Time-Resolved Spectroscopy of Sulfur- and Carboxy-Substituted *N*-Alkylphthalimides

Helmut Görner,*[a] Axel G. Griesbeck,[b] Thomas Heinrich,[b]
Wolfgang Kramer,[b] and Michael Oelgemöller[b]

Abstract: The photophysical and photochemical properties of *N*-phthaloylmethionine (**1**), *S*-methyl-*N*-phthaloylcysteine methyl ester (**2**) and *N*-phthaloyltranexamic acid (**3**) were studied by time-resolved UV/Vis spectroscopy, using laser pulses at 248 or 308 nm. The quantum yield of fluorescence is low ($\Phi_f < 10^{-2}$) for **1**–**3** in fluid and glassy media, whereas that of phosphorescence is large (0.3–0.5) in ethanol at −196 °C. The triplet properties were examined in several solvents, at room temperature and below. The spectra and decay kinetics are similar, but the population of the π,π* triplet state, as measured by T–T absorption, is much lower for **1** and **2** than for **3** or *N*-methyltrimellitimide (**5′**) at ambient temperatures. The quantum yield (Φ_Δ) of singlet molecular oxygen $O_2(^1\Delta_g)$ formation is substantial for **3** and **5′** in several air- or oxygen-saturated solvents at room temperature, but small for **2** and **1**. The quantum yield of decomposition is substantial (0.2–0.5) for **3** and small (< 0.05) for **2** and **1**. It is postulated that photoinduced charge separation in the spectroscopically undetectable ^{3}n,π* state may account for the cyclization products of **1** and **2**. In aqueous solution, this also applies for **3**, whereas in organic solvents cyclization involves mainly the lower lying ^{3}π,π* state. Triplet acetone, acetophenone and xanthone are quenched by **1**–**3** in acetonitrile; the rate constant is close to the diffusion-controlled limit, but smaller for benzophenone. While the energy transfer from the triplet ketone occurs for **3**, a major contribution of electron transfer to the *N*-phthalimide derivative is suggested for **1** and **2**, where the radical anion of benzophenone or 4-carboxybenzophenone is observed in alkaline aqueous solution.

Keywords: electron transfer · photochemistry · photocyclization · phthalimide · quantum yields

Introduction

The photochemical behaviour of *N*-phthaloylmethionine (**1**), *S*-methyl-*N*-phthaloylcysteine methyl ester (**2**) and a phthalimidocarboxylic acid containing a *trans*-cyclohexane-1,4-diyl spacer group between the nitrogen and the carboxyl group (**3**) has been intensively investigated.[1–11] Phthalimides have been the subject of various intramolecular photoprocess studies and some photophysical properties of *N*-substituted phthalimides have been reported.[12–25] *N*-Alkylphthalimides exhibit fluorescence with a quantum yield of 0.01 or less and a lifetime of 0.2–4 ns in solution at room temperature.[5, 18, 25] In aprotic media, fluorescence is absent for *N*-methylphthalimide (**5**) and *N*-propylphthalimide (**5″**).[20,21] For *N*-phthaloylvaline methyl ester (**4**) we have proposed that the formation of a photoisomer as the main product upon direct excitation occurs through an upper excited n,π triplet state.[11]

Charge separation prior to cyclization was assumed to occur either upon direct irradiation of **1**–**3** in acetonitrile or after energy transfer from triplet acetone or benzophenone, but different distributions of products were obtained for **1** and **2** in the absence and in the presence of high energy sensitizers.[1, 2] The role of energy and/or electron transfer has been discussed for various systems.[26–31] Examples for electron transfer substrates include sulfur-containing amino acids, in which, in alkaline aqueous solution, transfer occurs from the sulfur atom in methionine or cysteine derivatives to the triplet state of 4-carboxybenzophenone (CB).[30, 31] A further example for energy transfer versus electron transfer is the combination of ketones and DNA bases.[32]

In this study, the photophysics and photochemistry of three *N*-phthaloyl aliphatic amino acid derivatives (**1**–**3**) and, for comparison, *N*-methyltrimellitimide (**5′**) was studied by time-resolved spectroscopy. The features of the observable triplet states of **1**–**3** in polar solvents are discussed and the quantum yield of triplet formation (Φ_T) is compared with the quantum yields of decomposition (Φ_d) and formation of singlet molecular oxygen (Φ_Δ). Measurements of the quenching by

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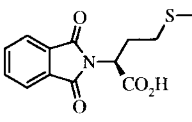
[a] Dr. H. Görner
Max-Planck-Institut für Strahlenchemie
45413 Mülheim an der Ruhr (Germany)

[b] Prof. Dr. A. G. Griesbeck, Dipl.-Chem. T. Heinrich, Dr. W. Kramer, Dr. M. Oelgemöller
Institut für Organische Chemie der Universität zu Köln
Greinstrasse 4, 50939 Köln (Germany)



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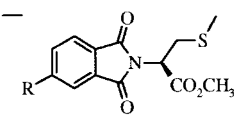
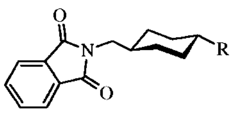
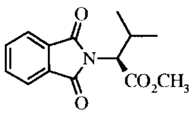


2 : R = H
2': R = CO_2CH_3



3 : R = COOH
3': R = CO_2CH_3



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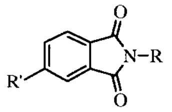


5 : R = CH_3, R' = H
5' : R = CH_3, R' = CO_2CH_3
5'': R = C_3H_7, R' = H

1–**3** of the triplet states of acetone, acetophenone, xanthone, CB and benzophenone were carried out in aqueous solution, acetonitrile or mixtures thereof.

Results

Photolysis: Phthalimides have two absorption maxima, around 220 and 295 nm. Upon irradiation (290 nm) of **3** in argon-saturated ethanol, the 290 nm absorption disappears and a new maximum appears at <250 nm (Figure 1, part a).

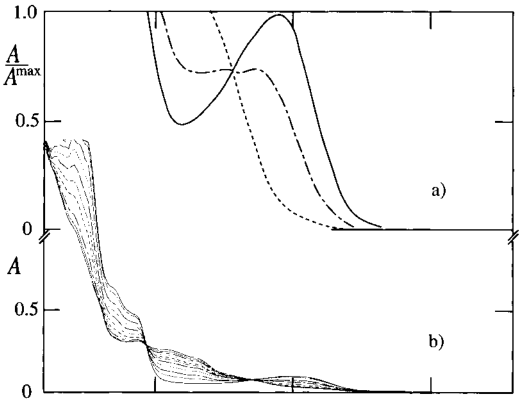


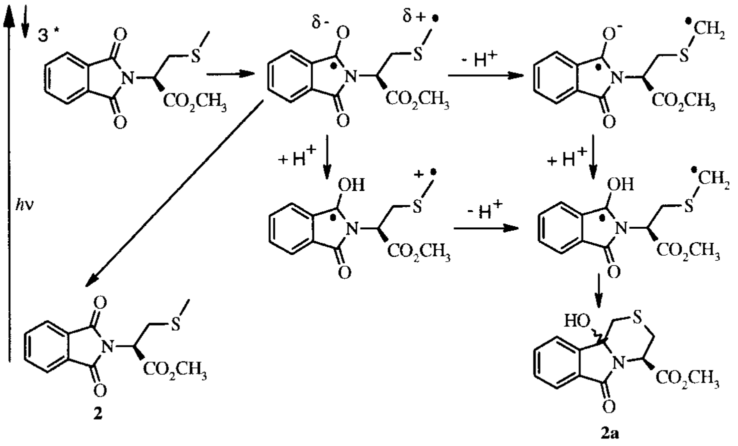
Figure 1. Absorption spectra of **3**, a) in argon-saturated ethanol prior to (full line) and after irradiation at 290 nm (broken and dashed lines: 1 and 2 min) and b) in aqueous solution at pH 7 (1–11: 2 s interval).

Similar changes were obtained for **3** in water (Figure 1, part b) and acetonitrile, and for **3'** and **4**,[11] whereas the degree of conversion is much smaller for **1**, **2** and the other compounds under examination. The quantum yield of decomposition ranges from $\Phi_d < 0.001$ for **5** or **5'** to $\Phi_d = 0.4$ for **3** in ethanol (Table 1). In contrast to **4**[11] and **3'**, in which the Φ_d values are not significantly changed in the presence of oxygen, Φ_d of **3** depends on the oxygen concentration. The value of Φ_d is drastically reduced in oxygen-saturated ethanol, but the effect of oxygen is smaller in aqueous solution (Table 1).

Table 1. Quantum yield Φ_d of decomposition of phthalimide derivatives.[a]

	1	2	3	3'	4[b]	5[b]	5'
CH_3CN	–[c]	< 0.005	0.2	0.06	0.08	0.001	< 0.01
EtOH	< 0.04	< 0.04	0.4 (0.05)[d]	0.1 (0.09)	0.16 (0.14)	< 0.02	< 0.01
H_2O		< 0.01	0.3 (0.2)	–[c]	0.12 (0.1)	0.01	0.003

[a] In argon-saturated solution upon irradiation at 290 nm. [b] Taken from ref. [11]. [c] Solubility too low. [d] Values in parentheses refer to oxygen-saturated solution.

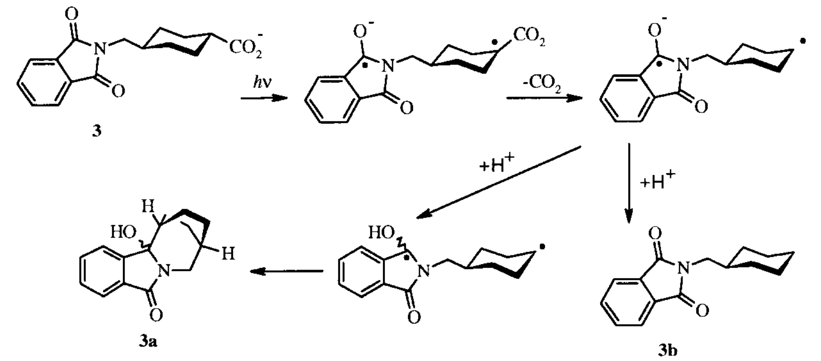


Scheme 1. Photocyclization of **2** by intramolecular charge separation between the thiomethyl and phthalimide moieties, yielding **2a** as the major product.

Practically no photoproducts were found for **1** and **2**.[1, 2] For **2** in deoxygenated acetonitrile, Φ_d is < 0.005, but upon acetone-sensitized excitation the quantum yield is 0.12, of which a value of 0.08[2] is accounted for by the major photoproduct **2a** (Scheme 1). Acetone-sensitized photolysis of **3** in the presence of 1 M water yielded **3a** as the major cyclization product (68%) and **3b** (12%), the product of decarboxylation without cyclization (Scheme 2).[3, 7] The results were similar when CB was used as sensitizer.[33]

Emission: The literature values for **5** in acetonitrile are $\lambda_f = 390$ nm, $\Phi_f = 8 \times 10^{-4}$ and $\tau_f = 0.19$ ns, while the rate constants are $k_f = 4 \times 10^6\,s^{-1}$ and $k_{isc} = 4 \times 10^9\,s^{-1}$.[25] The fluorescence properties are sensitive to solvent polarity and, in protic solvents, to hydrogen bonding.[21, 25] In ethanol or acetonitrile solutions at room temperature, the *N*-alkylphthalimides exhibit a weak fluorescence with quantum yields of $< 1 \times 10^{-3}$ for **1**–**5**. In aqueous solution, in which Φ_f is low for **1**, **2** (or **2'**) and **5'**, but larger than in ethanol, the emission maxima are around 430 nm (Figure 2 and Table 2).

Phosphorescence lifetimes (τ_p) of approximately 1 s at −196 °C and triplet energies of $E_T = 286–297$ kJ mol^{-1} are known for several phthalimides.[18–20] The phosphorescence spectra of **1**–**5** and **5'** in ethanol at −196 °C are very similar (Figure 2). They have a maximum at approximately 450 nm and an onset at ≈405 nm, corresponding to $E_T = 293$ kJ mol^{-1}. The phosphorescence excitation spectrum generally coincides with the absorption spectrum (at 24 °C). The decay follows a first-order law for **1**–**5** below −150 °C and $\tau_p = 0.7–0.9$ s at −196 °C. The quantum yield is $\Phi_p = 0.3–0.7$ (Table 2), whereas fluorescence is practically absent (on the overall luminescence intensity scale).



Scheme 2. Photoreactions of **3** yielding **3a** and **3b** as the major and a minor product, respectively.

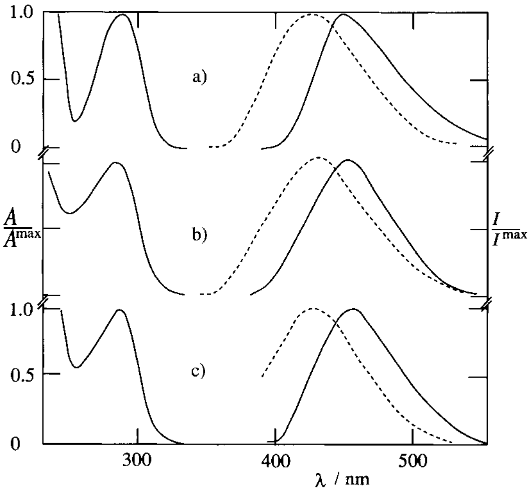


Figure 2. Absorption, fluorescence and phosphorescence spectra, in ethanol, in water, both at 24 °C and in ethanol at −196 °C (left, middle and right, respectively), of a) **5**, b) **1** and c) **3**; $\lambda_{exc} = 290$ nm.

Table 2. Fluorescence and phosphorescence maxima, quantum yields and phosphorescence lifetime of phthalimide derivatives.[a]

Compound	Solvent	λ_f [nm]	Φ_f ($\times 10^3$)	λ_p [nm]	Φ_p	τ_p [s]
1	H_2O	< 420	< 1			
	EtOH	< 420	< 0.1	445	0.3	0.85 ($\geq$0.3)[b]
2	H_2O	< 420	0.2			
	EtOH	< 420	< 0.1	450	0.3	0.85 ($\geq$0.3)
2′	EtOH	< 420	< 0.1	452	0.4	0.86
3	H_2O	430	4			
	EtOH	< 420	< 0.2	450	0.3	0.75 (0.6)
4[c]	EtOH	< 400	< 0.2	450	0.5	0.85
	H_2O	415	2			
5[c]	EtOH	< 405	< 0.5	450	0.6	0.75 (0.3)
5′	EtOH	< 400	< 0.5	455	0.6	0.73
	H_2O	422	0.5			
5″[c]	EtOH	< 400	< 0.5	453	0.7	

[a] In air-saturated solution at 24 and −196 °C for fluorescence and phosphorescence, respectively. [b] Values in parentheses: triplet lifetime (absorption) at −170 °C. [c] Values for **4**, **5** and **5″** were taken from ref. [11].

Transients observed upon direct excitation: The triplet properties of **3**, **4** and **5** are similar, and the assignment of the observed main transient to the lowest triplet state is based on the similarities with **5** (Table 3). The T–T absorption spectra of **3** in acetonitrile (Figure 3c) and other solvents show a $\lambda_{max} \leq 330$ nm; that of **1** (Figure 3a) is rather weak. Virtually no triplet could be detected for **2** or **2′** in acetonitrile upon 248 or 308 nm laser excitation, in contrast to the case of **2** in ethanol (Figure 3b) or water. The transient absorbance at λ_{max} (ΔA^{max}) in acetonitrile, using optically matched conditions and $\lambda_{exc} = 308$ nm, increases from < 0.04 to 0.3 and 1.0 (relative values) for **2** (or **1**) **3** and **5**, respectively. They are converted into quantum yields of population of the observable triplet (Φ_T) based on $\Phi_T = 0.8$ for **5** in acetonitrile. Similar values were obtained using $\lambda_{exc} = 248$ nm (Table 3). The ΔA^{max}

Table 3. Properties of the triplet state of phthalimide derivatives.[a]

Compound	Solvent	λ_{max} [nm]	τ_T [μs]	k_{ox} [$10^9 M^{-1} s^{-1}$]	Φ_T[b]
1	CH_3CN	310	3	1.5	0.05 (< 0.05)[c]
	EtOH	315 [320][d]	3	1.5	0.15 (< 0.05)
	H_2O	310	3	1.2	0.05 (< 0.05)
2	CH_3CN	< 330			< 0.03 (< 0.05)
	EtOH	325 [340][e]	2	1.6	0.03 (< 0.05)
	H_2O	325	3	1.2	0.08 (0.05)
2′	CH_3CN	< 330	3		< 0.05
3	dioxane	330	3	0.8	
	CH_2Cl_2	320	(3)	(1.1)	(0.4)
	CH_3CN	330	5	1.5	0.6 (0.4)
	EtOH	340 [335][e]	5	1	0.5 (0.4)
	H_2O	340	8	1.5	0.3 (0.2)
3′	CH_3CN	330	5	1.2	0.5
5′	dioxane	350	5	0.2	
	CH_2Cl_2	360	(1.2)	(0.3)	(0.8)
	CH_3CN	350	5	0.5	0.8
	EtOH	350	8	0.3	0.4

[a] In argon-saturated solution at room temperature, $\lambda_{exc} = 248$ nm. [b] Using $\Phi_T = 0.8$ for **5** in acetonitrile. [c] Values in parentheses refer to $\lambda_{exc} = 308$ nm. [d] Values in brackets refer to −165 °C. [e] A second (faster) component appears below −130 °C.

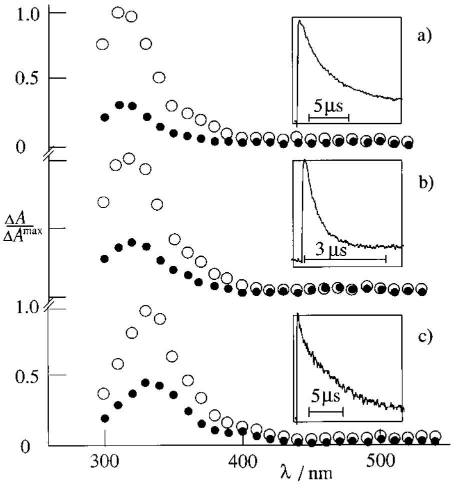


Figure 3. Transient absorption spectra in argon-saturated solution of a) **1** in ethanol, b) **2** in ethanol and c) **3** in acetonitrile (in the absence of additives) at 30 ns (○) and 5 μs (●) after the 248 nm pulse, $A_{248} \approx 2$; insets: decay kinetics at 330 nm.

values of **1** and **2** are much smaller than those of **3**, the last of which is fairly independent of solvent polarity. The triplet lifetimes of **1**–**3** in several solvents are in the 1–10 μs range. The decay is quenched by oxygen with rate constants of $k_{ox} = (1-2)\times 10^9\,M^{-1}s^{-1}$. For **3** in water an additional minor transient was observed, with the two $\lambda_{exc} = 248$ or 308 nm.

The T–T absorption of **5** in ethanol is observable in the temperature range down to $-196\,^\circ C$; the triplet lifetime under argon changes by five orders of magnitude (Figure 4). The ΔA_{330} value increases only slightly on going from 25 to $-196\,^\circ C$, using 308 or 248 nm laser pulses. This could be due to changes in the ground state at λ_{exc} and indicates that Φ_T at room temperature is close to its maximum value, which should be almost unity (assuming that internal conversion does not take place). For **1**–**5** in the -150 to $-196\,^\circ C$ range, virtually the same lifetime was observed both for phosphorescence and for T–T absorption (Table 2), demonstrating that the triplet states, observed by emission and absorption, are identical. The T–T absorption spectrum and triplet lifetime of **1**–**3** at intermediate temperatures under the same conditions are also similar to those of **5**, whereas the yield (measured by the ΔA_{330} value) is significantly smaller and increases on decreasing the temperature (Figure 4). It is noteworthy that for **2** a second decay component appears below $-130\,^\circ C$; its spectrum does not differ markedly from that of the major one, but the lifetime is about two orders of magnitude shorter. This species could be tentatively assigned to a second, higher-lying excited triplet state.

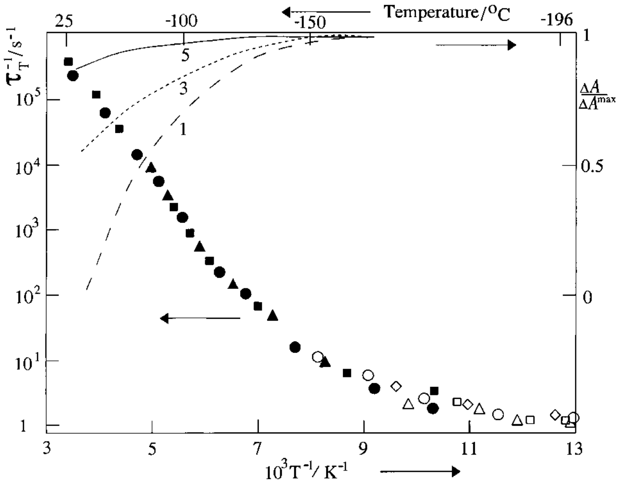


Figure 4. Effect of temperature on Φ_T^{rel} (right scale) and the reciprocal triplet lifetime (left scale) of **5** (circles), **1** (triangles), **2** (diamonds) and **3** (squares) in argon-saturated ethanol; open and full symbols refer to phosphorescence and absorption, respectively; $\lambda_{exc} = 248$ nm.

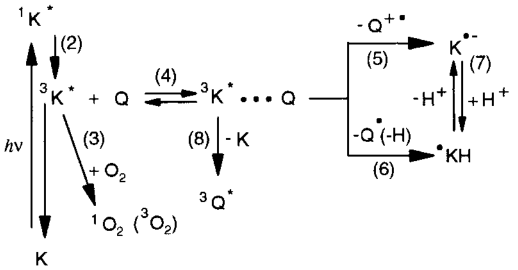
Formation of singlet molecular oxygen: The quantum yield Φ_Δ in several air- or oxygen-saturated solvents at room temperature is 0.1–0.25 for **3**, up to 0.7 for **5** and **5′**, but virtually zero for **1** and **2′** (Table 4). The largest change on going from air-saturated to oxygen-saturated solution was found for **5′**, for which the Φ_Δ values in dichloromethane are 0.18 and 0.44, respectively. This is in agreement with the k_{ox} and τ_T values (Table 3), since only 80% of the molecules in the triplet state are intercepted by oxygen. Generally, the fraction of the triplet state intercepted by oxygen is larger (typically >98%), on the basis of the triplet lifetimes of <70 ns and 3–10 μs in oxygen-saturated and argon-saturated solutions, respectively.

Table 4. Quantum yield of singlet molecular oxygen, Φ_Δ.[a]

	1	**2′**	**3**	**4**[b]	**5′**
toluene				0.4 (0.32)	0.3 (0.18)[c]
CH_3CN		<0.04	0.15 (0.10)	0.4 (0.38)	0.9 (0.65)
EtOH	<0.04	0.04	0.2 (0.20)	0.5 (0.38)	
D_2O	<0.05	<0.05	0.1 (0.06)	0.2	–[d]

[a] In oxygen-saturated solution (unless otherwise indicated), $\lambda_{exc} =$ 308 nm. [b] Taken from ref.[11] [c] Values in parentheses: in air-saturated solution. [d] Solubility too low.

Photoreactions upon ketone-sensitized excitation: In addition to energy transfer from the triplet state of the ketone ($^3K^*$) to the acceptor molecule (Q), electron transfer to $^3K^*$ may also occur; that is, the two are, in principle, competing processes (Scheme 3).[26–31] When T–T annihilation can be ignored, the decay of the triplet state is influenced by self-quenching and quenching by oxygen (Scheme 3, reaction 3). In the presence of an electron donor, the two major subsequent transients are the ketyl radical ($^\bullet$KH)—diphenylhydroxymethyl radical in the case of CB or benzophenone—and the radical anion ($K^{\bullet-}$). Electron transfer (Scheme 3, reactions 4,5) or hydrogen-atom abstraction (Scheme 3, reactions 4,6), both coupled by equilibrium (7) (Scheme 3), energy transfer (Scheme 3, reactions 4,8) or physical quenching of the collision complex may also occur.



Scheme 3. Primary ketone-sensitized reactions pathways of *N*-phthalimides (Q).

The pK_a of equilibrium (7) for benzophenone or acetophenone in aqueous solution is ≈9–10 and for CB, pK_a = 8.3.[30, 34] Acetone or xanthone, due to their low ε values for $^\bullet$KH and $K^{\bullet-}$, are not appropriate sensitizers for the detection of hydrogen-atom and/or electron transfer reactions in the presence of *N*-phthalimides.[11] These processes can be observed with acetophenone or benzophenone and even better with CB.

Transients observed with benzophenone and the carboxy derivative: Excitation of benzophenone in argon-saturated acetonitrile (or in a mixture with water) in the presence of **1**, **2** or **3**, using 248 or 308 nm laser pulses, produces $^3K^*$ (with $\lambda_{max} = 325$ and 525 nm) as an initial species. For **3**, a second transient with $\lambda_{max} = 330$ nm appears after a few μs (Figure 5, part a); we assign this to the lowest triplet state of **3**, reactions (4) and (8) (see Scheme 3). As secondary transients $^{\bullet}KH$ ($\lambda_{max} = 550$ nm) and $K^{\bullet -}$ ($\lambda_{max} = 640$ nm) could be detected for **1** in acetonitrile-water mixtures at pH 4–6 (Figure 5, part b) and pH 10–11 (Figure 5, part c), respectively (Table 5). Virtually no signal appears for **2′** after triplet quenching; that is, decay of $^3K^*$ occurs through physical quenching of the collision complex. The rate constant of decay increases linearly with the quencher concentration, and the rate constants k_4 are obtained from the slope (Table 6).

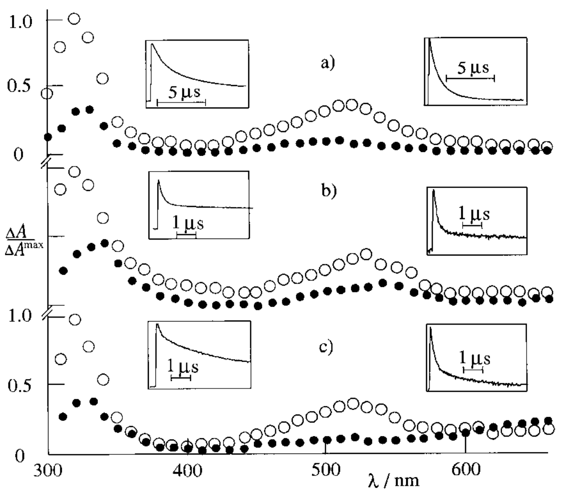


Figure 5. Transient absorption spectra of benzophenone in argon-saturated acetonitrile/water 4:1 in the presence of a) **3** (0.5 mM, pH 7), b) **1** (0.1 mM, pH 7) and c) **1** (pH 10) at 30 ns (○) and 3 μs (●) after the 248 nm pulse; insets: kinetics at 340 nm (left) and 530 nm (right).

Table 5. Transients obtained with phthalimide derivatives in the presence of ketones.[a]

Ketone	Phthalimide	Conditions[b]	λ_{max}[c] [nm]	$\tau_{1/2}$[d] [μs]	Species
benzophenone	none	I	320, 520	6	$^3K^*$[e]
	1	I	550	>3	$KH^{\bullet}$
	1	II′	660	>10	$K^{\bullet -}$
	3	I	330	4	^{3}**3***
	5	II′	330	5	^{3}**5***
CB	**1**	III	570	>3	$KH^{\bullet}$
	1	III′	660	>10	$K^{\bullet -}$
	2′	III	660	>10	$KH^{\bullet}$
	2′	III′	570	>3	$K^{\bullet -}$
xanthone	**3**	I	330	4	^{3}**3***
acetophenone	**1**	III′	440	>5	$K^{\bullet -}$
	3	I	330	4	^{3}**3***
acetone	**3**	I	330	<10	^{3}**3***
	3	III	330	<10	^{3}**3***

[a] In argon-saturated solution, using [phthalimide] ≥ 1 mM and $A(\lambda_{exc}) = 1-3$ for ketones; $\lambda_{exc} = 248$ nm. [b] I: in acetonitrile, II′: CH_3CN/H_2O 1:1 at pH > 9, III: water at pH ≤ 7, III′: pH > 9. [c] No remaining acceptor triplet was observable for **1** or **2**. [d] Half-life for the cases of radicals. [e]The $^3K^*$ triplet is the precursor in all cases.

Table 6. Rate constant for quenching of ketone triplet states by phthalimides, k_4 [$10^9\,M^{-1}s^{-1}$].[a]

	1	**2′**	**3**	**4**[b]	**5**[b]
benzophenone	3	2	1	0.9	2
CB[c]	4	4	2		2
xanthone	6	4	6	4	6
acetophenone	6	10			7
acetone[d]		5(9)[e]		9	9(9)

[a] In acetonitrile (unless otherwise indicated), $\lambda_{exc} = 248$ nm. [b] Taken from ref. [11]. [c] In water. [d] Build-up kinetics for the phthalimide triplet. [e] Values in parentheses refer to $\lambda_{exc} = 308$ nm.

Similar results were registered with CB, in which the three transients ($^3K^*$, $^{\bullet}KH$ and $K^{\bullet -}$) have maxima in the 335–360 nm range and, in addition, at $\lambda_{max} = 550$, 570 and 660 nm, respectively. The respective molar absorption coefficients are $\varepsilon_{550} = 5.2 \times 10^3$, $\varepsilon_{570} = 5.2 \times 10^3$ and $\varepsilon_{660} = 6.0 \times 10^3\,M^{-1}cm^{-1}$.[28–31] Excitation of CB in argon-saturated aqueous solution in the presence of **1** yields $^{\bullet}KH$ (Figure 6, part a) and $K^{\bullet -}$ (Figure 6, part b) as secondary transients at pH < 7 and 8.5–10, respectively. $K^{\bullet -}$ could also be detected for **2′** (Figure 6, part c and Table 5), but not for **3**. Electron transfer from triplet CB or benzophenone to **1** and **2′**, possibly in addition to energy transfer, is also indicated by the larger rate constant of quenching with respect to the cases of **3** or **5** (Table 6).

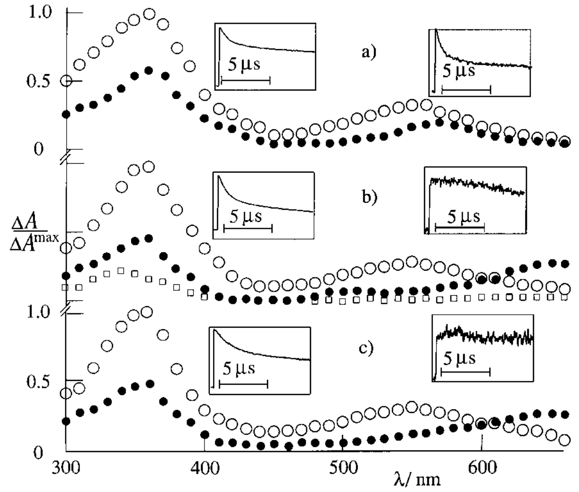


Figure 6. Transient absorption spectra of CB in argon-saturated aqueous solution in the presence of a) **1** (0.5 mM) at pH 7, b) **1** at pH 9.5, and c) **2′** (0.5 mM, pH 9.5) at 30 ns (○), 10 μs (●) and 100 μs (□) after the 248 nm pulse; insets: kinetics at 360 nm (left) and a) 550 nm, or b) and c) 650 nm (right).

Transients observed with xanthone, acetophenone and acetone: Excitation of xanthone produces $^3K^*$ ($\lambda_{max} = 300$ and 620 nm) in the absence and presence of Q (Table 5). The secondary transient in the presence of **5** with $\lambda_{max} = 330$ nm (not shown) is assigned to the triplet state of **5**, reactions (4) plus (8). A similar result was observed for **3**, but virtually no remaining signal (after a few μs) appears for **1** or **2** (not shown). For the system of **3** or **5** and xanthone, in contrast to the cases with benzophenone and acetophenone, the observed signal at 330 nm increases with time; that is, the ε_{330} value of ^{3}Q* is larger than that of ^{3}K*. The rate constant of triplet decay (at 620 nm) increases linearly with [Q], the rate constant is $k_4 = (4-6) \times 10^9\,\text{M}^{-1}\text{s}^{-1}$ (Table 6).

The triplet state of acetophenone has $\lambda_{max} < 330$ nm; addition of **3** (not shown) leads to a longer lived transient with $\lambda_{max} \approx 330$ nm in argon-saturated acetonitrile. The rate constant of decay of triplet acetophenone increases with the concentration of **3**, but this effect is partly obscured, due to comparable overlapping absorption of the secondary transients; e.g., K$^{\bullet-}$ or ^{3}Q*. Similar results were obtained in aqueous solution for **1** (pH 4–5) and **2** or **3** (pH 7–8). On increasing the pH to 11, K$^{\bullet-}$ ($\lambda_{max} = 440$ nm, $\varepsilon \approx 4000\,\text{M}^{-1}\text{cm}^{-1}$)[27] was observed for **1**.

Excitation of acetone in argon-saturated acetonitrile, using 248 or 308 nm laser pulses, produces the triplet state ($\lambda_{max} < 330$ nm with small ΔA). The same T–T absorption spectrum appears in aqueous solution at pH 7; with $\lambda_{exc} = 248$ nm at high intensities the hydrated electron (e^-_{aq}) also appears in low yield. Addition of **5′** to acetone in aqueous solution leads to a new transient with $\lambda_{max} = 330$ nm (Figure 7, part a). The value of ΔA_{330}, owing to the small ε value of ^{3}K* with respect to that of ^{3}**5′***, markedly increases, reaches a maximum (ΔA_{330}^{max}) and then decays within a few microseconds. For **3**, a build-up (increase of ΔA_{330} with time, see Figure 7, part c) with smaller ΔA_{330}^{max} than for **5′** was observed. The increase of ΔA_{330}^{max} versus [Q] is more pronounced with acetone than xanthone. The build-up rate constant increases linearly with [Q]; the slope equals k_4. For **1** (Figure 7, part b) or **2**, however, there was triplet quenching but virtually no new transient could be detected either in acetonitrile or in aqueous solution (on increasing the pH to 11). The lack of an observable triplet state of **1** and **2** after quenching of high-energy sensitizers indicates efficient higher excited state reactivity.

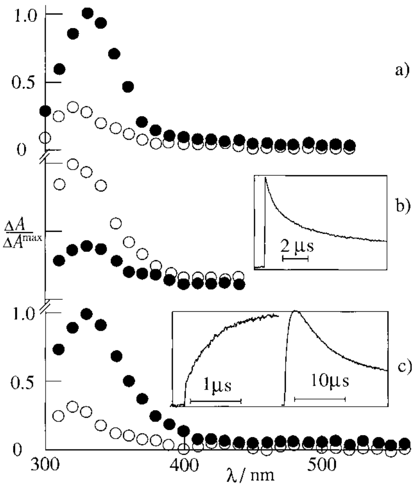


Figure 7. Transient absorption spectra of acetone in argon-saturated aqueous solution (1:9) in the presence of a) **5′** (0.1 mM, pH 7), b) **1** (0.1 mM, pH 4) and c) **3** (0.2 mM, pH 7) at 30 ns (○) after the 308 nm pulse and at 0.5 (○) and 2 μs (●) for **5′**, **1** and **3**, respectively; insets: grow-in and decay kinetics at 330 nm.

Discussion

Photoprocesses with *N*-alkylphthalimides: Generally, low Φ_f values were observed for compounds **1**–**5″** (Table 2). The fluorescing singlet state of *N*-substituted phthalimides is the $^1\pi,\pi^*$ state, which is believed to be above the ^{1}n,π^* state,[18, 19, 25] but could be below it.[11] The observed lowest triplet of **3** is probably a $^3\pi,\pi^*$ state. Whether the higher lying ^{3}n,π^* state is below the $^1\pi,\pi^*$ state is controversial even for **5** or **5″**, and this question cannot be conclusively answered in the cases of other *N*-substituted phthalimides, such as **1**–**3**. The quantum yield of intersystem crossing of **5** in acetonitrile is $\Phi_T = 0.7-0.8$.[11, 25] For **3** and **5′** Φ_T is slightly smaller, but it is much smaller for **1**, **2** and **2′** (Table 3).

Energy transfer to the phthalimide type acceptor (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 $300\,\text{kJ mol}^{-1}$, respectively. The quenching rate constants in acetonitrile at room temperature are close to the diffusion-controlled limit (Table 6). For benzophenone, with $E_T = 288\,\text{kJ mol}^{-1}$, this rate constant is significantly smaller, in agreement with the above estimate of $E_T = 293\,\text{kJ mol}^{-1}$ for the lowest triplet state of *N*-substituted phthalimides.

Direct and sensitized photoreactions with 3: In the case of direct excitation of **3** in several solvents at room temperature, the lowest triplet state is rather efficiently populated. This is confirmed by the Φ_T and Φ_Δ values in Table 3 and Table 4. A singlet pathway for cyclization of **3** under direct excitation conditions is unlikely in view of the large Φ_d value and the short singlet lifetimes for either **3** or those phthalimides (**5**, **5′** and **5″**) that are chemically unreactive. Intramolecular electron transfer should cause charge separation and CO_2 elimination, leading mainly to cyclization, to which the observed chromophore loss of **3** is ascribed. Triplet quenching by oxygen should strongly reduce the effect of intramolecular electron transfer. Therefore, one would expect that the Φ_d values should be much lower in the presence of oxygen. In fact, the results in ethanol are in agreement with this lowest triplet pathway (Table 1).

In aqueous solution, however, Φ_d is only 30% smaller under conditions of saturation with oxygen than with argon. Therefore, we propose that the observed $^3\pi,\pi^*$ state is mainly deactivated by intersystem crossing and that photodecomposition as a measure of photocyclization is a fast competing reaction, involving the spectroscopically undetectable ^{3}n,π^* state. For **3** in aqueous solution, this level should be equal to or only slightly above the $^3\pi,\pi^*$ state, but significantly lower in organic solvents, in ethanol particularly. An analogous argument that the $^3\pi,\pi^*$ state is not reactive with respect to cyclization (the Φ_d values are not affected by oxygen) has already been used for the isomerization in the case of **4** in the absence and in the presence of water.[11] The hypothesis of the $^3\pi,\pi^*$ state as the observed triplet and the ^{3}n,π^* state as a spectroscopically undetectable triplet has been suggested for other aromatic compounds containing a nitrogen atom, such as acridines, although the energy gap here is larger.[35]

For the methyl ester **3′**, cyclization is possible but decarboxylation is not. In fact, Φ_d is significantly smaller than for **3**

(Table 1). The triplet properties are reminiscent of those of *N*-alkylphthalimides, in which virtually no reactive ^{3}n,π^{*} state is involved.[11, 18, 19]

Efficient triplet population is also the case for ketone-sensitized excitation (reactions (4) and (8)), since the triplet of **3** was observed under all conditions investigated (Figure 5, part a and Figure 7, part c). Quenching by electron transfer is unlikely, since neither $^{\bullet}$KH or K$^{\bullet-}$ could be detected for the **3**/CB or **3**/benzophenone systems, in contrast to the cases of **1** or **2′**. To account for the rather effective acetone-sensitized photolysis of **3**,[3] we postulate population of the ^{3}n,π^{*} state in aqueous solution and of the $^{3}\pi,\pi^{*}$ state in the absence of water. Intramolecular electron transfer should cause charge separation, CO_2 elimination, cyclization and eventually protonation to complete the formation of **3a** (Scheme 2).

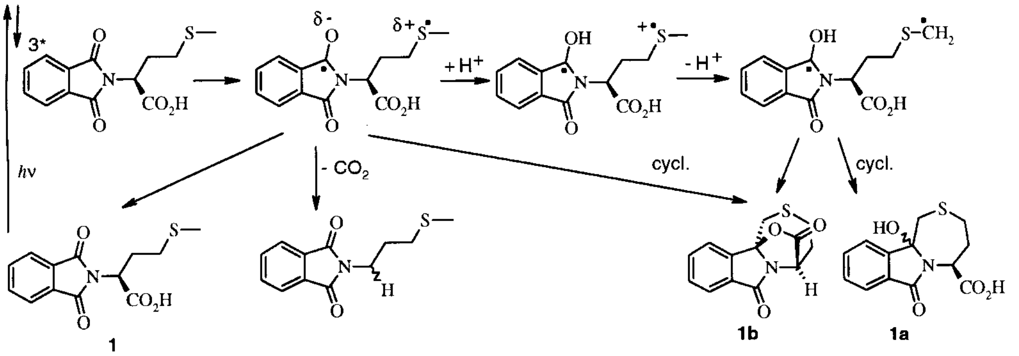
Photoreactions of 1 and 2 upon direct excitation: On the basis of flash photolysis studies of *N*-substituted phthalimides,[14, 19, 23] it is conceivable to assign the transient absorption spectrum of **1** or **2** (Figure 3, part a and b) at room temperature to the lowest triplet state. The phosphorescence results from the phthalimides in ethanol at −196 °C (Figure 2 and Table 2) support this. The shorter triplet lifetime of **1**–**3** with respect to rather unreactive *N*-alkylated phthalimides[19] could be due to subsequent reactions. However, the similar lifetimes for the *N*-phthalimides examined (Table 3), or at least those within the same order of magnitude, rule this out.

Singlet states have been assumed to contribute to the reactivity of *N*-substituted phthalimides upon direct excitation.[1, 2] The fluorescence lifetime of phthalimide esters in several solvents at room temperature are approximately 0.2 ns.[5, 18] Because of the similar Φ_f (Table 2) and τ_f values of reactive **1**, **2** and **2′** and unreactive **5** and **5′**, a triplet route upon direct excitation is more likely than a singlet route. Why, however, is almost no triplet state detectable for **1** and **2** at room temperature (Table 3)? The increase in ΔA_{330} on decreasing the temperature (Figure 4) indicates a fast reaction competing with population of the observed triplet state, and that this reaction is suppressed at lower temperatures. A possible explanation for the fast competing reaction in the cases of **1** and **2** (but not **4**)[11] is the population of an upper excited triplet state, followed by intramolecular electron transfer and then back-transfer.

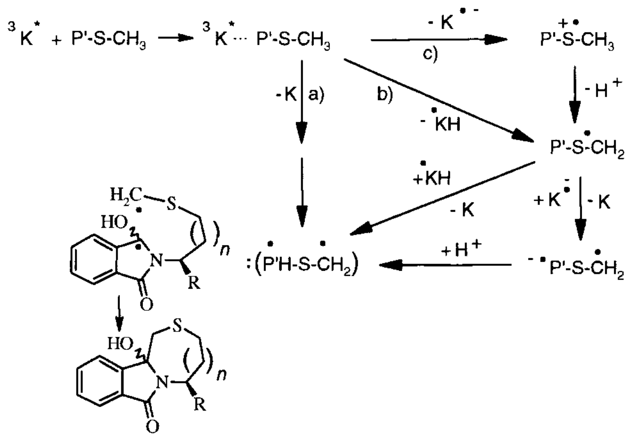
The radiation chemistry of methionine is well known.[36] The OH radical-induced decarboxylation involves a sulfur radical cation with $\lambda_{max} = 400$ nm and a lifetime of ≈ 0.2 μs and a longer lived dimeric sulfur radical cation with $\lambda_{max} = 480$ nm. However, under the applied conditions, no transient attributable to a sulfur-centred radical cation was found for **1** or **2**. Instead, the observed weak transient is most probably the lowest π,π triplet state. The proposed major cyclization of **1** and **2** after excitation occurs by means of intramolecular charge separation between the thiomethyl and phthalimide moieties (P′$^{\bullet-}$–S–Me$^{\bullet+}$), as illustrated in Scheme 4 and Scheme 1, respectively. Photoinduced charge separation has also been proposed for *N*-(2-methyl-2-propenyl)phthalimides, to account for the cyclization products.[2–16] The further reaction steps of **1** and **2** have already been discussed.[1, 2]

Sensitized photoreactions with 1 and 2: Reaction (4) of the ketone triplet state with the phthalimide is the major process, since the k_4 values of **1** and **2** are similar to those of **5** (Table 6). After quenching of ^{3}K*, however, practically no triplet could be generated for **1** (Figure 5, parts b and c, Figure 6, parts a and b) and **2′** (Figure 6, part c); that is, the energy transfer reaction (8) is too fast for observation or does not take place at all. The low amount of observed $^{3}\pi,\pi^{*}$ state should not be due to physical quenching without chemical reactivity, since the quantum yield of formation of photoproduct **2a** is 0.08 upon acetone-sensitized excitation.[2, 9] One possibility might be a too rapid charge separation in the ^{3}n,π^{*} state (^{3*}P′–S–Me → P′$^{\bullet-}$–S–Me$^{\bullet+}$) and another that quenching of ^{3}K* generates, to some degree, the ^{3}n,π^{*} state in which charge separation should occur. The most likely reason is intermolecular electron transfer (reaction (5) or reactions (6) plus (7)). In fact, for benzophenone or CB, formation of the radical and the radical anion was observed for **1** and gradually for **2′** in the presence of water at pH < 7 and > 9, respectively (Figure 5, part b—Figure 6, part c). This could be interpreted by the respective pathways b) and c) in Scheme 5.

Intermolecular electron transfer: The rate constant for quenching of the benzophenone or CB triplet state by **1** is significantly larger than that in the case of **3** (Table 6). This is in agreement with the redox properties. The measured oxidation potential (in acetonitrile vs. ferrocene) is E_{ox} =



Scheme 4. Photocyclization of **1** through intramolecular charge separation between the thiomethyl and phthalimide moieties, yielding **1a** and **1b** as products.



Scheme 5. Ketone-sensitized reactions pathways a–c accounting for cyclization of the thiomethyl and phthalimide (P′) moieties.

1.28, 1.47 and > 1.9 V for **1**, **2′** and **3**, respectively.[37] The free energy change for electron transfer is given by the Rehm–Weller relationship, where the term E_c takes account of ion pairing (< 0.06 V in acetonitrile or mixtures with water).[38]

$$\Delta G = E_{ox} - E^*_{red} - E_c \qquad (1)$$

Using the energy of the T_1 state of benzophenone (3.0 V) and the reduction potential (−1.83 V), it follows that the reduction potential in the triplet state is $E^*_{red} = 1.2$ V (versus SCE; note that E_{ox} versus SCE is approximately 0.3 V more positive than versus ferrocene). Thus, with $\Delta G = -0.2, \approx 0$ and > 0.4 V (versus SCE), for **1**, **2′** and **3**, respectively, electron transfer from the phthalimide to triplet benzophenone is feasible for **1** and **2**, but not for **3**. The results presented in Table 6 reveal that the choice of ketone sensitizers examined does not seem to be critical concerning the reaction step (4). The possibility, for a given phthalimide, of observing $^{\bullet}$KH or $K^{\bullet -}$ (Table 5) is a consequence of the specific sensitizer properties: essentially the ε values. For time-resolved measurements, benzophenone or CB are favoured, whereas for product composition analysis acetone may be better.

Pathways of photocyclization: Four cases can be distinguished mechanistically, and results supporting the different types of photochemical reactivity are summarized in Table 7. Virtually no photochemical reactivity at all (low Φ_d) is expected for **5**, **5′** or **5″**. This case (*D*) is characterized by efficient triplet population (large Φ_T and Φ_Δ values). The other extreme, case *A*, of high photochemical reactivity (large Φ_T, Φ_Δ and Φ_d values), through the $^3\pi,\pi^*$ state accounts for **3** in organic solvents. A second triplet route (case *B*), of cyclization through the higher lying $^3n,\pi^*$ state for **4** in the absence and presence of water and for **3** in aqueous solution, has large Φ_d and somewhat reduced Φ_T and Φ_Δ values. In case *C*, intermolecular electron transfer from **1** and **2** to triplet benzophenone or CB was observed. Inefficient triplet population (small Φ_T and Φ_Δ values) and low Φ_d (as a measure of cyclization) upon direct excitation of **1** or **2** can be explained by intramolecular back electron transfer as a major effect.

Table 7. Quantum yields of phthalimide derivatives.[a]

Compound	Φ_f	Φ_T	Φ_p[b]	Φ_Δ	Φ_d	IET[c]	Type[d]
1	< 0.001	0.05	0.3	< 0.05	< 0.02	yes	*C*
2	< 0.001	0.05	0.3		< 0.01	yes	*C*
2′	< 0.001		0.4	< 0.05		yes	*C*
3	< 0.002	0.5	0.3	0.13	0.3	no	*A*/*B*
3′		0.5			< 0.02	no	*B*
4[e]	< 0.002	0.2	0.5	0.3	0.16	no	*B*
5[e]	< 0.005	0.5	0.6	0.6	< 0.01	no	*D*

[a] From Tables 1–4 at 24 °C using averages of values in acetonitrile and water. [b] At −196 °C. [c] Intermolecular electron transfer upon benzophenone- or CB-sensitized excitation. [d] See text. [e] Values taken from ref. [11].

Conclusion

The excited singlet states of all *N*-phthalimides investigated are too short-lived and decay preferentially by intersystem crossing to the corresponding triplet states and only marginally ($\Phi_f < 0.01$) by fluorescence. The observable triplet state is of π,π^* type and shows strong phosphorescence ($\Phi_p = 0.3-0.5$). The photoreactive *N*-phthalimides are converted into products with remarkable differences in their quantum yields of chromophore decomposition: $\Phi_d = 0.2-0.4$ for **3** and < 0.05 for **1** and **2**. For **3** in ethanol and water, Φ_d is too large for the involvement of the singlet pathway. The quantum yields for formation of phthalimide triplet states and singlet oxygen are substantial ($\Phi_T = 0.2-0.5$, $\Phi_\Delta = 0.1-0.2$) for **3** and **4**, but small for **1** and **2**. A new triplet pathway and intramolecular electron transfer are postulated for the photocyclization. The involvement of the spectroscopically undetectable higher lying $^3n,\pi^*$ state prior to intramolecular electron transfer accounts for the difference between Φ_d and Φ_T in **4** (photoconversion into an isomer) and is suggested for the photocyclization (in low yield) of **1** and **2**. In the case of **3**, photodecarboxylation and product formation involve the $^3\pi,\pi^*$ and $^3n,\pi^*$ states in organic solvents and aqueous solution, respectively. Thus, the chemical behaviour of excited **3** and **4** points to a situation in which the classical Kasha rule (in its photochemical version) is circumvented.

Under conditions of sensitized excitation (acetone, acetophenone, xanthone and, less efficiently, benzophenone) product formation is enhanced for **1** or **2**, in contrast to **4**. The evidence for intermolecular electron transfer from **1** or **2** to triplet benzophenone or the carboxy derivative is based on spectroscopic and kinetic characterization of the radical anion of the ketone and its conjugated acid. Thus, the triplet state of the ketone acts as an electron acceptor.

Experimental Section

Compounds **1**–**3** were as used previously.[1–3] The molar absorption coefficient of **2** is $\varepsilon_{296} = 1.7 \times 10^3$ and $\varepsilon_{219} = 4.7 \times 10^4$ $M^{-1}cm^{-1}$.[2] *N*-Methylphthalimide (**5**, EGA), the sensitizers and most solvents (acetone and acetonitrile: Merck, Uvasol) were used as commercially available; ethanol was purified by distillation and water was deionized by a Millipore (Milli Q) system. Where indicated, the pH values refer to ordinary aqueous solution; otherwise they were adjusted with NaOH. *N*-Alkylphthalimides in alkaline solution are known to hydrolyze;[21] that is, they are thermally unstable. The stability in acetonitrile-water mixtures (1:1) at pH 10.5 was found to increase in the order **5**, **2** and **1**; the last two could be used within a few minutes after establishing the pH, to record transient absorption spectra. Compound **2′** was used rather than **2** in some cases, due to its better solubility.

Absorption and emission spectra were recorded on spectrophotometers (Perkin–Elmer 554 and Hewlett Packard 8453) and spectrofluorimeters (Perkin–Elmer LS5 and Spex-Fluorolog), respectively. Note that the fluorescence excitation spectrum does not generally coincide with the absorption spectrum, owing to a very small Φ_f value and superposition of fluorescence from trace impurities. Phosphorescence of $O_2(^1\Delta_g)$ at 1269 nm[39–41] was detected after the pulse, using a cooled Ge detector (North Coast, EO 817FP), a silicon filter, an interference filter and an amplifier (Comlinear, CLC-103) as described elsewhere.[11] The lifetimes range from 10–14 μs in ethanol to 60–90 μs in dichloromethane. The signal, extrapolated to the end of the 20 ns pulse (I_Δ), was found to show a linear dependence on the absorbed energy and on the laser intensity; the slope of the latter plot is denoted as q_Δ. The quantum Φ_Δ in toluene was obtained from q_Δ values using optically matched solutions ($A_{308} = 0.8$) and acridine as reference $\Phi_\Delta^{\text{ref}} = 0.71$.[40] For the values in other oxygen-saturated solvents a correction has to be applied, using the rate constant k_r for radiative deactivation of $O_2(^1\Delta_g)$ relative to that in benzene (k_r^o). The k_r/k_r^o ratios taken from the literature range from 0.12 in D_2O to 0.96 in toluene.[41] The 248 or 308 nm output from one of two excimer lasers (Lambda Physik EMG 200 and EMG 210 MSC; energy less than 100 mJ, pulse width 20 ns) was used for excitation. The laser flash photolysis apparatus and the detection system have been described elsewhere.[11, 39] For selective production of ${}^{\bullet}$KH, 2-propanol was used; the radical anion was generated by electron transfer from 1,4-diazabicyclo[2.2.2]octane or in the presence of 2-propanol in water at pH 10–11.[11]

For photodecomposition, λ_{irr} of 290 nm from a 1000 W Xe/Hg lamp combined with a monochromator or 254 nm from a low pressure Hg lamp was used. The concentration was adjusted such that the absorbance (in a 1 cm cell) was 1–3 at λ_{irr}. The quantum yield Φ_d was obtained by using the decrease of absorbance at 290 nm (or the increase in absorbance at the initial minimum $\approx$ 250 nm). Actinometry was performed with Aberchrome 540 for $\lambda_{\text{irr}} = 290$ nm.[42] The measurements (unless specified otherwise) were carried out after purging with argon prior to and during irradiation at $24 \pm 2\,^\circ$C.

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