and 4: 3×10^{-7} , 5×10^{-6} and 1×10^{-5} moles absorbed quanta, respectively.

Φ is not significant although a tendency to decreased quantum yields with lower pH is observed (Table 1).

Irradiation of air-saturated solutions results in a drastic decrease of Φ_d : extremely low (0.001) in neat acetonitrile, only 1–4% of the values obtained with argon saturation at 0–5% H_2O , but still 10–50% at 10–25% H_2O (Table 1). This means that the intensifying effect of water on Φ_d remains observable even under air atmosphere. Inspection of the conversion (decomposition of 1- or 2-NGA and formation of the naphthaldehydes and naphthoic acids) versus irradiation

Table 1
Quantum yield of photodecomposition of 1- and 2-naphthylglyoxylic acids^a

%H ₂ O	1-NGA				2-NGA			
	Argon		Air		Argon		Air	
	280 nm	336 nm	280 nm	336 nm	280 nm	336 nm	280 nm	336 nm
0 ^b	0.080	0.086	0.001	0.001	0.05	0.03	0.001	0.002
1.0	0.17	0.33	0.008	0.005	0.27	0.22	0.002	0.004
2.5	0.25	0.36	0.005	0.005	0.23	0.28	0.002	0.004
5.0	0.26	0.40	0.011	0.012	0.27	0.34	0.003	0.005
10	0.29	0.46	0.031	0.044	0.28	0.37	0.007	0.011
25	0.18	0.27	0.091	0.16	0.32	0.36	0.04	0.091
100 (pH 2)	0.021	0.014	c	c	0.011	0.003	c	c
100 (3–4)	0.015	0.018	c	c	0.035	0.030	c	c
100 (10)	0.026	0.018	c	c	0.041	0.028	c	c

^aIn argon- or air-saturated solution at 25°C; H₂O: vol. %.

^b0.002–0.003% water.

^c $\Phi < 0.03$.

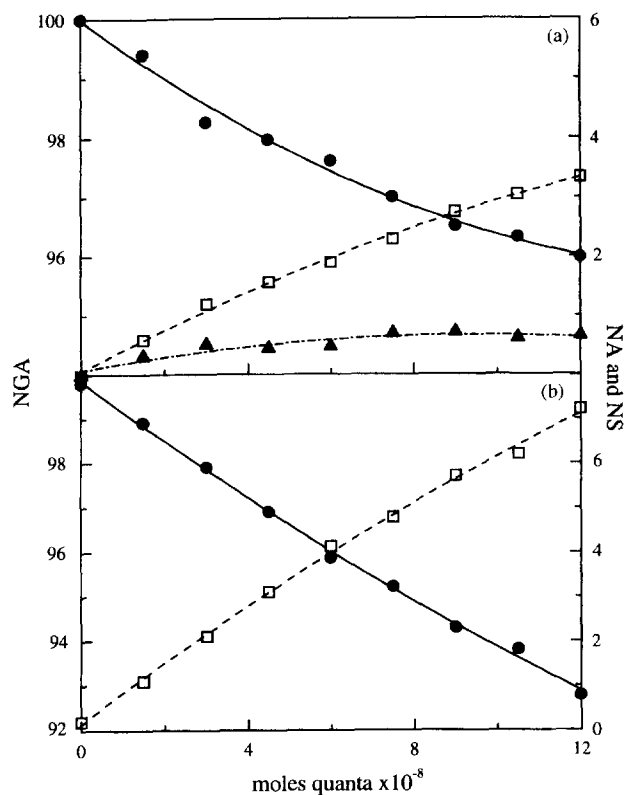


Fig. 4. Photolysis ($\lambda_{irr} = 336$ nm) of 1-NGA (\bullet , 250 μ M) and formation of 1-NA (\square) in argon-saturated acetonitrile in the presence of (a) 1% H₂O (\blacktriangle , formation of 1-NS) and (b) 10% H₂O.

dose diagrams for air-saturated conditions shows slight curvatures indicating an acceleration with light dose.

Carbon dioxide could be detected by GC both in the presence and absence of water as a major product of both naphthylglyoxylic acids. The quantum yields, however, do not conform well to those obtained by HPLC. At least partly, this may be due to experimental problems at the low concen-

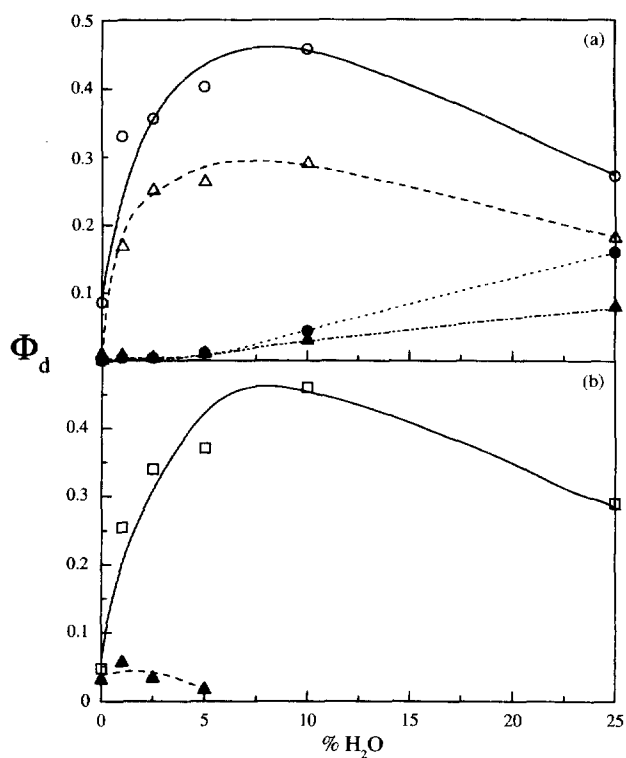


Fig. 5. Quantum yields of (a) photodecomposition of 1-NGA (250 μ M) in argon- and air-saturated H₂O/CH₃CN mixtures (open and full symbols, respectively; $\lambda_{irr} = 280$ and 336 nm, triangles and circles, respectively) and (b) of formation of 1-NA (\square) and 1-NS (\blacktriangle) at $\lambda_{irr} = 336$ nm under argon.

trations applied. The quantum yields of formation of naphthoic acids are lowest for 0% water and higher for 1-NS compared with 2-NS (Table 2). The naphthils are formed with quantum yields of 0.005–0.02 at both wavelengths (under argon), and in even smaller amounts at 1–10% water content.

Table 2
Quantum yields of formation of naphthaldehydes and naphthoic acids^a

%H ₂ O	1-NA		1-NS		2-NA		2-NS	
	280 nm	336 nm	280 nm	336 nm	280 nm	336 nm	280 nm	336 nm
0 ^b	0.055	0.047	0.048	0.031	0.018	0.016	0.024	0.017
1.0	0.14	0.28	0.015	0.074	0.15	0.14	0.060	0.036
2.5	0.24	0.34	0.021	0.033	0.16	0.185	0.065	0.050
5.0	0.24	0.37	0.018	0.017	0.19	0.195	0.077	0.036
10	0.29	0.46	0.050	— ^c	0.25	0.30	— ^c	0.039
25	0.18	0.29	— ^c	— ^c	0.23	0.285	— ^c	0.043

^aIn argon-saturated solution at 25°C.

^b0.002–0.003% water.

^c $\Phi \leq 0.01$.

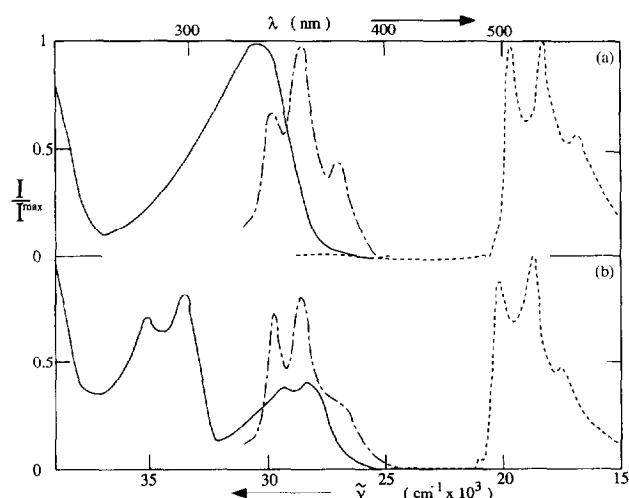


Fig. 6. Emission and excitation spectra (broken and full lines, respectively) of (a) 1-NGA and (b) 2-NGA in ethanol at -196°C ($\lambda_{\text{exc}} = 254$ nm, $\lambda_{\text{p}} = 520$ nm).

3.2. Fluorescence and phosphorescence

The emission and corresponding excitation spectra of the two naphthylglyoxylic acids in glassy ethanol at -196°C are shown in Fig. 6. The emission spectra reveal two well-separated parts. For energetic reasons the band in the 300–400 nm range is to be attributed to fluorescence and that above 500 nm to phosphorescence. This is supported by kinetic results (see below). While the maximum of the fluorescence band is similar for both naphthylglyoxylic acids, the phosphorescence maximum of 2-NGA is displaced to shorter wavelengths than that of 1-NGA (Tables 3 and 4). In particular, the phosphorescence maxima of the naphthylglyoxylic acids are markedly red-shifted compared to phenylglyoxylic acids [12]. From the onset of the phosphorescence, triplet energies of 259, 242 and 234 kJ mol^{-1} were derived for phenylglyoxylic acid, 2-NGA and 1-NGA, respectively.

The quantum yields of fluorescence (Φ_{f}) and phosphorescence (Φ_{p}) are listed in Tables 3 and 4 for various conditions. At room temperature the main emission of the naphthylglyoxylic acids in all solvents used is fluorescence ($\lambda_{\text{max}} \approx 350$ –

Table 3
Fluorescence maxima and quantum yield of NGAs in glassy and fluid media^a

Compound	Solvent	Temp. ($^{\circ}\text{C}$)	λ_{f} (nm)	Φ_{f}	
1-NGA	butyronitrile	-196	339,355	0.02	
	ethanol	-196	338,352	0.02	
	EG/H ₂ O	pH 4	-196	354	
		pH 0.5	-196	354	
		acetonitrile	25	350	0.006
2-NGA	water	pH 4	25	346	0.006
		pH 0.5	25	343	
	butyronitrile	-196	336,352	0.005	
	ethanol	-196	338,353	0.006	
	EG/H ₂ O	pH 4	-196	353	
pH 0.5		-196	353		
	acetonitrile	25	355	0.009	
	water	pH 4	25	354	0.006
		pH 0.5	25	351	

^aIn aerated solution; EG/H₂O: ethylene glycol/water (2:1, vol.), pH refers to neat water; $\lambda_{\text{exc}} = 265$ and 313 nm at 25 and -196°C ; Φ_{f} is not corrected for changes in the refractive index and quenching by oxygen ($\leq 30\%$).

Table 4
Phosphorescence maxima, quantum yield and lifetime of NGAs in glassy media^a

Compound	Solvent	λ_{p} (nm)	Φ_{p}	τ_{p} (s)	
1-NGA	butyronitrile	514,555,597sh	0.2	0.3	
	ethanol	515,554,597sh	0.3	0.23	
	EG/H ₂ O	pH 4	517,552,600sh	0.2	0.2
pH 0.5		520,556	0.2	0.2	
2-NGA	butyronitrile	490,526,568sh	0.5	0.7	
	ethanol	488,526,565sh	0.6	0.68	
	EG/H ₂ O	pH 4	497,530,570sh	0.4	0.7
		pH 0.5	500,535	0.4	0.6

^aIn aerated solution at -196°C , $\lambda_{\text{exc}} = 313$ nm.

370 nm). In glassy media at -196°C Φ_{p} is larger for 2-NGA than for 1-NGA. On the other hand, Φ_{p} is much larger than Φ_{f} which is rather small both at 25 and -196°C . This points to the importance of photoprocesses involving a triplet state.

The fluorescence lifetime (τ_f) of both naphthylglyoxylic acids in ethanol at 25°C is in the range of 2–3 ns; at –196°C two components with $\tau_f \leq 1$ and ≈ 30 ns were observed. The fluorescence intensity at ≈ 350 nm of both naphthylglyoxylic acids in acetonitrile at room temperature decreases with increasing oxygen concentration, the change between oxygen- or air-saturated solution and argon-saturated solution is about 0.45 or 0.77, respectively. This is matched by a two-fold decrease in the triplet yield (see below) on going from argon to oxygen saturation.

The phosphorescence lifetime (τ_p) of the naphthylglyoxylic acids at –196°C is in the 0.2–0.7 s range. This is two orders of magnitude longer than that of phenylglyoxylic acid [12]. Changing pH from 0.5 to 4 in a 2:1 mixture of ethylene glycol and water has no discernible effect on λ_p , Φ_p and τ_p ; the values are practically the same as in butyronitrile or ethanol. An example for the monoexponential decay is shown in Fig. 7 (inset) for 1-NGA in butyronitrile at a slightly higher temperature. The temperature dependence of the phosphorescence could be measured only in the range of high viscosities. Plots of τ_p^{-1} vs. T^{-1} show a variation with temperature and level off below ca. –160°C (Fig. 7).

3.3. Transient absorption

For the two naphthylglyoxylic acids in several organic solvents at room temperature two transients were detected by laser flash photolysis. Examples of the time-resolved transient absorption spectra in acetonitrile are shown in Fig. 8. The main transient, showing a broad absorption spectrum with a maximum around 540 nm for 1-NGA and $\lambda_{\max} = 430$ nm for 2-NGA is assigned to a triplet state. For comparison, λ_{\max} of 1- and 2-NA is around 490 and 440 nm, respectively [30–33], i.e., a blue-shift of the maximum of the T–T absorption spectrum has also been reported for 2- versus 1-NA. In addition, a bleaching was recorded for 1-NGA in the 300–340 nm range.

The triplet is formed within the laser pulse width and decays by mixed first- and second-order kinetics, the second-order component could be reduced by using a low laser intensity. Some spectral and kinetic properties of the triplet are compiled in Table 5. The half-life of the triplet decay in argon-saturated solution is about 2–5 μ s under our conditions and is limited by self-quenching. Variation of the excitation wavelength (248, 308, and 354 nm) has virtually no effect on the T–T absorption spectrum, while the kinetic changes can be attributed to differences in the concentrations which were generally higher for longer λ_{exc} . The triplet was also detected for both naphthylglyoxylic acids in neat 2-propanol where ketones generally exhibit H-atom abstraction. For 2-NGA in ethanol ΔA_{430} ($\lambda_{\text{exc}} = 248$ nm) was found to be almost the same at 25 and –185°C, indicating that temperature has only a small effect on the triplet yield. Moreover, ΔA_{430} is the same under optically matched conditions in ethanol and acetonitrile.

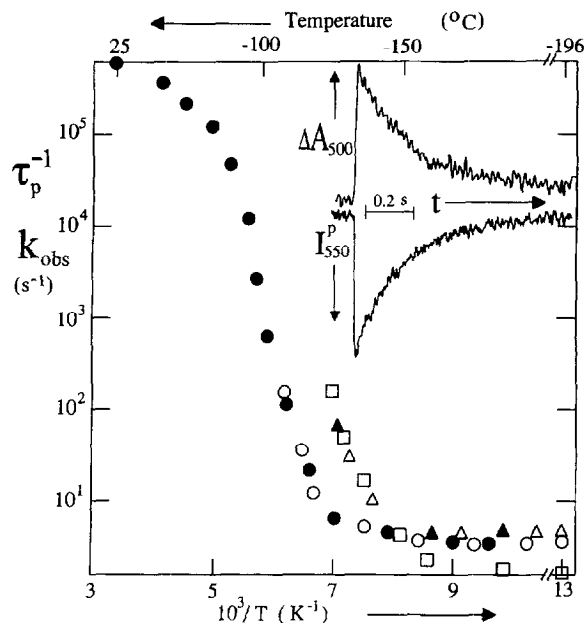


Fig. 7. Temperature dependence of the rate constant for triplet decay (full symbols) and the reciprocal phosphorescence lifetime (open symbols) for 1-NGA (Δ , \blacktriangle) and 2-NGA (\square) in ethanol ($\lambda_{\text{exc}} = 354$ nm) and 1-NGA in butyronitrile (\circ , \bullet , $\lambda_{\text{exc}} = 248$ nm); inset: triplet decay of 1-NGA in ethanol at –168°C monitored by emission and absorption.

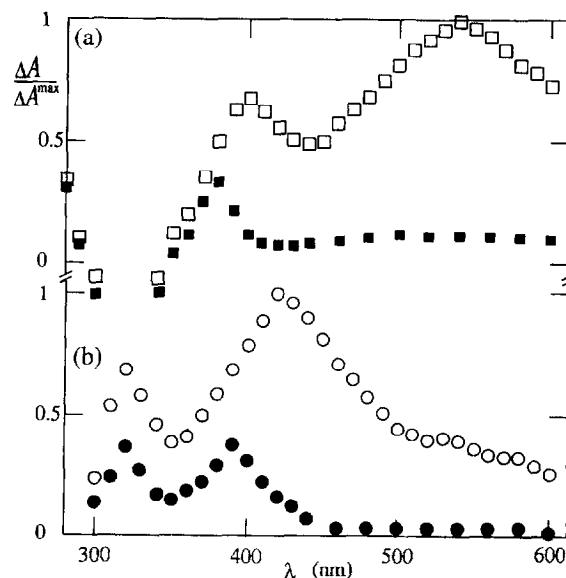


Fig. 8. Transient absorption spectra of (a) 1-NGA and (b) 2-NGA in argon-saturated acetonitrile 0.1 μ s (open symbols) and 10 μ s (full symbols) after the 248 nm pulse.

Quenching measurements by oxygen and 1,3-cyclohexadiene support the triplet nature for both naphthylglyoxylic acids. The rate constant for triplet quenching by oxygen in several solvents at room temperature is approximately 3×10^9 $\text{M}^{-1} \text{s}^{-1}$ and that by 1,3-cyclohexadiene is nearly diffusion-controlled (Table 5). The assignment to a triplet state is in agreement with energy transfer measurements. Application of thioxanthone-sensitized excitation at 354 nm in acetonitrile reveals the above triplet as the remaining transient (using

Table 5
Properties of the triplet state of NGAs observed by laser flash photolysis^a compound solvent

Compound	Solvent	λ_{exc} (nm)	λ_{T} (nm)	$t_{1/2}$ (μs)	k_{ox} ($\text{M}^{-1} \text{s}^{-1} \times 10^9$)
1-NGA	acetone	354	520	≈ 2	
	acetonitrile	354	400,530	> 2	2 (10) ^b
		308	400,530	> 2	2 (10) ^b
		248	400,540	> 2	
		308	400–540	> 2	3
	2-propanol	248	400,530	≥ 5	3
acetonitrile/H ₂ O ^c	248	400,540	2		
2-NGA	acetone	354	420	> 4	3
	acetonitrile	308	440	≥ 5	2
		248	430	> 3	2.5
		308	420	> 4	2.5
	2-propanol	308	440	> 4	3
	acetonitrile/H ₂ O ^c	248	420	3	

^aIn argon-saturated solution at 24°C.

^bValues in parentheses refer to 1,3-cyclohexadiene as quencher.

^c(9:1).

[NGA] ≥ 1 mM) (not shown), its extinction coefficient for 1-NGA being about 1/5 of that ($3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ [33]) of the thioxanthone triplet at 640 nm. The triplet yield of 1- and 2-NGA in acetonitrile is estimated to be 0.7 and 0.5, respectively. This follows from a comparison of the ΔA values at the maximum with benzophenone in benzene ($\epsilon_{520} = 7.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ [33]) under otherwise equal conditions ($A_{354} = 2.0$), using $\epsilon_{435} = 6 \times 10^3$ and $\epsilon_{535} = 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ for 1- and 2-NGA, respectively. This coincides with the above estimate for 2-NGA from T-T absorption and phosphorescence.

Upon direct excitation of 1 or 2-NGA, also a minor (longer lived) transient (radical: R) appears in several solvents in the absence of oxygen. The spectra in acetonitrile show $\lambda_{\text{max}} = 380$ nm for 1-NGA and 325 and 390 nm for 2-NGA (Fig. 8). R decays essentially by second-order kinetics (half-life $t_{1/2} \geq 10 \mu\text{s}$) and $t_{1/2}$ is reduced by oxygen. The yield of R is not much different in 2-propanol compared to acetonitrile which is significantly less reactive. This is evidence against H-atom abstraction from the solvent. Because of spectral overlap of R in the 320–400 nm range with the triplet state, it cannot be distinguished kinetically whether or not R is formed within the laser pulse, i.e., from a singlet or triplet state. However, in the presence of 1,3-cyclohexadiene in a concentration sufficient to quench 50–80% of the triplet lifetime, the decay of R is not markedly affected by the triplet quencher but its yield is reduced instead. This excludes a triplet nature of R and indicates a radical.

When the naphthylglyoxylic acids were excited at 248 nm in neat aqueous solution at pH 4, mainly the hydrated electron was detected. Its identity is based on the well-known absorption spectrum ($\lambda_{\text{max}} = 715$ nm) and the effects of additives such as N₂O and oxygen which strongly reduce its lifetime, cf. [12]. Control measurements showed that no hydrated electron was observable at excitation wavelengths 354 or 308 nm. In aqueous solution, different to organic solvents, prac-

tically no triplet could be detected. In mixtures of acetonitrile with water it was found that the triplet yield (as measured by ΔA at λ_{T}) decreases with increasing [H₂O]; for 1- and 2-NGA the effect is similar, $\approx 10\%$ and 50% for 10% and ca. 35% H₂O, respectively. This feature of the triplet of the naphthylglyoxylic acids is reminiscent to that of phenylglyoxylic acid. However, water affects the lifetime of the 1- or 2-NGA triplet only moderately (k_{obs} increases by $\leq 50\%$ on going from 0 to 10% water), while this reaction is more efficient for phenylglyoxylic acid [12].

3.4. Formation and decay of singlet molecular oxygen

Formation of O₂(¹ Δ_{g}) was detected upon 353 nm excitation of 1- and 2-NGA in oxygen-saturated solution. The quantum yield (Φ_{Δ}) was obtained from the linear dependences of the initial phosphorescence signals on the incident laser intensity. The Φ_{Δ} values are 0.35, 0.75 and 0.65 for 1-NGA and 0.33, 0.62 and 0.55 for 2-NGA in butyronitrile, acetonitrile and ethanol, respectively. This indicates both efficient triplet population (in agreement with the absorption measurements in Section 3.3) and energy transfer to oxygen.

3.5. Time-resolved conductivity

Transient conductivity measurements in water at pH = 9–12 show a decrease in the signal amplitude ($\Delta\kappa$) after the laser pulse (Fig. 9). The decay kinetics are pH-dependent in a characteristic way, as already found for phenylglyoxylic acid [12]. The rate constant increases from $k(\Delta\kappa) \approx 0.7 \text{ s}^{-1}$ at pH 10 to about 60 s^{-1} at pH 12. The decrease in $\Delta\kappa$ within seconds is ascribed to the formation of hydrogen carbonate which has a smaller equivalent conductivity than OH⁻



The obtained rate constant for this reaction is $k_2 =$

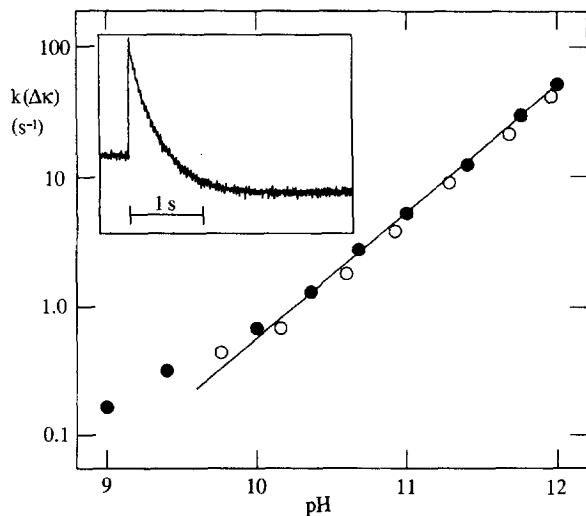


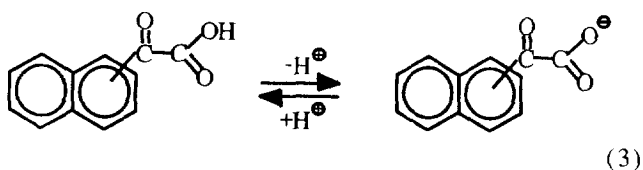
Fig. 9. Rate constant for the slow conductivity decrease of 1-NGA (●) and 2-NGA (○) in argon-saturated aqueous solution versus pH; $\lambda_{\text{exc}} = 248 \text{ nm}$; inset: signal for 1-NGA at pH = 11.

$(6 \pm 1) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in agreement with the literature value of $6.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [34].

4. Discussion

4.1. Ground state

As for phenylglyoxylic acid [12] the photochemistry of the naphthylglyoxylic acids in aqueous solution is governed by the equilibrium between the acid and the corresponding base in the ground state, Eq. (3).



The $\text{p}K_{\text{a}}$ of both naphthylglyoxylic acids is around 1.2, compared to 1.1 for phenylglyoxylic acid [12]. Apart from this, the photochemical properties (spectra, lifetimes and yields) of the excited states of the naphthylglyoxylic acids are quite different from those of phenylglyoxylic acid and its 4-substituted derivatives.

4.2. Emission from excited singlet and triplet states

Fluorescence occurs in low yield both at 25 and -196°C (Table 3). The acid or anion nature of the excited singlet state has no marked effect on λ_{f} and Φ_{f} . For 2-NGA in glassy media intersystem crossing is the main deactivation step of ^1NGA . This follows from the rather large value of Φ_{p} (Table 4) which is a lower limit for the quantum yield of intersystem crossing (Φ_{isc}) due to relationship (4a) and (4b),

$$\Phi_{\text{isc}} = \Phi_{\text{p}} / \tau_{\text{p}} \times k_{\text{p}} \quad (4a)$$

$$\tau_{\text{p}} = 1 / (k_{\text{p}} + k_{\text{nr}}) \quad (4b)$$

where k_{p} and k_{nr} are the rate constants for the radiative and non-radiative triplet decay, respectively. Assuming that internal conversion from the excited singlet state can be neglected it follows from $\Phi_{\text{p}} = 0.4\text{--}0.6$ and $\tau_{\text{p}} = 0.6\text{--}0.7 \text{ s}$ that $k_{\text{p}} = 0.8 \text{ s}^{-1}$ and $k_{\text{nr}} = 0.8 \text{ s}^{-1}$ for 2-NGA. The shorter phosphorescence lifetime and the smaller Φ_{p} value for 1-NGA could lead to the assumption that k_{p} is similar for both and k_{nr} larger for 1-NGA, e.g., 3 s^{-1} .

Intersystem crossing is also suggested to be the main deactivation step of the excited singlet state at room temperature since the estimated triplet yield of both naphthylglyoxylic acids in acetonitrile is 0.5–0.7 (see Section 3.3). Keeping in mind that the triplet lifetime changes in this range from approximately $5 \mu\text{s}$ to 0.2–0.7 s, it is not surprising that practically no phosphorescence could be measured at room temperature; the estimation leads to $\Phi_{\text{p}} \leq 10^{-5}$. This differs significantly from phenylglyoxylic acid where phosphorescence is observable in acetonitrile at 25°C [12].

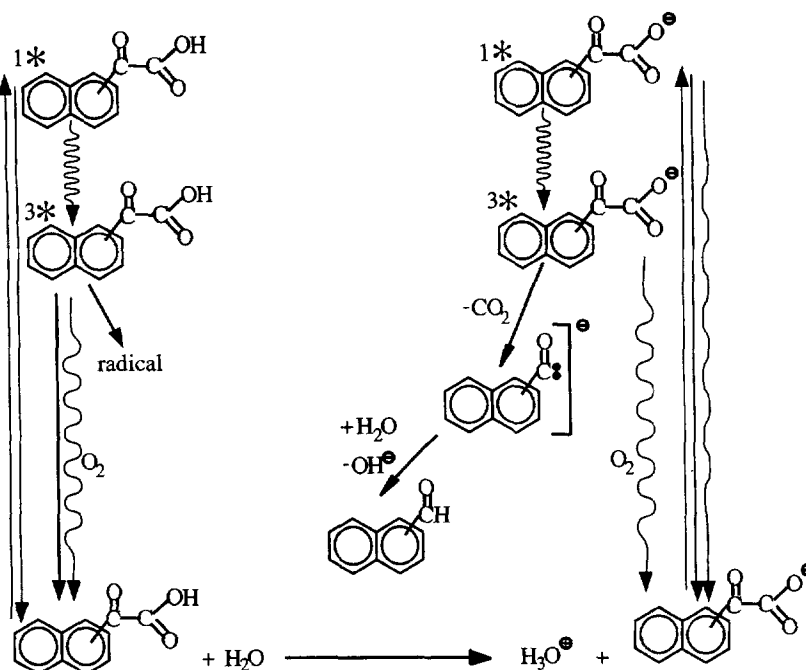
4.3. Transients

The main transient (Fig. 8 and Table 5) is assigned to the lowest triplet state of the naphthylglyoxylic acids on the basis of energy transfer from triplet thioxanthone in acetonitrile and quenching measurements in several organic solvents at room temperature. The rate constant for quenching by 1,3-cyclohexadiene is nearly diffusion-controlled and that by oxygen is slightly smaller (Table 5). Moreover, the results shown in Fig. 7 are in line with this assignment since the same triplet lifetimes were obtained both in emission and absorption.

The nature of R is more difficult to reveal. Although the ratio of the yields of R and the triplet change somewhat with the solvent, there is indication for the formation of R in all deoxygenated organic solvents used. The rate constant for H-atom abstraction from alcohols is smaller than $2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ (the limiting value in 2-propanol). This and the small solvent effect of the yield of R differ from the case of phenylglyoxylic acid, where the α -carboxy- α -hydroxybenzyl radical is formed by H-atom abstraction from an alcohol [12]. If non-occurrence of H-atom abstraction from 2-propanol is anticipated for the naphthylglyoxylic acids, there is, however, still the possibility that H-atom abstraction occurs intramolecularly. Alternatively, R may be assigned to a naphthoyl radical.

4.4. Photochemical reactions

The photoconversion of 1-NGA into 1-NA (Fig. 5) and 2-NGA into 2-NA in deoxygenated aqueous acetonitrile solution are rather clean reactions (Tables 1 and 2). Decarboxylation is in accordance with the conductivity results in deoxygenated alkaline aqueous solution which indicate OH^-



elimination according to Scheme 1. The reactive intermediate is suggested to be a triplet state. The excited singlet state is excluded since Φ_d (Tables 1 and 2) is much larger than Φ_f (Table 3). Moreover, the significant quenching of Φ_d by oxygen is not in line with the much smaller effect on Φ_f .

The following conclusions can be drawn from the data in Tables 1 and 2. (1) Φ_d is similar for 1- and 2-NGA for virtually all conditions examined and the differences in values may be regarded as small. (2) A pronounced effect is the (10–20)-fold increase in Φ_d in deoxygenated acetonitrile with increasing water content up to maximum values of 0.3–0.4 in mixtures containing 5–20 M of water. (3) The enhancing effect of water is reflected in both quantum yields, decomposition of 1- or 2-NGA and formation of 1- or 2-NA, whereas that of formation of naphthoic acid is more or less independent of water. (4) The Φ values show a complete material balance. (5) Oxygen strongly reduces the photoconversion into naphthaldehydes, as Φ_d in air-saturated aqueous acetonitrile (<10% water) is only a few percent of the values in the absence of oxygen.

In order to account for the role of water we suggest that a prerequisite for an efficient photoconversion of the naphthylglyoxylic acids into naphthaldehydes is that 1- or 2-NGA are present as anions. Under these conditions photodecarboxylation occurs in substantial yield (Scheme 1). On the other hand, a too high concentration of water reduces this effect as the lifetime and yield of the observed triplet were found to be reduced on addition of water to acetonitrile solution. A remarkable effect is the wavelength dependence of Φ_d ; the quantum yields are generally larger for $\lambda_{irr} = 336$ nm than for 280 nm (Tables 1 and 2). One may hypothesize that the

reactive triplet state is a n, π state which is populated with higher efficiency at a longer irradiation wavelength.

The effect of oxygen on Φ_d is larger than one might expect on the basis of flash photolysis results since the product $k_{ox} \times [O_2]$ in air-saturated acetonitrile (Table 5) is ca. 3×10^6 s⁻¹, which, compared to a half-life of 2 μ s, would result in $\approx 90\%$ triplet quenching. The decay of the triplet under steady-state conditions, however, should not be limited by annihilation and therefore the amount of triplet quenching in air-saturated acetonitrile is probably larger and in agreement with that observed for Φ_d in the presence and absence of air (Table 1). This contrasts with the behaviour of phenylglyoxylic acid, where the triplet lifetime in aqueous acetonitrile is too short to be accessed by oxygen ($\tau_T = 44$ and < 20 ns for 10 and 20% water, respectively [12]), and thus no effect of oxygen on Φ_d was detected under these conditions [7,8].

Nevertheless, the results for the naphthylglyoxylic acids are compatible within the framework derived from a series of phenylglyoxylic acid and 4-substituted derivatives [12,13] in so far as Φ_d is strongly dependent on the percentage of water in other polar solvents such as acetonitrile or acetone. Radical reactions essentially account for the results in dry acetonitrile and heterolytic α -splitting (an ionic mechanism) accounts for the results in the presence of water. Interestingly, Krogh and Wan [35], studying the photodecarboxylation of diarylacetic acids in aqueous solution, have concluded that an ionic mechanism is involved where the C–C bond cleavage may be concerted with protonation from the solvent [35,36].

The parallels between phenylglyoxylic acid and the naphthylglyoxylic acids are the pK_a values, high quantum

yields of phosphorescence at -196°C (0.2–0.6) and intersystem crossing at 25°C and the characteristic maximum in the quantum yields of triplet population and decarboxylation in acetonitrile as a function of water concentration. The type of reaction mechanism changes from a radical one in the absence to an ionic one in the presence of water. The differences are the fluorescence, the influence of the wavelength of irradiation and the effect of oxygen on Φ_d for 1- and 2-NGA; the independence of oxygen for the photodecarboxylation of phenylglyoxylic acid in aqueous acetonitrile is due to the fast reaction of the triplet state with water which is much less reactive in the case of the naphthylglyoxylic acids.

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References

- [1] L. Claisen, Ber. Dtsch. Chem. Ges. 10 (1877) 844.
- [2] P.A. Leermakers, G.F. Vesley, J. Am. Chem. Soc. 85 (1963) 3776.
- [3] D.S. Kendall, P.A. Leermakers, J. Am. Chem. Soc. 88 (1966) 2766.
- [4] T. Fujisawa, B.M. Monroe, G.S. Hammond, J. Am. Chem. Soc. 92 (1970) 542.
- [5] T. Fujisawa, G.S. Hammond, J. Am. Chem. Soc. 94 (1972) 4175.
- [6] Y. Sawaki, Y. Ogata, J. Am. Chem. Soc. 103 (1981) 6455.
- [7] A. Defoin, R. Defoin-Straatmann, H.J. Kuhn, J. Labelled Comp. Radiopharm. 19 (1982) 891.
- [8] H.J. Kuhn, A. Defoin, EPA Newsletter, No. 26 (1986) 23.
- [9] W. Amrein, J. Gloor, K. Schaffner, Chimia 28 (1974) 185.
- [10] A. Defoin, R. Defoin-Straatmann, K. Hildenbrand, E. Bittersmann, D. Krefit, H.J. Kuhn, J. Photochem. 33 (1986) 237.
- [11] H.J. Kuhn, S.E. Braslavsky, R. Schmidt, Pure Appl. Chem. 61 (1989) 187.
- [12] H.J. Kuhn, H. Görner, J. Phys. Chem. 92 (1988) 6208.
- [13] H. Görner, H.J. Kuhn, XII IUPAC Symp. Photochem., Bologna (1988).
- [14] H. Görner, L.J. Currell, H.J. Kuhn, J. Phys. Chem. 95 (1991) 5518.
- [15] J. Cymerman-Craig, J.W. Loder, B. Moore, B. Austr. J. Chem. 9 (1956) 222.
- [16] D.R. Arnold, Adv. Photochem. 6 (1968) 301.
- [17] A.J.L. Cooper, J.Z. Ginos, A. Meister, Chem. Rev. 83 (1983) 321.
- [18] E. Adlerova, P. Vejdelhova, M. Protiva, Coll. Czech. Chem. Comm. 29 (1964) 97.
- [19] M. Gomberg, W.E. Bachmann, J. Am. Chem. Soc. 50 (1928) 2762.
- [20] M. Gomberg, F.J. van Natta, J. Am. Chem. Soc. 51 (1929) 2242.
- [21] J.D. Fulton, R. Robinson, J. Chem. Soc. (London) 1939, 200.
- [22] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 22 (1993) 113.
- [23] R.W. Redmond, S.E. Braslavsky, Chem. Phys. Lett. 148 (1988) 523.
- [24] G. Martinez, S.G. Bertolotti, O.E. Zimmerman, D.O. Mártire, S.E. Braslavsky, N.A. Garcia, J. Photochem. Photobiol. B: Biol. 17 (1993) 247.
- [25] R.D. Scurlock, S. Nonell, S.E. Braslavsky, P.R. Ogilby, J. Phys. Chem. 99 (1995) 3521.
- [26] R. Schmidt, E. Afshari, J. Phys. Chem. 94 (1990) 4378.
- [27] A.P. Darmanyan, Chem. Phys. Lett. 215 (1993) 477.
- [28] A. Defoin, R. Defoin-Straatmann, H.J. Kuhn, Tetrahedron 40 (1984) 2651.
- [29] H. Görner, H.J. Kuhn, J. Phys. Chem. 90 (1986) 5946.
- [30] B.W. Boldridge, B.L. Justus, G.W. Scott, J. Chem. Phys. 80 (1984) 3179.
- [31] A.M.J. van Eijk, P.F.A. Verhey, A.H. Huizer, C.A.G.O. Varma, J. Am. Chem. Soc. 109 (1987) 6635.
- [32] A. Samanta, R.W. Fessenden, Chem. Phys. Lett. 153 (1988) 406.
- [33] I. Carmichael, G.L. Hug, Phys. Chem. Ref. Data 15 (1986) 1.
- [34] M.N. Schuchmann, C. von Sonntag, Z. Naturforsch. 37b (1982) 1184.
- [35] E. Krogh, P. Wan, J. Am. Chem. Soc. 114 (1992) 705.
- [36] P. Wan, D. Budac, Chap. 31, in: W.M. Horspool, Pill-Soon Song (Eds.), CRC Handbook of Organic Photochemistry and Photobiology, CRC Press, Boca Raton, 1995, pp. 384.