

Laser flash photolysis study of *N*-alkylated phthalimides

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Abstract

The photophysical and photochemical properties of *N*-phthaloylvaline methyl ester (**2**) in comparison with *N*-methylphthalimide (**1a**) and *N*-propylphthalimide (**1b**) were studied by nanosecond laser flash photolysis ($\lambda_{\text{exc}} = 248$ or 308 nm). The quantum yield of fluorescence of the three compounds is low ($\Phi_{\text{f}} = 10^{-2}$), whereas that of phosphorescence at -196°C is large (0.3–0.7). The triplet properties were examined in several solvents at room temperature and in ethanol at low temperatures. Formation of singlet molecular oxygen $\text{O}_2(^1\Delta_{\text{g}})$ was observed in several air- or oxygen-saturated solvents at room temperature; the quantum yield is substantial (up to 0.7) for **1a** and only slightly smaller ($\Phi_{\Delta} = 0.3\text{--}0.5$) for **2**. Triplet acetone, acetophenone and xanthone in acetonitrile are quenched by **1** and **2** via energy transfer, the rate constant is almost diffusion-controlled and smaller for benzophenone. Product formation in preparative photolysis was not observed for **1a** or **1b**, whereas **2** (in the absence of a sensitizer) mainly gives a product of photoisomerization and two cyclization products in minor amounts. Formation of these products via the observed π,π triplet state is unlikely and an upper excited n,π triplet pathway is, therefore, proposed. ©1999 Elsevier Science S.A. All rights reserved.

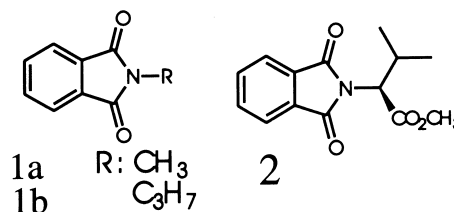
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1. Introduction

The photochemistry of *N*-alkylated phthalimides has been intensively investigated [1–10] and major aspects of the synthetic work have been reviewed [11–14]. The phthalimide chromophore is the subject of various intra- and intermolecular photoprocess studies [14–21]. Some photophysical properties of several *N*-substituted phthalimides have been reported [22–31]. Charge separation occurs either upon direct irradiation or after energy transfer in the presence of acetone or benzophenone [1–21]. The initial species upon excitation of a given ketone (K) in inert solvents is its triplet state ($^3\text{K}^*$) [32–53] and in addition to energy transfer from $^3\text{K}^*$ to the acceptor molecule, electron transfer to $^3\text{K}^*$ may occur, i.e. both are, in principle, competing processes. Examples for energy versus electron transfer are ketones and sulfur-containing amino acids [41–50] or DNA bases [51,52].

In this paper we studied the photochemistry of methyl (*S*)-3-methyl-2-phthalimidobutanoic acid (*N*-phthaloylvaline methyl ester: **2**) in comparison with *N*-methylphthalimide (**1a**) and *N*-propylphthalimide (**1b**) by time resolved spectroscopy (Chart 1). The objective is towards a better understanding of the photophysical and photochemical reactions

involved. Formation of singlet molecular oxygen from triplet excited phthalimides was observed. The quantum yield of $\text{O}_2(^1\Delta_{\text{g}})$ formation (Φ_{Δ}) was determined in several solvents and compared with the quantum yields of triplet formation (Φ_{T}) and decomposition (Φ_{d}) obtained under comparable conditions. Energy transfer measurements to the triplet states of phthalimides were carried out with acetone, acetophenone, xanthone and benzophenone in aqueous solution, acetonitrile or their mixtures.



2. Experimental details

N-methylphthalimide (**1a**, EGA) and **1b** were purchased and (*S*)-*N*-phthaloylvaline methyl ester (**2**) is the same as used previously [iv]. The molar absorption coefficients of **2** [5], **1a** and **1b** in acetonitrile are $\epsilon_{294} = 1.3 \times 10^3$,

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$\varepsilon_{295} = 1.5 \times 10^3$ and $\varepsilon_{296} = 1.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, respectively. The sensitizers and solvents (Merck) were used as commercially available, e.g. dichloromethane; acetone and acetonitrile were Uvasol quality; ethanol was purified by distillation and water was deionized by a millipore (Milli Q) system. Absorption and emission spectra were recorded on a spectrophotometer (Perkin–Elmer, 554) and spectrofluorimeters (Perkin–Elmer, LS5 and Spex-Fluorolog), respectively. The 248 or 308 nm output of two excimer lasers (Lambda Physik, EMG 200 and EMG 210 MSC; energy below 100 mJ, pulse width 20 ns) was used for excitation. The laser flash photolysis apparatus and the detection system have been described elsewhere [53].

Phosphorescence of singlet molecular oxygen at 1269 nm [54–61] was detected after the pulse using a cooled Ge detector (North Coast, EO 817FP), a silicon and interference filter and an amplifier (Comlinear, CLC-103) as described elsewhere [54,55]. The signal, which can be overlapped by fluorescence and/or scatter, was extrapolated to the end of the 20 ns pulse (I_{Δ}). At a fixed laser intensity (I_b , I_{Δ}) was found to show a linear dependence on the absorbed energy, being proportional to $(1-10^{-A})$, and on I_L with a curvature at higher intensities; the slope of the latter plot is denoted as Q_{Δ} . The quantum yield of formation of $\text{O}_2(^1\Delta_g)$ in toluene was obtained from Q_{Δ} values using optically matched solutions ($A_{308} = 0.8$) and acridine as reference $\Phi_{\Delta}^{\text{ref}} = 0.71$ [56,57]. For the values in other oxygen-saturated solvents a correction has to be applied using the rate constant k_r for radiative deactivation of $\text{O}_2(^1\Delta_g)$ relative to that in benzene (k_r°).

$$\Phi_{\Delta} = \Phi_{\Delta}^{\text{ref}} \left(\frac{Q_{\Delta}}{Q_{\Delta}^{\text{ref}}} \right) \left(\frac{k_r^{\circ}}{k_r} \right) \quad (1)$$

The k_r/k_r° ratios in toluene, dichloromethane, acetonitrile, ethanol and D_2O are 0.96, 0.75, 0.30, 0.23 and 0.12, respectively [59–61].

For photodecomposition $\lambda_{\text{irr}} = 290 \text{ nm}$ of a 1000 W Xe-Hg lamp combined with a monochromator or 254 nm from a low pressure Hg lamp were used. The concentration was adjusted such that the absorbance (in a 1 cm cell) was 1–3 at λ_{irr} . The relative quantum yield of decomposition was obtained by using the decrease in absorbance at 290 nm (or the increase in absorbance at the initial minimum at $\approx 250 \text{ nm}$). Actinometry was performed with either aberchrome 540 or ferrioxalate for $\lambda_{\text{irr}} = 290 \text{ nm}$ [62,63]. The measurements (unless otherwise specified) were carried out after purging with argon prior to and during irradiation at $24 \pm 2^{\circ}\text{C}$.

3. Results

3.1. Emission

The compounds under examination have a *N*-phthalimide chromophore which has two maxima around 220 and 295 nm (Fig. 1) and absorbs most of the UV light.

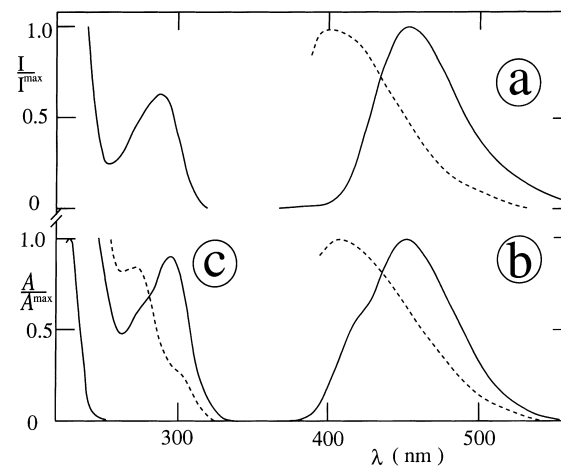


Fig. 1. Fluorescence, phosphorescence (right) and phosphorescence excitation (left) spectra in ethanol at 24 and -196°C (broken and full lines, respectively) of (a) **1a** and (b) **2**; $\lambda_{\text{exc}} = 290 \text{ nm}$. (c) Absorption spectra of **2** in argon-saturated aqueous solution at 24°C prior to (full line, left $\times 10$) and after irradiation at 290 nm (broken line).

Table 1

Fluorescence and phosphorescence maxima, quantum yields and phosphorescence lifetime of phthalimide derivatives^a

Compound	Solvent	λ_f (nm)	$\Phi_f (\times 10^3)$	λ_p (nm)	Φ_p	τ_p (s)
1a	MeCN	<420	<0.6 [0.8] ^b			
	EtOH	<405	<0.5	450	0.6	0.75 (0.6) ^c
	H ₂ O	425	6			
1b	EtOH	<400	<0.5	453	0.7	
	H ₂ O	420	0.5 [25] ^d			
2	EtOH	<400	<0.2	450	0.5	0.85
	H ₂ O	415	2			

^a In air-saturated solution at 24 and -196°C for fluorescence and phosphorescence, respectively.

^b Taken from ref. [31].

^c Value in parenthesis: triplet lifetime (absorption) at -170°C .

^d Taken from ref. [24].

N-alkylphthalimides in solution at room temperature exhibit fluorescence (Fig. 1a and b) with a low quantum yield (Φ_f). For **1** and **2** in ethanol or acetonitrile the limit of Φ_f is below 1×10^{-3} . Φ_f is larger in aqueous solution than in acetonitrile or ethanol. For these cases the emission maximum is around 420 nm and the fluorescence excitation spectrum is similar to that of absorption. Even in aqueous solution Φ_f is low for **1b** and increases for **1a** and **2** (Table 1).

The phosphorescence spectra of **1a** and **2** in ethanol at -196°C are shown in Fig. 1a and b, respectively. They have a maximum at ca. 450 nm and an onset at $\approx 405 \text{ nm}$, corresponding to a triplet energy of $E_T = 293 \text{ kJ mol}^{-1}$. The quantum yield is $\Phi_p = 0.5\text{--}0.7$ (Table 1). The phosphorescence excitation and absorption spectra coincide. The decay follows a first-order law below -150°C and the phosphorescence lifetime is ca. 0.8 s at -196°C . These results are in agreement with literature data for *N*-phthalimides, e.g. $\tau_p \approx 1 \text{ s}$ and $E_T = 286\text{--}297 \text{ kJ mol}^{-1}$ [22–24].

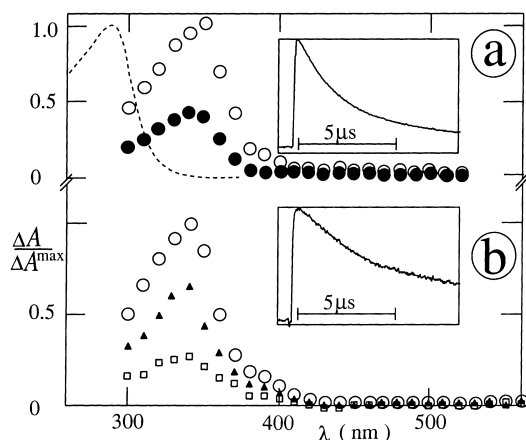


Fig. 2. Transient absorption spectra in argon-saturated acetonitrile (in the absence of additives) of (a) **1a** at 30 ns (○) and 5 μ s (●) after the 248 nm pulse, $A_{248} \approx 2$, and (b) **2** at 30 ns (○), 3 μ s (▲) and 10 μ s (□); insets: decay kinetics at 350 nm.

Table 2
Properties of the triplet state of phthalimide derivatives^a

Compound	Solvent	λ_{\max} (nm) ^b	τ_T (μ s)	k_{ox} ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	Φ_T ^c
1a	dioxane	<u>350</u> , 640	5	0.2	
	CH ₂ Cl ₂	<u>340</u> , 600	(1.2)	(0.3)	(0.8) ^d
	MeCN	<u>350</u> , 560	5	1.4	0.8 ^e
	EtOH	345	9	1.1	0.4
	H ₂ O	345	10	1	0.2
1b	MeCN	345	10	1.4	0.7
	EtOH	340 ^f	15	1.2	0.4
	H ₂ O	340	20	1.3	0.5
2	dioxane	<u>340</u> , 640	2	0.8	
	MeCN	340	9	1.2	0.5
	EtOH	335	9	1.2	0.4
	H ₂ O	340	10	1.2	0.2

^a In argon-saturated solution at room temperature, $\lambda_{\text{exc}} = 248$ nm.

^b Max. underlined.

^c Using $\Phi_T = 0.8$ for **1a** in acetonitrile.

^d Values in parentheses refer to $\lambda_{\text{exc}} = 308$ nm.

^e Using **1a** in acetonitrile as reference.

^f Remaining transient at 320–350 nm.

3.2. Triplet state properties

Coyle et al. [23] have carried out flash photolysis of several *N*-substituted phthalimides. The T-T absorption spectra exhibit $\lambda_{\max} < 350$ nm, level off at ca. 400 nm and extend weakly to ca. 600 nm. The triplet lifetime in oxygen-free ethanol is $\tau_T = 10$ –40 μ s. The triplet state of **1a** with $\lambda_{\max} = 350$ nm and a much weaker band around 600 nm was monitored using $\lambda_{\text{exc}} = 248$ nm (Fig. 2a) or $\lambda_{\text{exc}} = 308$ nm. The triplet lifetime of **1a** in argon-saturated solution is in the 5–10 μ s range (Table 2). The rate constants for quenching of the triplet state of **1a** by oxygen in ethanol, acetonitrile and water are $k_{\text{ox}} = (1.0$ – $1.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. They are smaller than the published value of $k_{\text{ox}} = 3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [23]. A weak long lived transient with $\lambda_{\max} = 380$ nm was registered for **1a** and **2** in argon-saturated ethanol. It is absent in acetonitrile and may, therefore, be due to the ketyl radical.

Table 3
Quantum yield of singlet molecular oxygen, Φ_{Δ} ^a

Compound	1a	1b	2
Toluene	0.42 (0.30)	0.41 (0.32)	0.48 (0.32) ^b
CH ₂ Cl ₂	0.30 (0.21)		
MeCN	0.82 (0.70)	0.70 (0.7)	0.47 (0.38)
EtOH	0.42 (0.40)	0.40 (0.39)	0.51 (0.38)
D ₂ O	0.4	0.41 (0.39)	0.2

^a In oxygen-saturated solution (unless otherwise indicated), $\lambda_{\text{exc}} = 308$ nm.

^b Values in parentheses: in air-saturated solution.

The triplet properties of **2** with $\lambda_{\max} = 345$ nm (Fig. 2b) and **1b** are similar to those of **1a** (Table 2).

The assignment of the observed main transient of **2** to the lowest triplet state is based on the similarities with **1a**. The transient absorbance of **2** at λ_{\max} (ΔA^{\max}), using optically matched conditions and $\lambda_{\text{exc}} = 248$ or 308 nm, is slightly smaller than those of **1a** and **1b** (Table 2). The triplet lifetime of **2** in several solvents is in the 1–10 μ s range and the triplet state is quenched by oxygen with $k_{\text{ox}} = (1.0$ – $1.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The triplet state of **1a** in ethanol is observable in the temperature range down to -196°C . The T-T absorption spectrum is the same, whereas the lifetime under argon changes by five orders of magnitude (Fig. 3). The ΔA_{340} value increases only slightly on going from 25 to -196°C using 308 or 248 nm laser pulses, indicating that the quantum yield of population of the observed triplet (Φ_T) at room temperature is relatively large (see Section 4.1). For **1a** and **2** in the -150 to -196°C range, virtually the same lifetimes were observed for both phosphorescence and T-T absorption (Fig. 3 and Table 1), demonstrating that the triplet state, observed by emission and absorption, is identical. The triplet properties of **2** at moderate temperatures under the same conditions are also similar to those of **1a**.

3.3. Formation of singlet molecular oxygen

Formation of $\text{O}_2(^1\Delta_g)$ was observed for the three compounds in several air- or oxygen saturated solvents at room temperature (Fig. 4). The lifetime in toluene, dichloromethane, acetonitrile, ethanol and D₂O is typically 25, 70, 60, 13 and 50 μ s, respectively. The initial signal (I_{Δ}) shows a linear dependence on the laser intensity and is curved at higher intensities. The quantum yield (Φ_{Δ}) for optically matched toluene solutions is proportional to the slope of these plots, whereas in the other solvents the above mentioned correction was applied. Φ_{Δ} is 0.2–0.5 for **2** and up to 0.8 for **1a** and **1b** (Table 3). The smallest change on going from air- to oxygen-saturated solution was found for **1b**, where the triplet lifetime (Table 2) is largest. The respective increase of the Φ_{Δ} values for **1a** and **2** is in agreement with the k_{ox} and τ_T values since under air only ca. 85% of the molecules in the triplet state are intercepted by oxygen. In oxygen-saturated solution the fraction of triplet state which is intercepted by oxygen is larger (typically 96–99%), based

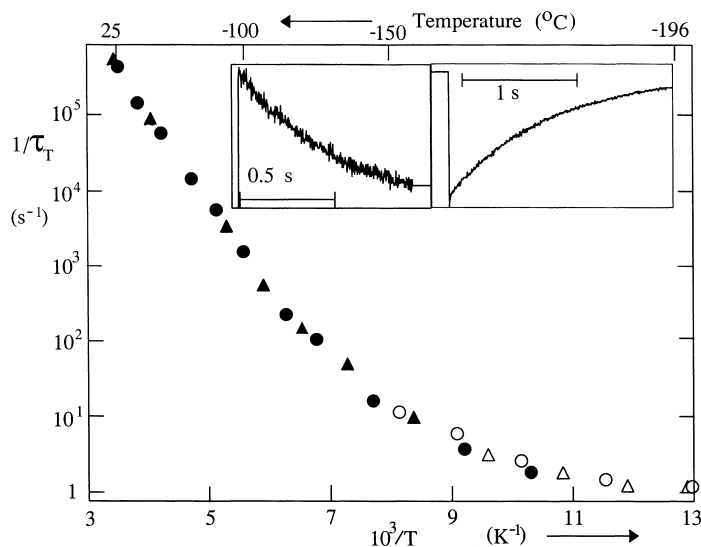


Fig. 3. Effect of temperature on the reciprocal triplet lifetime of **1a** (circles) and **2** (triangles) in argon-saturated ethanol; open and full symbols refer to phosphorescence and absorption, respectively; insets: decay kinetics for **1a** of T-T absorption at -170°C (left) and phosphorescence at -196°C (right), $\lambda_{\text{exc}} = 248 \text{ nm}$.

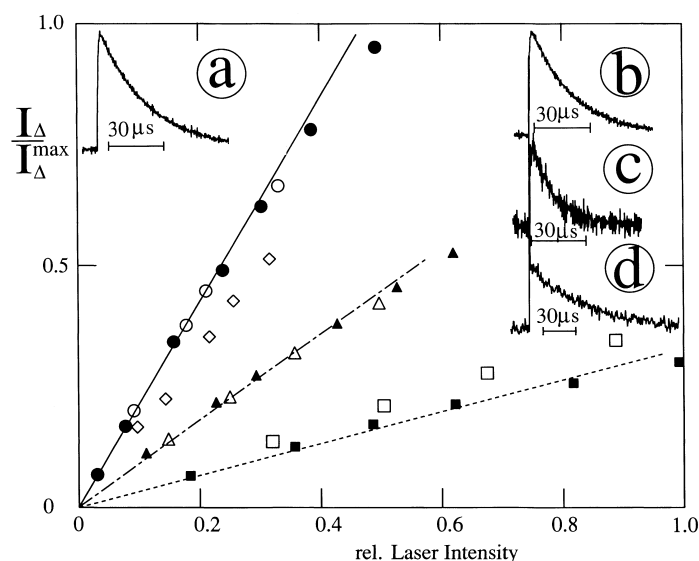
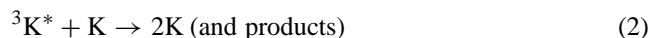


Fig. 4. Signal of $\text{O}_2(^1\Delta_g)$ extrapolated to the pulse end, as a function of the laser intensity (max: 2 MW cm^{-2}) for **1b** (open symbols) and **2** (full symbols) in air-saturated toluene (circles), acetonitrile (\diamond), ethanol (triangles) and heavy water (squares); insets: decay kinetics of (a) **1a** in toluene, **2** in (b) toluene, (c) ethanol and (d) D_2O .

on the triplet lifetimes of $\leq 100 \text{ ns}$ and $5\text{--}20 \mu\text{s}$ in oxygen- and argon-saturated solution, respectively.

3.4. Photoreactions upon ketone sensitized excitation

The only transient on a nanosecond time scale of a given ketone, e.g., benzophenone, in aqueous solution (when electron ejection is avoided [64]) or in acetonitrile is the triplet state ($^3\text{K}^*$). When T-T annihilation can be ignored, the decay of the triplet state is influenced by self-quenching (2) and quenching by oxygen (3).



Values of k_2 and k_3 are close to the diffusion controlled limit in most cases. The decay kinetics are first-order (at sufficiently reduced intensity) and the observed lifetimes are compiled in Table 4.

The two major subsequent transients in the presence of a phthalimide (A-DH), e.g. an electron donor, are the ketyl radical ($^{\bullet}\text{KH}$, the diphenylhydroxymethyl radical in the case of benzophenone) and the radical anion $\text{K}^{\bullet-}$. H-atom abstraction (4, 5) or electron transfer (4, 6), both coupled by

Table 4
Transients obtained with phthalimide derivatives in the presence of ketones^a

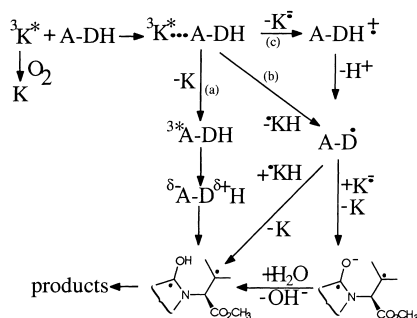
Ketone	Additive	Conditions ^b	λ_{\max} (nm)	τ_T (μs) ^c	Species
Benzophenone	none	A	320, 525	6	$^3\text{K}^*$ ^d
	1a	A	340	6	$^3\mathbf{1a}^*$
	1a	B	340	5	$^3\mathbf{1a}^*$ (no $\text{K}^{\bullet-}$)
	2	A	340	4	$^3\mathbf{2}^*$
	2	B	340	4	$^3\mathbf{2}^*$
Xanthone	none	A	320, <u>620</u>	4	$^3\text{K}^*$
	1a	A	340	6	$^3\mathbf{1a}^*$
	2	A	340	6	$^3\mathbf{2}^*$
Acetophenone	none	A	<330	5	$^3\text{K}^*$
	1a	A	340	6	$^3\mathbf{1a}^*$
	2	A	340	4	$^3\mathbf{2}^*$
Acetone	none	A	<340	3	$^3\text{K}^*$
	none	C	<330	5	$^3\text{K}^*$
	1a	A	340	5	$^3\mathbf{1a}^*$
	2	A	340	4	$^3\mathbf{2}^*$

^a In argon-saturated solution, using [phthalimide] ≥ 1 mM and $A(\lambda_{\text{exc}}) = 1-3$ for ketones; $\lambda_{\text{exc}} = 248$ nm.

^b A: in acetonitrile, B: MeCN-H₂O (1 : 1) at pH > 9, C: water at pH > 9.

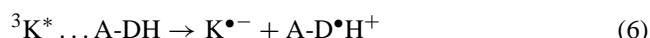
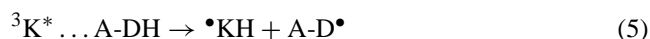
^c Half-life for the cases of radicals.

^d The $^3\text{K}^*$ triplet state is always the precursor.



Scheme 1.

equilibrium (7), energy transfer (4, 8) or physical quenching (4, 9) may occur (Scheme 1).



For selective production of $\bullet\text{KH}$ and $\text{K}^{\bullet-}$, 2-propanol or DABCO were used, respectively. Alternatively, $\text{K}^{\bullet-}$ can be generated in the presence of 2-propanol and water at pH 10–11. The pK_a of equilibrium (7) for benzophenone or acetophenone in aqueous solution is $\approx 9-10$ [65]. Note that *N*-alkylphthalimides in alkaline aqueous solution are known to exhibit hydrolysis [27].

The results reveal that acetone or xanthone, due to their low ϵ values of $\bullet\text{KH}$ and $\text{K}^{\bullet-}$, are not appropriate sensitizers

for detection of H-atom and/or electron transfer reactions in the presence of *N*-phthalimides. These processes can be observed with acetophenone or even better with benzophenone.

3.5. Transients observed with benzophenone

The three transients of benzophenone have maxima in the 320–350 nm range and in addition at $\lambda_{\max} = 520, 550$ and 640 nm for $^3\text{K}^*$, $\bullet\text{KH}$ and $\text{K}^{\bullet-}$, respectively. Excitation of benzophenone in argon-saturated acetonitrile in the presence of **1a** or **1b** by 248 or 308 nm laser pulses produces $^3\text{K}^*$ with $\lambda_{\max} = 325$ and 520 nm as initial species. The relatively strongest remaining signal appears with $\lambda_{\max} = 340$ nm (Fig. 5a). This species is assigned to the triplet state of **1a**, reactions (4) plus (8). A similar result was observed for **2** (not shown). The rate constant of decay of $^3\text{K}^*$ increases linearly with the quencher concentration (Fig. 6). From the slope, the rate constant of quenching of $^3\text{K}^*$ was obtained, $k_q = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for **1a** (Table 5). As secondary transients $\bullet\text{KH}$ and $\text{K}^{\bullet-}$ are conceivable (Scheme 1), but they could only be observed in acetonitrile-water mixtures (Table 4).

3.6. Transients observed with xanthone

Excitation of xanthone in argon-saturated acetonitrile by 248 or 308 nm laser pulses produces $^3\text{K}^*$ with $\lambda_{\max} = 300$ and 620 nm as initial species in the absence and presence of A-DH (Table 4). Selective production of $\text{K}^{\bullet-}$ in the presence of DABCO yields a weak transient with $\lambda_{\max} = 700$ nm; the transient for $\bullet\text{KH}$ in the presence of 2-propanol is even weaker. The secondary transient in the presence of **1a** with $\lambda_{\max} = 340$ nm (Fig. 5b) is assigned to the triplet state of **1a**, reactions (4) plus (8). A similar result was observed for **2** (Fig. 5c). For the system of **1a** and xanthone, in contrast to the cases with benzophenone and acetophenone, the observed signal at 340 nm (formation of $^3\text{A-DH}^*$) is larger than that of $^3\text{K}^*$. Also with xanthone in acetonitrile the rate constant of triplet decay (e.g., at 620 nm) increases linearly with the quencher concentration (Fig. 6). The rate constant of triplet quenching is close to the diffusion controlled limit (Table 5).

3.7. Transients observed with acetophenone

The triplet state of acetophenone has $\lambda_{\max} < 330$ nm; in the presence of DABCO a transient with $\lambda_{\max} = 450$ nm due to $\text{K}^{\bullet-}$ was observed, whereas $\bullet\text{KH}$ is virtually not observable. The ϵ values of $\bullet\text{KH}$ and $\text{K}^{\bullet-}$ at 365 and 445 nm are ≈ 3000 and $\approx 4000 \text{ M}^{-1} \text{ cm}^{-1}$, respectively [39,40], i.e., <30% with respect to that of the triplet precursor. Addition of **1a** (Fig. 7a) leads to a longer lived transient with $\lambda_{\max} \approx 340$ nm in argon-saturated acetonitrile. The rate constant of decay of $^3\text{K}^*$ increases with the quencher concentration, but this effect is partly overlapped by a comparable

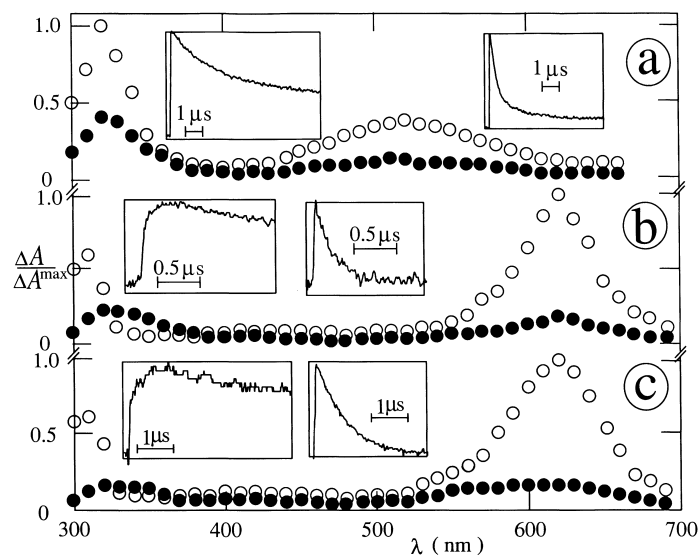


Fig. 5. Transient absorption spectra in argon-saturated acetonitrile in the presence of (a) benzophenone and **1a** (0.5 mM) and (b, c) xanthone and (b) **1a** (0.5 mM) and (c) **2** (0.3 mM) at 30 ns (○) and 1 μs (●) after the 248 nm pulse; insets: decay kinetics at 330 nm (left) and (a) 530 nm and (b, c) 620 nm (right).

Table 5

Rate constant for quenching of ketone triplet states by phthalimides, k_q ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)^a

Ketone	1a	2
Benzophenone	2	0.9
Xanthone	6	4
Acetophenone	7	
Acetone ^b	9 (9) ^c	9

^a In acetonitrile, $\lambda_{\text{exc}} = 248 \text{ nm}$.

^b Build-up kinetics for **2**.

^c Value in parenthesis refers to $\lambda_{\text{exc}} = 308 \text{ nm}$.

absorption of the secondary transients, e.g. $\text{K}^{\bullet-}$ or ${}^3\text{A-DH}^*$. Similar results were obtained in aqueous solution for **2** (pH 7–8).

3.8. Transients observed with acetone

UV irradiation of acetone is known to populate the lowest n, π^* triplet state which is responsible for most of its photochemistry. Triplet properties and reactivity of acetone have been extensively studied in various organic solvents and in aqueous solution [32–50]. The rate constant of self-quenching is $k_2 = 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile [34,35], but the typical half-life of the triplet state of acetone in aqueous solution is below 5 μs [37,38]. In order to simulate the conditions of preparative photochemistry by flash photolysis, neat acetone was replaced by acetone dissolved in acetonitrile, water or their mixtures. Excitation of acetone in argon-saturated acetonitrile by 248 or 308 nm laser pulses produces the triplet state ($\lambda_{\text{max}} < 330 \text{ nm}$ with small ΔA). The same T-T absorption spectrum appears in aqueous solution at pH 7; only with $\lambda_{\text{exc}} = 248 \text{ nm}$ at high intensities does the hydrated electron appear.

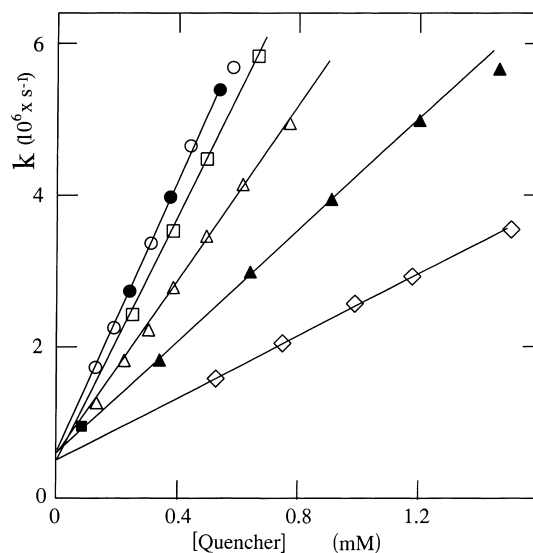


Fig. 6. Rate constants of triplet decay as a function of the concentration of **1a** (open symbols) and **2** (full symbols) for quenching of acetone (circles), xanthone (triangles), acetophenone (squares) and benzophenone (◇) in argon-saturated acetonitrile; $\lambda_{\text{exc}} = 248 \text{ nm}$.

Addition of **1a** to acetone in aqueous solution leads to a new transient with $\lambda_{\text{max}} = 340 \text{ nm}$ (Fig. 7b). Owing to the small and larger ϵ values of ${}^3\text{K}^*$ and ${}^3\text{1a}^*$, respectively, ΔA_{340} markedly increases, reaches a maximum value ($\Delta A_{340}^{\text{max}}$) and then decays within a few microseconds. This build-up (increase of ΔA_{340} with time) and the increase of $\Delta A_{340}^{\text{max}}$ with the quencher concentration is more pronounced than with xanthone. The build-up rate constant increases linearly on the quencher concentration, the slope equals k_q . A smaller maximum build-up was observed for **2** (Fig. 7c).

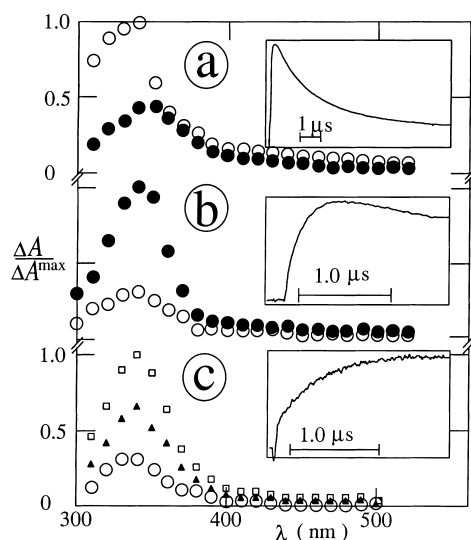


Fig. 7. Transient absorption spectra of (a) acetophenone in argon-saturated acetone in the presence of **1a** (0.2 mM) at 30 ns (○) and 2 μs (●) after the 248 nm pulse; inset: decay kinetics at 340 nm, (b, c) spectra of acetone (5 M) in argon-saturated aqueous solution (pH 7) in the presence of (b) **1a** (0.5 mM) at 30 ns (○) and 5 μs (●) and (c) **2** (0.2 mM) at 30 ns (○), 300 ns (▲) and 2 μs (□); insets: grow-in and decay kinetics at 340 nm.

3.9. Steady-state photolysis

Upon continuous irradiation at 290 nm of **2** in argon-saturated aqueous solution the phthalimide chromophore absorbing around 290 nm disappears and a new maximum at <250 nm appears (Fig. 1c). Similar changes were obtained in ethanol and acetonitrile. The quantum yield of decomposition ranges from $\Phi_d = 0.001$ for **1a** in acetonitrile to $\Phi_d = 0.16$ for **2** in ethanol (Table 6). The Φ_d values of **2** are not significantly changed in the presence of oxygen.

When **2** was irradiated (<300 nm) in acetonitrile, the photoisomerization product **3** was formed with high chemoselectivity. The quantum yield of conversion of **2** into **3** ($\lambda_{irr} = 290$ nm) is ca. 0.01 in acetonitrile, but much smaller upon sensitized excitation [10]. Solvents of low polarity, such as hexane, benzene or toluene, favour the additional formation of products **4** and **5**. These photoproducts originate from biradical cyclization following δ - and γ -hydrogen abstraction, respectively. In benzene a **3** : **4** : **5** ratio of 80 : 12 : 8 was determined by ^1H NMR spectroscopy and comparison with analogous product structures (Scheme 2). In acetone which could act as triplet sensitizer, the efficiency is strongly reduced with respect to acetonitrile.

4. Discussion

4.1. Photoprocesses with *N*-alkylphthalimides

N-alkylphthalimides exhibit fluorescence with a quantum yield of 0.01 or less in ethanol solution at room temperature and a lifetime of 3–4 ns [23]. For *N*-phenylphthalimide the

Table 6
Quantum yield Φ_d of decomposition of phthalimide derivatives^a

	1a	2
Benzene		0.02
Acetonitrile	0.001	0.08
Ethanol	0.02	0.16 (0.14) ^b
Water	0.01	0.12 (0.1)

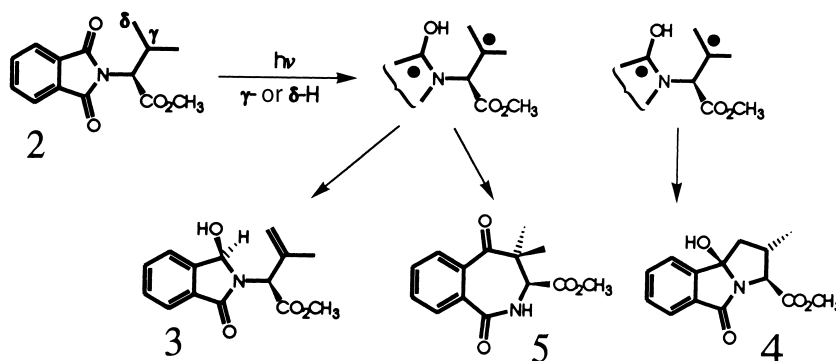
^a Upon irradiation (290 nm) in argon-saturated solution.

^b Values in parentheses: in oxygen-saturated solution.

fluorescence maximum is red-shifted with $\lambda_f \approx 500$ nm [29]. In aprotic media fluorescence is absent for *N*-methylphthalimide (**1a**) and *N*-propylphthalimide (**1b**) [24–26]. The literature values of **1a** in acetonitrile are $\lambda_f = 390$ nm, $\Phi_f = 8 \times 10^{-4}$, $\tau_f = 0.19$ ns, the rate constants are $k_f = 4 \times 10^6$ s⁻¹ and $k_{isc} = 4 \times 10^9$ s⁻¹ [31]. The fluorescence properties are sensitive to solvent polarity and in protic solvents to hydrogen bonding with the excited molecule [25,26,31]. Generally, low Φ_f values were observed, for **1b** Φ_f increases from 0.004 in ethanol to 0.025 in water [24], the latter value under our conditions, however, is lower (Table 1).

Concerning the nature of the fluorescing singlet state of *N*-substituted phthalimides, it is noteworthy that $^1n, \pi^*$ and $^1\pi, \pi^*$ states, which are in close proximity have been discussed [22–30]. The observed triplet of **1a** or **1b** can, in principle, be a $^3n, \pi^*$ or $^3\pi, \pi^*$ state, which are also in close proximity [22,31]. The order of levels of *N*-substituted phthalimides is controversial, the level of the n, π triplet state is slightly below or above the lowest singlet level [22–27]. The proposed order for **1a** in polar solvents is $^1n, \pi^*$, $^1n, \pi^*$, $^3(n, \pi)^*$ and $^3\pi, \pi^*$ with energy levels of 395, 334, 298 and 288 kJ mol⁻¹ [23] or 384, 368, 343 and 297 kJ mol⁻¹ [31], respectively. Further modifications are likely since the data for the triplet states are obtained at -196°C and the levels of the n, π states depend strongly on the solvent polarity. For *N*-alkylphthalimides in alcohols the proposed order is $^1n, \pi^*$, $^3\pi, \pi^*$, $^1\pi, \pi^*$ and $^3n, \pi^*$, whereas in water the two triplet states are exchanged [25,26]. To account for the small Φ_f (Table 1) and large Φ_T and Φ_Δ values (Tables 2 and 3) for the three compounds in both the absence or presence of water we propose that the lowest excited singlet and upper triplet states are almost isoenergetic. One possibility is shown in Scheme 3.

Energy transfer to the phthalimide type acceptor molecule, reactions (4) and (8), occurs from the triplet state of high energy sensitizers, such as acetone, acetophenone or xanthone with $E_T = 309, 305$ or 300 kJ mol⁻¹, respectively. The quenching rate constant in acetonitrile at room temperature is close to the diffusion-controlled limit (Table 5). For benzophenone with $E_T = 288$ kJ mol⁻¹, this rate constant is significantly smaller, in agreement with the estimate of $E_T = 293$ kJ mol⁻¹ for the *N*-substituted phthalimides (see Section 3.1). From the results of **1a** with acetone (Fig. 7b), acetophenone (Fig. 7a) and xanthone (Fig. 5b), a value of $\epsilon_{350} = 5 \times 10^3$ M⁻¹ cm⁻¹ is obtained by an extrapolation to 100% quenching. Then, from a comparison of the ΔA^{\max} value with benzophenone under optically matched



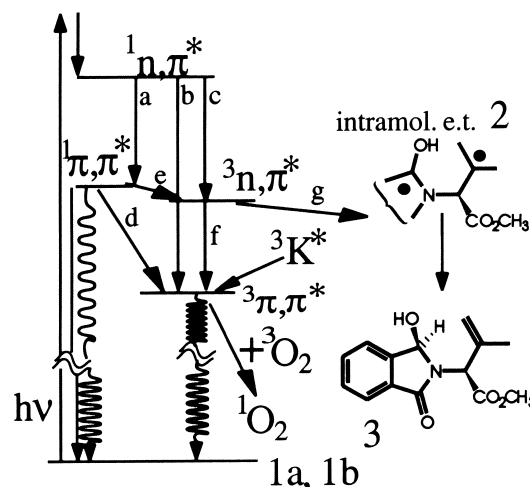
Scheme 2.

conditions, the quantum yield of intersystem crossing is derived. For **1a** in acetonitrile $\Phi_T = 0.8 \pm 0.2$ which approximates the literature value of $\Phi_T = 0.70$ [31]. According to this and the Φ_T values in other solvents (Table 2) it follows that internal conversion is not the major deactivation step. It may not play a role if intersystem crossing into an upper excited triplet state is involved. The same conclusion can be made for **1b**, in contrast to *N*-phenylphthalimide in cyclohexane and acetonitrile, where $\Phi_T = 0.17$ and 0.03, respectively, have been reported [29]. The Φ_T values are in agreement with the Φ_Δ values, which were obtained under comparable conditions (Tables 2 and 3).

The choice of solvent is related to the effect of H-atom abstraction from the excited ketone. If this effect (which takes place in toluene or alcohols) is avoided, the reaction step (4) is efficient. The effect of solvent on τ_T gives no distinct indication for H-atom abstraction by ethanol, as in the case of ketones. Although τ_T is slightly shorter than in acetonitrile, a comparable value was found in dichloromethane, where H-atom abstraction is unlikely to occur. The weak longer lived transient for **1a** or **1b** in argon-saturated ethanol (but not in acetonitrile) may be due to the ketyl radical. For **1a** and *N*-propylphthalimides, however, two other possibilities for a longer lived transient have been considered [23]. On the other hand, the data of photodecomposition of **2** in ethanol with respect to the lower Φ_d values in acetonitrile (Table 6) point to the possibility of H-atom abstraction from the alcohol.

4.2. Photoreactions with **2**

The fluorescence data (Table 1) and the observable triplet features (Table 2) of **2** are similar to those of **1a**. Based on the Φ_f values of **2** and **1a** $\tau_f = 0.2$ – 1 ns can also be estimated for **2**. In both cases fluorescence from the $^1\pi, \pi^*$ state is practically insignificant. Similar τ_f values for **2** and **1a** are not in agreement with a singlet pathway in the isomerization of **2**. Here several deactivation channels of the $^1n, \pi^*$ state have to be considered (a–c, Scheme 3). A major deactivation channel is population of the triplet state which should be assigned to the $^3\pi, \pi^*$ state. This intersystem crossing



Scheme 3.

step (a plus d, c plus f or b) is efficient since the Φ_T values are large (Table 2). It is interesting to note that both the relatively large Φ_Δ/Φ_T ratio (Tables 2 and 3) and the quenching rate constants of $k_{ox} = (1.0$ – $1.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 2) are indicative for the π, π^* nature of the observed triplet state of the three compounds [58].

In order to judge on the involvement of an upper excited state or the lowest triplet state in the isomerization of **2** into **3** under direct excitation, one should consider the Φ_d values. They are substantial for **2** in ethanol and water and somewhat smaller in acetonitrile (Table 6). For comparison, the Φ_d values of **1a** in the three solvents are much smaller. A possible reason for decomposition of **2** could be the isomerization reaction into **3** via the $^3\pi, \pi^*$ state. The large Φ_d values are not consistent with a singlet pathway. However, if a triplet state were involved the reaction should be strongly retarded by oxygen, thereby mainly generating $\text{O}_2(^1\Delta_g)$ (Tables 2 and 3). The Φ_d values in the presence and absence of oxygen are similar (Table 6). We, therefore, conclude that deactivation of the lowest triplet state cannot lead to the isomerization. This is in agreement with the result that the quantum yield of formation of **3** is very low upon sensitized excitation [10]. Note that energy transfer is possible (Table 4) and that the quenching rate constant is sufficiently large (Table 5).

For **2** it is now proposed that intersystem crossing into the upper excited n, π triplet state is significant and its subsequent deactivation involves the isomerization reaction (pathway g in Scheme 3) and leads to photodecomposition. On the other hand, to account for the low product yield under sensitized conditions we postulate energy transfer to the non-reactive $^3\pi, \pi^*$ state.

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