Journal of Photochemistry and Photobiology A: Chemistry 151 (2002) 27–37

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Investigation of the photochemical properties of an important class of photobase generators: the *O*-acyloximes

J. Lalevée [a], X. Allonas [a,*], J.P. Fouassier [a], H. Tachi [b], A. Izumitani [b], M. Shirai [b], M. Tsunooka [b]

[a] *Département de Photochimie Générale, UMR No. 7525, Ecole Nationale Supérieure de Chimie, 3, rue Alfred Werner, 68093 Mulhouse Cedex, France*
[b] *Department of Applied Chemistry, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan*

Received 5 October 2001; received in revised form 10 April 2002; accepted 18 April 2002

Abstract

The influence of the molecular structure and the required conditions for bond breaking in the triplet state of 10 carefully selected *O*-acyloximes (eight of them are original) usable as photobase generators are deeply investigated for the first time. Ground state absorption and fluorescence spectra revealed that the transitions involved exhibit a $\pi\pi^*$ character. A clear nonvertical character in triplet–triplet energy transfer was found in compounds exhibiting a flexible aryl–C=N–O– moiety. An important and new point is concerned with this effect which strongly affects the triplet sensitized decomposition process, due to the possible formation of a highly vibrationally excited triplet state from which dissociation can occur. Laser experiments enabled to detect the primary free radicals formed from both direct and sensitized dissociation and to measure the relative quantum yields in iminyl radicals. Comparison of these laser experiments with steady state quantum yields of photolysis demonstrates the involvement of in-cage reactions that influence the overall efficiency of base generation, depending on the acyl moiety. All these facts were rationalized in a global mechanism of photodissociation and found to explain well the results of photoinitiated thermal crosslinking experiments performed in a model media with the starting oxime esters.

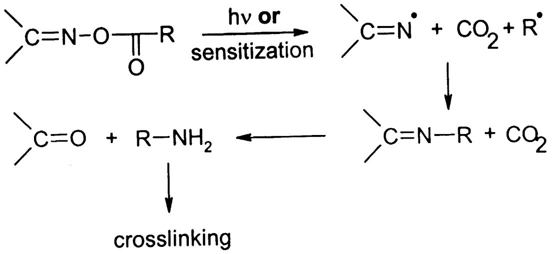
Keywords: Photobase; Oxime; Energy transfer; Photopolymerization; Iminyl radical

---

1. Introduction

The design of compounds generating acids or bases upon irradiation of light presents a great interest in the field of polymeric photosensitive systems [1–7]. Photogenerated acid has been an essential component in chemically amplified photoresists for some time, and many papers have been published in this field [1]. On the other hand, the idea of photochemically generated bases is a relatively new concept, which appeared in the end of the 1980s. Actually, these compounds are not used as initiators of ionic polymerization, but principally as catalysts for base-catalyzed crosslinking reactions. Indeed, the highly sensitive photoresist systems involve reactions such as the transformation of functional groups in polymer chains or crosslinking of polymers that can be catalyzed by photochemically generated bases. Among the different structures that can be used as photobase generators, *O*-acyloximes have been proved to be quite efficient [1,3–6,8].

In case of phenylacetyloximes, a schematic process for amine production can be given



For carbamoyl derivatives, direct hydrogen abstraction from the substrate to R$^\bullet$ leads to the formation of amine without requirement of water.

Light induced reactions of compounds possessing a carbon–nitrogen double bond (in contrast with C–O and C–C double bond based systems) have not been the subject of extensive studies [9–11]. Although some works have been carried out principally on other oximes structures to demonstrate the involvement of the triplet state in the formation of radicals [7,12–18], the influence of the molecular

---

[*] Corresponding author. Tel.: +33-389-336874; fax: +33-389-336895.
E-mail address: x.allonas@uha.fr (X. Allonas).

1010-6030/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(02)00174-0

structure and the required conditions for bond breaking in the triplet state were not yet elucidated. In addition, the relative importance of the singlet versus the triplet pathway remains unclear.

In this paper, several points will be investigated in details: the photophysical and photochemical properties of well selected *O*-acyloximes (AO), absorption and emission spectra, triplet state energy levels characterized by energy transfer experiments, bond breaking in the singlet and triplet states, generation of radicals, photolysis and crosslinking ability. All these data will allow the proposal of a global reaction mechanism and the discussion of the structure/properties relationships.

2. Experimental section

2.1. Steady state spectroscopy

The UV spectra were carried out in benzene and acetonitrile (spectroscopic grade, Fluka). Fluorescence spectra at room temperature were recorded on a Fluoromax 2 (Jobin-Yvon). The experiments of luminescence at 77 K have been realized in ethanol with a special accessory adapted to a LS-5B (Perkin-Elmer).

2.2. Laser spectroscopy

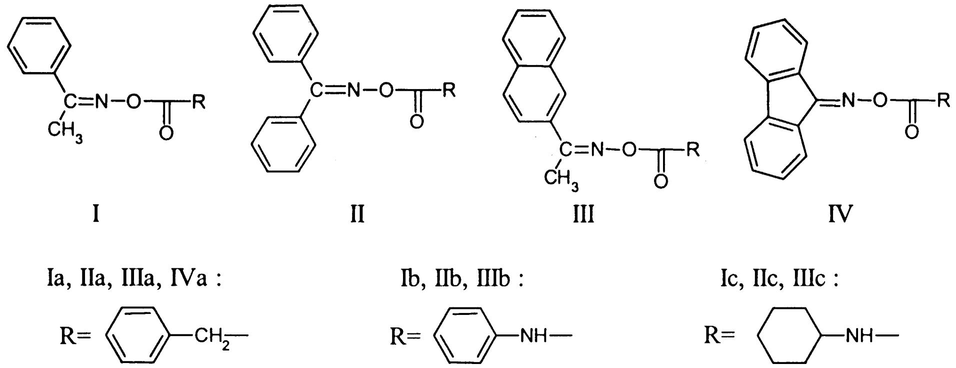
The nanosecond transient absorption setup is based on a pulsed solid state tunable laser. It includes a Nd:Yag laser (Powerlite 9010, continuum) operating at 10 Hz with an injection seeding system that improves the single longitudinal mode output and the shot to shot stability. After amplification, the output is frequency doubled and tripled. This laser can deliver nanosecond pulses at 355 nm with an energy of about 500 mJ that are used to pump an optical parametric oscillator (OPO, Sunlite, Continuum) and an optical parametric amplifier (OPA) generating a narrowband radiation in the visible and near-infrared spectral region. The wavelength is tunable continuously from 450 to 1800 nm. A frequency doubling system (FX1, continuum) pumped by the OPO–OPA output is able to deliver a nanosecond pulse from 225 to 450 nm with an average energy about 8 mJ. The transient absorption analysis system (LP900, Edinburgh Instruments) used a 450 W pulsed xenon arc lamp, a Czerny–Turner monochromator, a fast photomultiplier and a transient digitizer (TDS 340, Tektronix). This experimental setup is characterized by an instrumental response of about 7 ns.

2.3. Photolysis experiments

The irradiation lamp was a medium pressure mercury lamp (Ushio UM102, 100W) for experiments at 254 and 366 nm. The line at 366 nm was selected with a filter (Toshiba UV-36B). The intensity was 1.30 mW cm^{-2}. The photolysis have been conducted in films (0.3 g polystyrene film 40–50 μm thickness, 0.015 g of acyloxime, 0.03 g of benzophenone, BP) or in solvent (benzene, [acyloxime] = 0.1 mol dm^{-3}, [BP] = 0.1 mol dm^{-3}). The photolysis was followed through infrared spectroscopy by probing the bleaching of the characteristic absorption band of the oxime at 1760 cm^{-1} (Jasco FTIR 7300). The quantum yields of photolysis were calculated after evaluation of the energy absorbed.

2.4. Photoinitiated thermal crosslinking experiments

The photoinitiated thermal crosslinking of poly(glycidyl methacrylate) films (PGMA) was carried out: PGMA films (0.35 μm thick) were prepared by casting (on a quartz plate) a tetrahydrofuran solution of PGMA (30 mg), carbamoyloximes (3.0 mg) and BP (3.0 mg). The films were irradiated at 366 nm under air with a low pressure mercury lamp (Ushio ULO-6DQ, 6W, 1.00 mW cm^{-2}). Post-baking at 80 °C for 10 min was then achieved. Insoluble fractions were determined by the ratio of the film thickness before and after dipping in THF by the use of two beam interferometry with a metallurgical microscope (Nikon optiphot XPF-UM).



Scheme 1.

2.5. *Compounds studied*

The different oximes, presented in Scheme 1, were synthesized by a procedure described elsewhere [4,6,16]. Four different basic structures (i.e. acetophenone (I), BP (II), acetonaphthone (III) and fluorenone (IV) oximes) substituted by *O*-phenylacetyl (a), *N*-phenylcarbamoyl (b), *N*-cyclohexylcarbamoyl (c) groups were studied. Compounds I and III are supposed to be in the *E* form.

3. Results and discussion

3.1. *Absorption and emission properties*

Table 1 gathers the different wavelengths of absorption maximum for the oximes (eight of them are original) and the parent ketones, as well as the corresponding molar absorption coefficients in acetonitrile and methanol. It can be seen that the absorption properties are only slightly influenced by the acyl group. This is attributed to a $S_0 \rightarrow S_1$ transition localized on the oxime moiety. Due to their structural analogy and the presence of electron lone pair on the heteroatom, ketones were often compared with the corresponding oximes [17,19], the question being the nature of the electronic transitions. A solvent effect on Ia, IIa, IIIa and IVa, clearly demonstrates the character $\pi\pi^*$ of the transitions for all the oximes studied. The lone pair of nitrogen atom seems to influence slightly the electronic transitions, in contrast to parent ketone for which a lone pair of oxygen atom can lead to a red shifted transition with important $n\pi^*$ character (see for example acetophenone versus Ia or BP versus IIa, Table 1). On the contrary, the UV spectra of III and IV are very similar to the corresponding ketones, all the electronic transitions being of $\pi\pi^*$ nature.

As for the corresponding ketones, no fluorescence has been observed for the compounds I and II with our experimental setup. Only acetonaphthone and fluorenone oxime esters exhibit fluorescence. A parallel can be drawn between absorption and fluorescence properties: the fluorescence features of acetonaphthone oxime derivatives (IIIa, IIIb or IIIc) in benzene are not influenced by the acyl moiety (Fig. 1). In addition, the fluorescence spectra of IVa and fluorenone exhibit a striking resemblance: the maxima of emission correspond to 478 and 487 nm, respectively, for IVa and fluorenone in benzene, and 494 and 515 nm in acetonitrile (Fig. 1). The relative fluorescence quantum yield in acetonitrile of IVa corresponds to the half of the fluorenone one. In order to increase the intensity, fluorescence experiments were carried out in ethanol at low temperature (77 K). For compounds I and II, the fluorescence spectra reflect the absence of any $n\pi^*$ transition. Indeed, despite the expected hypsochromic shift of the fluorescence between room temperature and 77 K, the position of the maximum does not agree with a $n\pi^*$ transition localized above 310 nm. The emission maxima were located at 315, 310 and 310 nm for IIa, Ia and Ic, respectively, demonstrating the $\pi\pi^*$ character of the lowest singlet states. All these facts agree very well with the above remark of a $S_0 \rightarrow S_1$ transition involving orbitals only localized on the oxime moiety.

The transitions observed for the present oxime derivatives are of $\pi\pi^*$ nature and the presence of a lone pair on the nitrogen atom do not lead to any observable $n\pi^*$ transition.

Table 1
Absorption properties of *O*-acyloximes and corresponding ketones

Compounds	Methanol		Acetonitrile		Electronic character
	λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	λ_{max} (nm)	ε_{max} ($M^{-1}\,cm^{-1}$)	
Acetophenone	–	–	239	12070	$\pi\pi^*$
	–	–	316	50	$n\pi^*$
Ia	243	16200	243	14950	$\pi\pi^*$
Ib	250	24800	246	–	$\pi\pi^*$
Ic	245	14300	245	–	$\pi\pi^*$
Benzophenone	–	–	251	18360	$\pi\pi^*$
	–	–	337	130	$n\pi^*$
IIa	254	15000	251	16050	$\pi\pi^*$
IIb	259	18800	254	–	$\pi\pi^*$
IIc	260	20600	251	–	$\pi\pi^*$
Acetonaphthone	–	–	246	50990	$\pi\pi^*$
	–	–	339	1550	$\pi\pi^*$
IIIa	247	45150	246	49460	$\pi\pi^*$
IIIb	248	43900	247	–	$\pi\pi^*$
IIIc	247	46500	245	–	$\pi\pi^*$
Fluorenone	–	–	255	101500	$\pi\pi^*$
	–	–	378	270	$\pi\pi^*$
Iva	255	59400	255	58680	$\pi\pi^*$

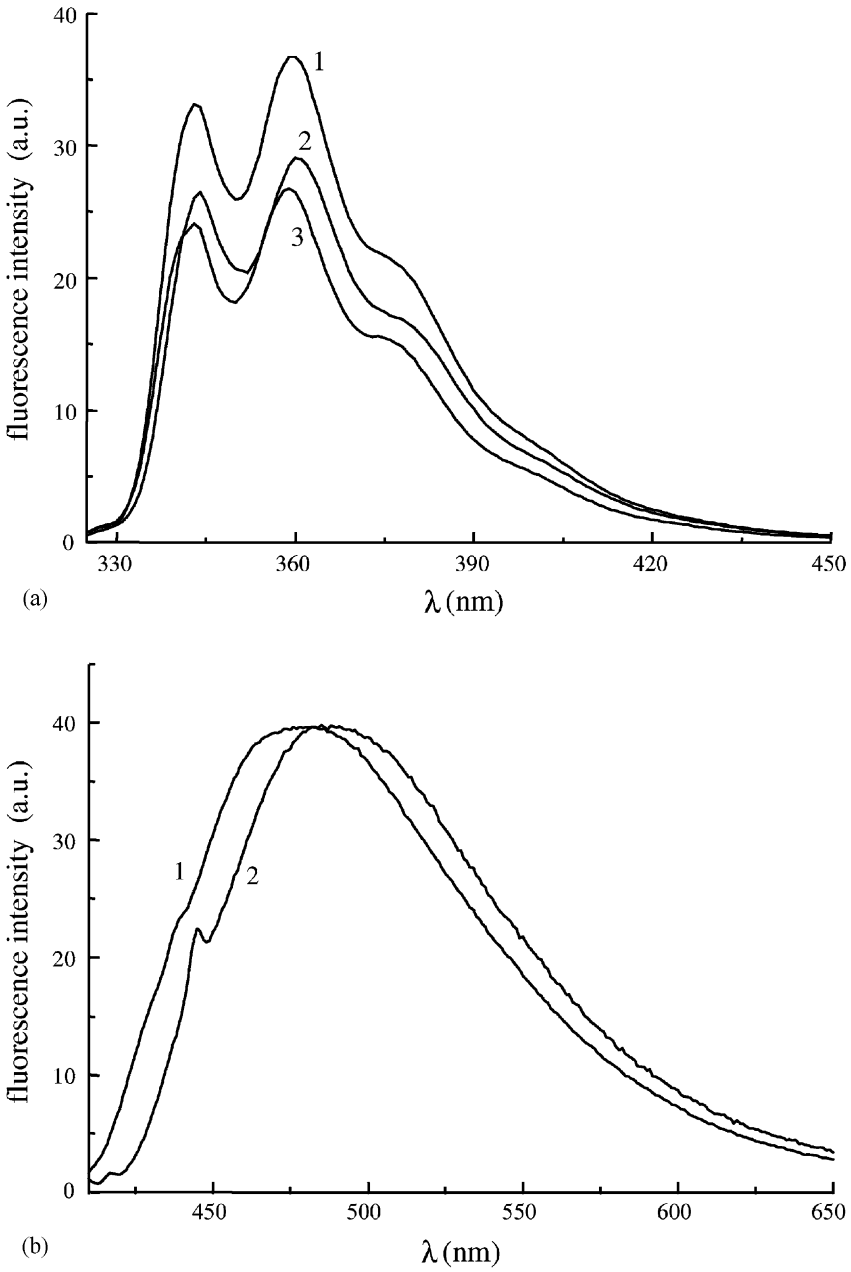


Fig. 1. (a) Fluorescence spectra of (1) IIIa, (2) IIIb, (3) IIIc; (b) fluorescence spectra of (1) IVa and (2) fluorenone in benzene.

3.2. Direct and sensitized photolysis

In order to check the photoreactivity of the studied *O*-acyloximes, steady-state photolysis experiments were carried out in film and in benzene. The quantum yields of photolysis ϕ_{ph} are collected in Table 2. From these results, it is clear that both the direct and the sensitized excitation of *O*-acyloximes can lead to dissociation. However, no information on the process involved is available. Discussion of the results obtained both in direct excitation or in sensitized experiments will be presented below.

3.3. Photoinitiated thermal crosslinking experiments

The ability of oxime derivatives to generate amine has been already evidenced [3,6,7,16]. In order to evaluate the efficiency of the studied compounds, experiments of photoinitiated thermal crosslinking of epoxides (polyglycidyl methacrylate films) were carried out on *N*-phenylcarbamoyl and *N*-cyclohexylcarbamoyl derivatives with the use of BP as sensitizer. The results are shown in Fig. 2. The overall efficiency of the systems was determined by following the insoluble fraction as a function of the energy dose and they order as follows: IIIb > IIIc > Ib > IIb > Ic > IIc.

Table 2
Steady-state photolysis quantum yields ϕ_{ph} (see Section 2)

Compound	ϕ_{ph}			
	Direct excitation in film[a] (under N_2)	Sensitization in film[b] (under N_2)	Sensitization in solution[c]	
			Under N_2[d]	Under air
Ia	n	0.41	0.6 (0.65)	0.6
Ib	0.86	n	0.91 (1)	0.79
Ic	0.59	n	0.46 (0.5)	0.45
IIa	n	0.35	0.42 (0.7)	0.42
IIb	0.73	n	0.58 (1)	0.5
Iic	0.08	n	0.28 (0.48)	0.27
IIIa	n	0.59	0.62 (0.66)	0.63
IIIb	n	n	0.94 (1)	0.81
IIIc	n	n	0.63 (0.67)	0.62
Iva	n	0.06	0.07	0.07

n: not available (see text).

[a] Irradiation at 254 nm in a polymethylmethacrylate film.

[b] Irradiation at 366 nm in a polystyrene film in the presence of BP.

[c] Irradiation at 366 nm in benzene.

[d] The values in parenthesis correspond to the quantum yields of photolysis normalized to the maximum obtained for a given oxime structure.

3.4. Direct laser excitation

Direct excitation of *O*-acyloximes did not reveal any absorbing transient that can be ascribed to triplet states in our experimental conditions. In the literature [13], a short lifetime of 10 ns has been measured for the triplet state of dibenzophenone oxime hexamethylene diurethane, the intersystem crossing was found low and the extinction coefficient seemed weak. All these facts render the direct detection of acyloxime triplet state rather difficult. For oximes based on other chemical structures, it has been noticed that direct irradiation can lead to photolysis and formation of radicals, albeit with very poor yields [14,15,17]. In our case, some compounds (Ib and IIb) lead to transients that are ascribed to iminyl radicals (see below). The efficiency of direct excitation and particularly the possibility of singlet state cleavage will be examined in details (see below).

3.5. The triplet state

3.5.1. The triplet energy level

Phosphorescence in glassy matrix allows the determination of triplet energies of about 305 kJ mol^{-1} for BP oxime (IIb, c) and about 245 kJ mol^{-1} for acetonaphthone oxime (IIIa, b, c) derivatives. These values agree very well with results reported in the literature for other BP oximes [17].

Energy transfer experiments have been carefully done in order to study the quenching rate constant k_q of triplet donors by *O*-acyloximes; results have been already reported with the use of donors defined in [20]. The plots of k_q versus E_T^D have been fitted according to the classical Sandros treatment [21], leading to the estimation of vertical energy levels. The agreement between this model and the experimental data has been found to be very good for IVa and, to a lesser extent, for III(a, b, c). However, the behavior of compounds I and II has been poorly described by the Sandros plots. In the endergonic region, the experimental points exhibit a slope lower than that calculated from the Sandros model, i.e. 0.17 mol kJ^{-1} (Fig. 3) [20]. As observed in other molecular structures, this departure from the classical model is generally ascribed to a change in the geometry of the molecule between ground and excited states [22–24], an effect called nonvertical energy transfer (NVET). To describe this particular behavior, the Agmon–Levine–Balzani (ALB) model can be applied [25,26]. The mechanism for energy transfer process is shown in Scheme 2, where k_d, k_{-d}, k_{en} and k_{-en} represent the rate constants for formation and dissociation of the encounter complex and the rate constants of energy transfer and back transfer, respectively. The quenching rate

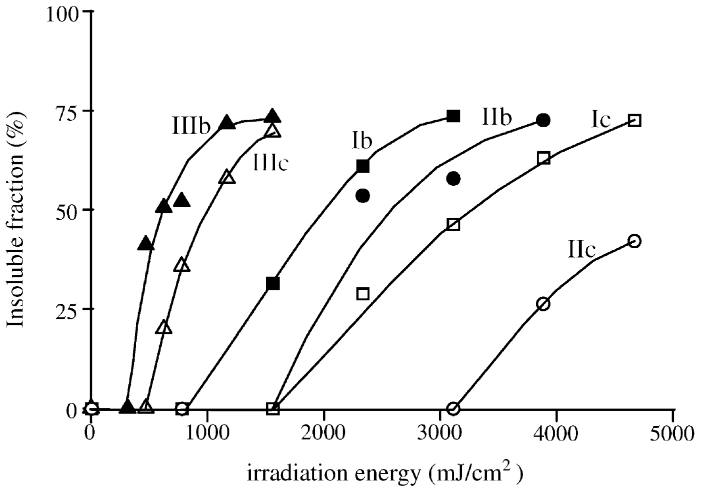


Fig. 2. Insoluble fraction of PGMA films with *O*-carbamoyloximes and BP vs. the irradiation energy dose *E* at 366 nm. Post-baking at 80 °C for 10 min.

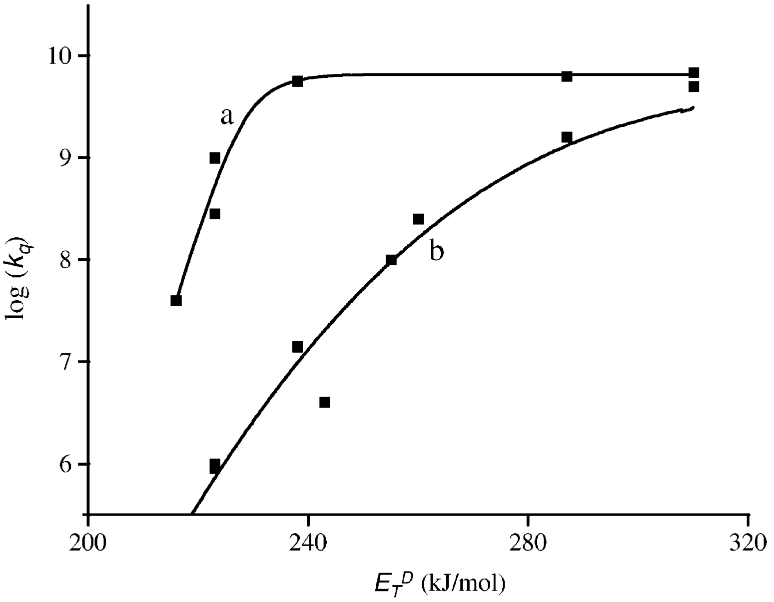
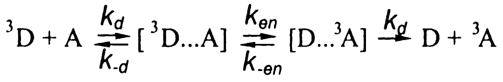


Fig. 3. Plots of the quenching rate constants k_q vs. the donor triplet energy E_T^D (a) for IVa and (b) for Ia. The experimental data were fitted to the ALB model (see text).



$$ {}^3D + A \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [{}^3D...A] \underset{k_{-en}}{\overset{k_{en}}{\rightleftharpoons}} [D...{}^3A] \xrightarrow{k_d} D + {}^3A $$

Scheme 2.

constant k_q is given by

$$k_q = \frac{k_d}{1 + k_{-d}/k_{en} + \exp(+\Delta G/RT)} \quad \text{with}$$

$$k_{en} = k_{en}^0 \exp\left(\frac{-\Delta G^*}{RT}\right) \qquad (1)$$

where $\Delta G = E_T^O - E_T^D$ with E_T^O the oxime triplet energy; k_{en}^0, ΔG^* are the preexponential factor and the standard free activation energy, respectively. In this treatment, ΔG^* is related to the free energy change of the process by using following expression

$$\Delta G^* = \Delta G + \frac{\Delta G^*(0)}{\ln 2} \ln\left(1 + \exp\left(-\frac{\Delta G \ln 2}{\Delta G^*(0)}\right)\right) \qquad (2)$$

where $\Delta G^*(0)$, the reorganizational intrinsic barrier, is related to the changes in nuclear positions that have to occur prior to energy transfer [26].

Results are given in Table 3. Compound IVa, which is essentially planar, does not lead to any difference in the triplet

Table 3
Triplet energies obtained from phosphorescence at 77 K and energy transfer in solution at room temperature (results of the best fits obtained with the Sandros and the ALB models)

Compound	Phosphorescence (E_T^O, kJ mol^{-1})	Energy transfer			
		Sandros	ALB		
		E_T^O (kJ mol^{-1})	E_T^O (kJ mol^{-1})	$\Delta G^*(0)$ (kJ mol^{-1})	k_{en}^0 (10^{-10}) s^{-1}
Ia	–	250	222[a]	23[a]	0.8[a]
Ib	–	258	249	10.5	0.6
Ic	–	250	232	17	0.8
IIa	–	255	244	15	1
IIb	307	255	244	10.5	0.5
Iic	300	257	239	15	0.8
IIIa	246	229	218	14.5	1.5
IIIb	249	230	222[a]	11[a]	1.5[a]
IIIc	249	228	222	11	1.5
Iva		228	228	3.7	2.21

[a] Obtained with a fixed value of k_{en}^0 in the fitting procedure.

$$^{3}\mathrm{BP} + \mathrm{AO} \rightarrow {}^{3}\mathrm{AO} + \mathrm{BP}$$

$$^{3}\mathrm{AO} \rightarrow \mathrm{radicals}$$

Scheme 3.

energy determined by using the different methods. The ALB model leads to the determination of the relaxed triplet energies, that are lower than the spectroscopic triplet energies due to the increase of the flexibility of the molecules. This fact has been already reported on a series of oximes and the influence of flexibility on the nonvertical character clearly evidenced [27]. Compounds I and II having important possibilities of geometry changes between ground and excited states exhibit important NVET characters. The free rotation of the phenyl rings at room temperature is responsible for the large difference between the spectroscopic energy determined by phosphorescence at 77 K and the relaxed energy determined in solution at room temperature. For instance, in case of compound IIb this difference is about 63 kJ mol^{-1}. Similar behaviors have been observed for benzil derivatives [28].

The relaxed triplet energy levels are only slightly dependent of the acyl substituents. The nature of the acyl moiety (in the a, b and c series) does not affect by more than 10 kJ mol^{-1}, the energy level of the ketone oxime triplet state in agreement with previous data of steady-state photolysis experiments on other derivatives [18]. It follows that the triplet character is localized on the ketone oxime part of the molecule, a fact supported by the values of the triplet energies which decrease when the delocalization increases.

3.5.2. The sensitized cleavage in the triplet state

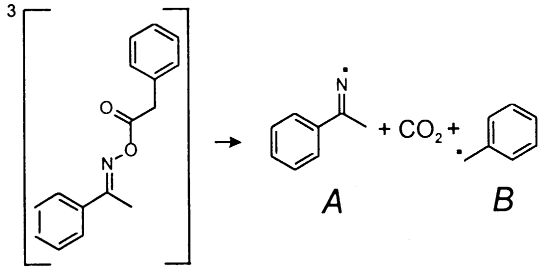
Although sensitization experiments with BP form quantitatively the triplet state through energy transfer [20] (Scheme 3), no triplet state absorption was observed. A fast deactivation of the triplet is expected to occur [13] through the cleavage of the N–O bond, leading nearly quantitatively to the formation of radicals.

Different transients attributable to radicals were detected in acetonitrile or benzene. The different results obtained for I and II derivatives are summarized in Table 4 and typical transient absorption curves versus time are represented in Fig. 4. Unfortunately, for the compounds III and IV, their own absorption at the excitation wavelength (355 nm) prevent to realize this kind of experiments. Three different transients were observed. For a and b derivatives of I and II, a very long-lived transient (called A) is obtained around 300 nm (Fig. 4) with a decreasing absorption falling down at 350 nm. This transient has been already observed by laser spectroscopy for a derivative of BP oxime [13] and was ascribed to the iminyl radical (A in Scheme 4). This transient is very stable and insensitive to O_2. No decrease of the absorption in 50 μs range is observed in acetonitrile and benzene.

Table 4
Different transients observed with I and II derivatives in benzene and their maximum absorption wavelengths obtained through triplet–triplet sensitization

Oxime	Transient A (nm)	Transient B (nm)	Transient C (nm)
Ia	300	316	n.o.
Ib	300	–	330
Ic	n.o.	–	300
IIa	300	316	n.o.
IIb	300	–	n.o.
IIc	n.o.	–	n.o.

n.o.: not observed.



Scheme 4.

In the case of Ia and IIa (phenylacetyl moiety), another transient (called B) with a very narrow absorption band is detected near 320 nm (Fig. 4). This transient corresponds to the typical absorption of the benzyl radical [29]. The corresponding half-lifetime is shorter than for the iminyl radical, and an estimate about 4 and 7 μs can be given in acetonitrile and benzene, respectively. All these facts strongly support a mechanism based on an N–O bond scission occurring in the triplet state and followed by a very fast decarboxylation of the acyloxyl radical (Scheme 4) yielding a benzyl radical. The fast rise of this radical occurs within the time resolution of the setup in the sensitizing conditions (competitive absorption of ground state sensitizer and oxime). This leads to a rate constant of decarboxylation above $2 \times 10^{7}\ \mathrm{s}^{-1}$. Lower values for rate constant of decarboxylation (10^{5} to $10^{6}\ \mathrm{s}^{-1}$) have been reported in the case of the benzoyloxyl radical [30], but this particular behavior can be probably ascribed to a stabilization of the radical by a delocalization of the lone electron on the phenyl ring. In the present case, this phenomenon cannot take place. On the other hand, very high rates have been observed in other studies of decarboxylation reactions of acyloxyl radicals (about $10^{10}\ \mathrm{s}^{-1}$) [31].

In the case of compounds I(b, c) a third transient (called C) due to secondary reaction was observed at different wavelengths (Fig. 4). This transient cannot be formed from the iminyl radical A, because the decay of A does not correspond to the rise of C. This transient C may involve an aminyl radical. Such a secondary reaction of the aminyl radical with a ground state oxime has been already observed [15].

The observation of iminyl radicals for I(a, b, c) and II(a, b, c) allows to determine the relative quantum yields ϕ_{Im} for both type of oxime derivatives by comparison of the optical

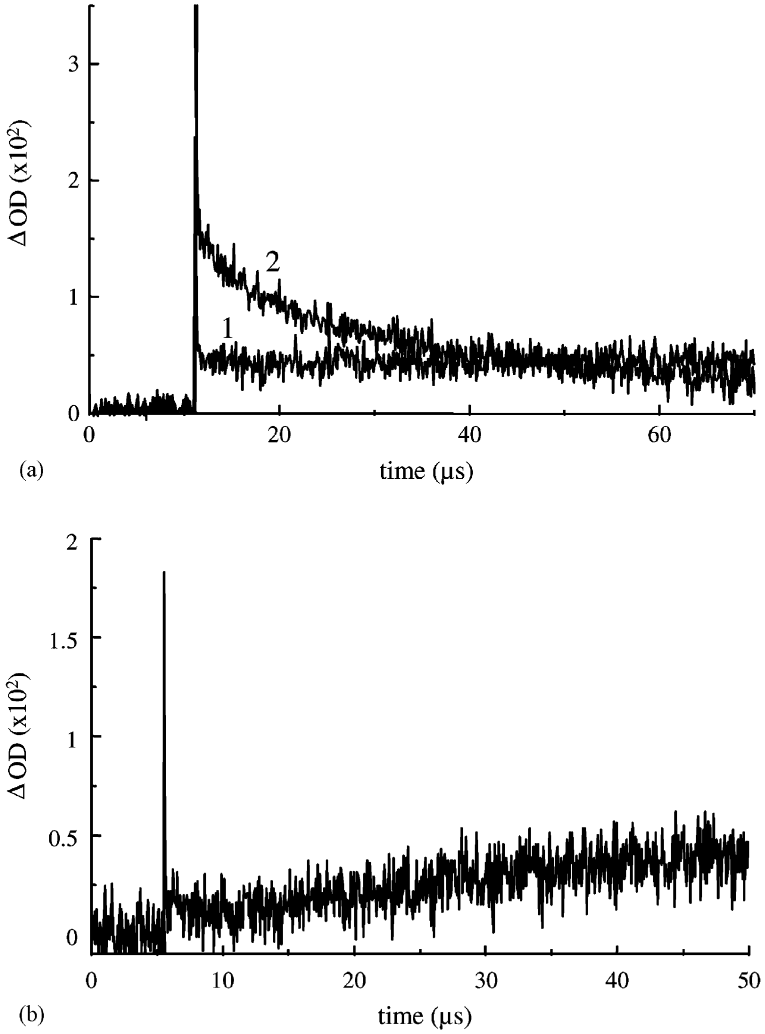


Fig. 4. The different transients observed in sensitization experiments: (a) BP + Ia in benzene, (1) observed at 300 nm iminyl radical (A) and (2) observed at 320 nm (benzyl radical B); (b) transient observed at 330 nm (species C for the system BP + Ib in benzene).

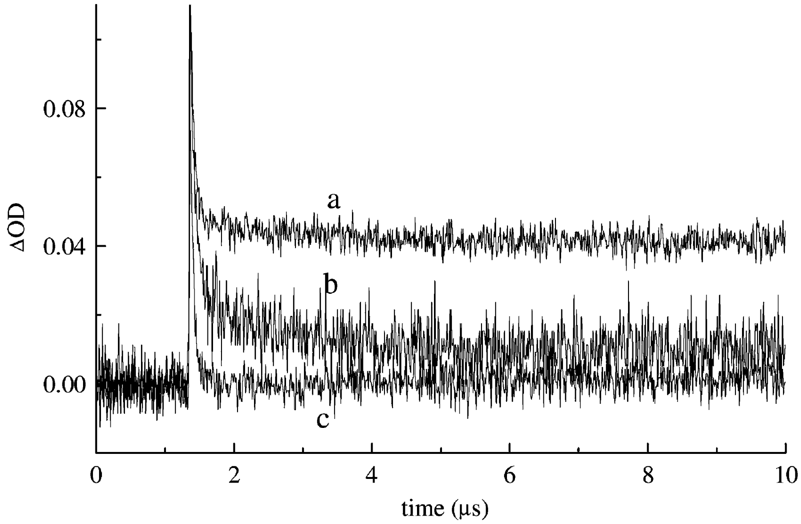


Fig. 5. Transient absorption probed at 300 nm (in benzene) for (a) BP + Ib, (b) BP + Ia, (c) BP + Ic. The long-lived component is ascribed to iminyl radicals.

densities at 300 nm. Relative quantum yields in iminyl radicals are: 0.4, 1, and <0.05 for Ia, Ib and Ic, respectively; 1, 0.9 and <0.05 for IIa, IIb and IIc, respectively. For a given oxime, the a and b derivatives give high yields in iminyl radicals, contrary to c derivatives for which nearly no iminyl radical was observed (Fig. 5).

3.5.3. *The triplet versus singlet state cleavage*

For IIb, the amount of iminyl radicals produced under direct excitation at 270 nm and through sensitization with BP at 355 nm were measured in acetonitrile. The triplet state of BP was used as an actinometer in order to compare these two experiments. The different kinetics, monitored at 310 nm, were normalized to the same absorbed light intensity and it was found that the iminyl radical formation under direct excitation is about two times more efficient. This higher efficiency clearly demonstrates for this compound that a large part of the mechanism occurs through the singlet excited state.

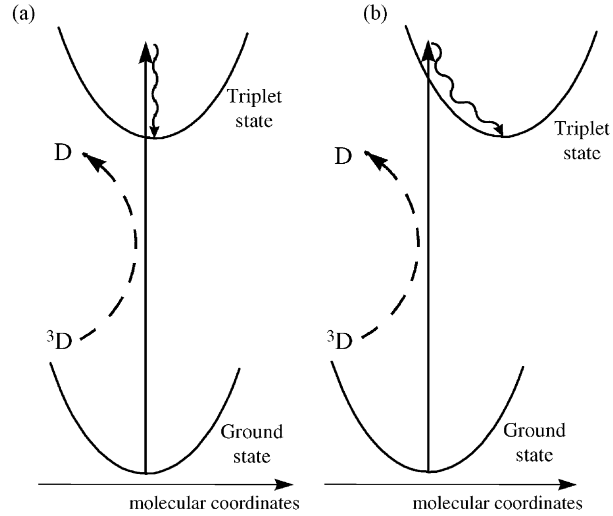


Fig. 6. Schematic representation of (a) vertical energy transfer from a donor D to a rigid molecule, and (b) nonvertical energy transfer to a flexible molecule.

4. Proposition of a global mechanism of dissociation

4.1. *Triplet sensitized dissociation through energy transfer*

Assuming a bond dissociation energy (BDE) of about 225 kJ mol^{-1} for the nitrogen–oxygen bond, [17] it is reasonable to suppose that the reactivity of the triplet states of *O*-acyloximes is related to the value of the triplet energy levels: compounds characterized by triplet energies higher than the BDE should exhibit high reactivity. This is indeed the case for compounds I and II which have triplet energy levels higher than 225 kJ mol^{-1}, and are characterized by high values of ϕ_{ph} when sensitized by BP (Table 2). However, during sensitization, the energy transferred to the oximes depends on the relaxed triplet energy of the donor $E_{\mathrm{T}}^{\mathrm{D}}$. If $E_{\mathrm{T}}^{\mathrm{D}}$ is higher than the relaxed triplet energy of the oxime $E_{\mathrm{T}}^{\mathrm{O}}$, this latter is formed in a highly vibrationally excited state from which dissociation can occur. From Table 5, it can be seen that the ϕ_{ph} values of Ia and IIIa decrease with $E_{\mathrm{T}}^{\mathrm{D}}$. This result supports the hypothesis of a dissociation from a vibrationally excited triplet state. A similar short lived precursor has been invoked to explained the photoisomerization of acetophenone *O*-methyloxime [9,10].

More insights into the photodissociation mechanism can be obtained from the comparison of compounds IIIa and IVa that exhibit a very different photoreactivity (Table 2), although they are characterized by comparable relaxed triplet energy levels. Indeed, IVa is stable under irradiation while IIIa is characterized by a high quantum yield of photolysis. Therefore, assuming an identical BDE, the dissociation does not take place from the relaxed triplet state. In order to rationalize this fact, it should be noted that IVa exhibits a clear vertical behavior which places its spectroscopic triplet energy level at about 230 kJ mol^{-1}. On the contrary, the spectroscopic triplet energy level of IIIa is higher, determined as 246 kJ mol^{-1} by phosphorescence at 77 K, and this compound exhibits a nonvertical behavior indicating a flexibility of the molecule. In that situation, the geometry of the triplet state, reached spectroscopically or from energy transfer, is different from the relaxed one (Fig. 6) [27]. During the relaxation process, the excited flexible molecule (IIIa) explores more different geometries than the rigid molecule (IVa), giving the possibility to reach more easily the transition state for the dissociation. Therefore, the higher spectroscopic triplet energy of IIIa should explain the high photodissociation efficiency, that can depends on the changes in geometry accompanying the relaxation.

4.2. *Importance of in-cage reactions*

The very slight influence of O_2 on the photolysis results (Table 2) can be explained by the short lifetime of the acyloxime triplet state, a fact already mentioned. In sensitization experiments, it was found that the quantum yields of

Table 5
Quantum yields of decomposition of *O*-acyloximes in films under irradiation at 366 nm with various sensitizers and at the same quenching efficiency

	Xanthone ($E_{\mathrm{T}}^{\mathrm{D}} = 310$ kJ mol^{-1})	Benzophenone ($E_{\mathrm{T}}^{\mathrm{D}} = 288$ kJ mol^{-1})	Benzil ($E_{\mathrm{T}}^{\mathrm{D}} = 223$ kJ mol^{-1})
Ia	0.57	0.44	∼ 0.00
IIIa	0.68	0.54	0.39

photolysis strongly depend on the substituent. For a given oxime, the cyclohexylcarbamoyl derivative (c) always gives the lower photolysis quantum yield, next is the phenylacetyl derivative (a); finally the phenylcarbamoyl derivative (b) gives the higher yield. The same trend was observed between the photolysis results and the values of quantum yields in iminyl radical, giving confidence to the results obtained. These observations cannot be accounted for by a change in the N–O bond dissociation energy with the substituent. Indeed, such a behavior should be strongly dependent on the triplet energy: this is not observed since it has been shown to be constant for a given oxime (normalized values in Table 2). The large difference in the relative iminyl yields determined just after flash indicates that in-cage reactions occur prior to the separation of the photoproduced radicals. The back-formation of a N–O bond (with spin change) after cleavage results in lower quantum yields of photolysis and in iminyl radical. Dissociation of oxime leads to iminyl radical and acyloxyl radical ($RCO_2^\bullet$). If the decarboxylation is not fast enough, these two radicals can recombine to give the starting oxime, and therefore the global efficiency of the photodissociation is decreased [15]. On the contrary, the occurrence of the decarboxylation process leads to the formation of carbon dioxide and a new radical ($R^\bullet$). The latter can also react in-cage with the iminyl radical to form an imine, resulting in a decrease of the free iminyl radical quantum yield (Scheme 5).

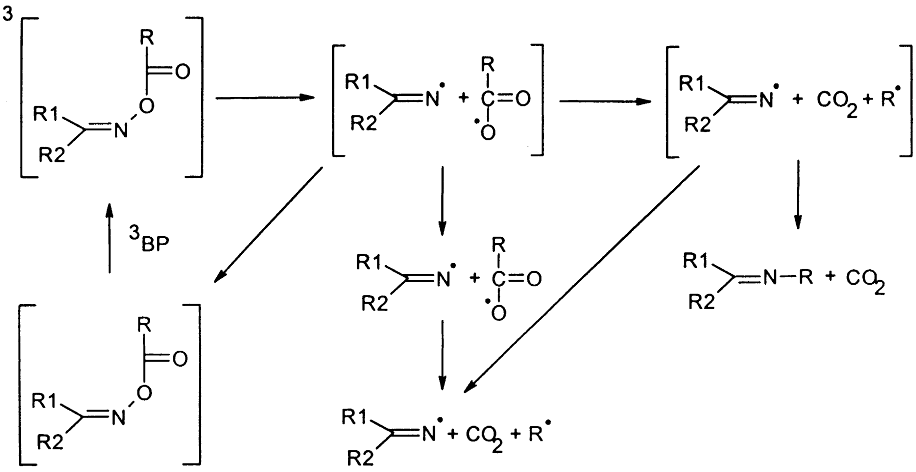
These hypothesis are clearly supported by the experiments. For example, the photodissociation of Ib was nearly complete although that of Ia is only 0.6, a trend also observed from laser experiments. The situation was more pronounced for Ic for which no iminyl radical was observed by laser spectroscopy, although a clear photolysis occured. In that case, in-cage reactions governs the overall efficiency. The observed degradation of the oxime is well explained by the competition between decarboxylation followed by subsequent reaction of the radical ($R^\bullet$) with the iminyl radical to form an imine, and the separation of the system to give the observable species (Scheme 5).

Comparing the influence of the oxime part for a given acyl moiety let show that the photolysis quantum yields always increase from compounds II to compounds I and III. This effect evidences the reactivity of the iminyl radicals toward $RCO_2^\bullet$ which decreases ϕ_{ph}. Iminyl radicals from compounds II are more reactive than that produced with the compounds I and III.

Under direct excitation, *N*-phenylcarbamoyl derivatives were more reactive in photolysis than other acyl moieties (Table 2). This fact qualitatively agrees with results from laser excitation experiments, previously reported for IIb. The high yields of photolysis for these compounds give evidence to the possibility of a dissociation from the singlet state. Moreover, the higher quantum yield of photolysis obtained under direct excitation for Ic clearly demonstrates the involvement of a singlet mechanism. In this case, the lack of detectable radicals, as in the case of the sensitization experiments, has already been explained in the former paragraph. Therefore, it seems clear that under direct excitation, even if photodissociation can occur from the triplet state, the singlet state can also give rise to an efficient dissociation for some *O*-acyloximes.

4.3. Quantum yields of photolysis and crosslinking efficiency

Despite the different processes involved in the photosensitized crosslinking experiments, the results clearly show that the increase of efficiency (expressed as the time—deduced from Fig. 2 required to reach 50% of insolubilization) agrees quite well with that of the photolysis quantum yields (Fig. 7) and follow the order: IIIb > IIIc > Ib > IIb > Ic > IIc. Therefore, it seems clear for these systems that the photolysis efficiency, representative of the production of amine,



Scheme 5.

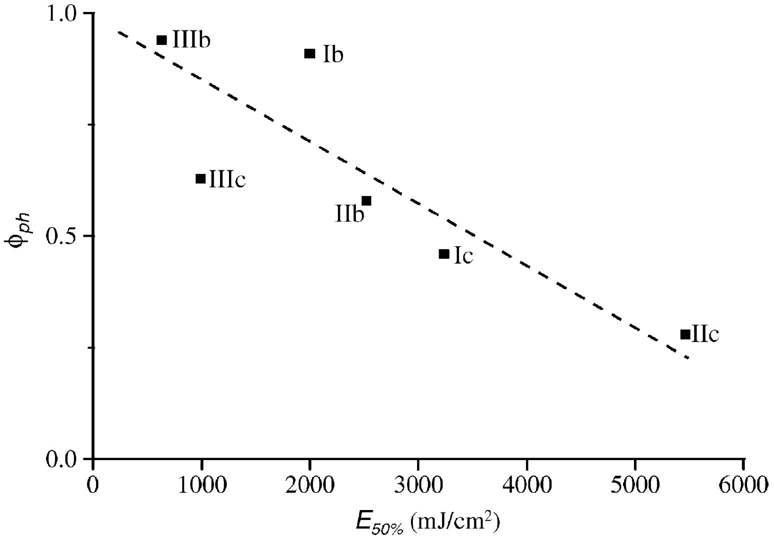


Fig. 7. Representation of the quantum yields of photolysis ϕ_{ph} vs. the energy required for 50% of insolubilization $E_{50\%}$ (photosensitized conditions).

governs directly the efficiency of the photoinitiated thermal crosslinking.

5. Conclusion

In this study, the photophysical and photochemical properties of original *O*-acyloximes have been examined together with their efficiency in crosslinking experiments. It was shown that the $S_0 \rightarrow S_1$ transition and the triplet state are localized on the oxime moiety. The study of the triplet state has pointed out a clear non-vertical behavior for the flexible molecules that affects the efficiency of the sensitized mechanism. The direct observation of radicals allowed to propose a mechanism of dissociation which includes the substituent effects. Moreover, a good correlation between the photolysis results and the efficiency observed in photoinitiated thermal crosslinking experiments has been established. Therefore, the main factors governing the photodissociation of *O*-acyloximes have been unraveled in details, allowing to relate for the first time the molecular structure with the reactivity of these systems in crosslinking experiments. The study of other photobase generators as well as the investigation of the nonvertical energy transfer mechanism on a new set of oximes will be developped in forthcoming papers.

References

[1] M. Shirai, M. Tsunooka, Bull. Chem. Soc. Jpn. 71 (1998) 2483.
[2] M. Shirai, J. Nakanishi, M. Tsunooka, T. Matsuo, M. Endo, J. Photopolym. Sci. Technol. 11 (1998) 641.
[3] K.-H. Song, M. Tsunooka, M. Tanaka, J. Photochem. Photobiol. A.: Chem. 44 (1988) 197.
[4] K. Ito, M. Nishimura, M. Sashio, M. Tsunooka, J. Polym. Sci. Part A: Polym. Chem. 32 (1994) 2177.
[5] K. Ito, Y. Shigeru, Y. Kawata, K. Ito, M. Tsunooka, Can. J. Chem. 73 (1995) 1924.
[6] M. Tsunooka, H. Tachi, K. Asakino, K. Suyama, J. Photosci. 6 (1999) 145.
[7] K.-H. Chae, Macromol. Rapid Commun. 19 (1998) 1.
[8] M. Shirai, M. Endo, M. Tsunooka, J. Photopolym. Sci. Technol. 12 (1999) 669.
[9] A. Padwa, F. Albrecht, J. Am. Chem. Soc. 96 (1974) 4849.
[10] A. Padwa, Chem. Rev. 77 (1977) 37.
[11] M.F. Haley, K. Yates, J. Org. Chem. 52 (1987) 1817.
[12] G. Bucher, J.C. Scaiano, R. Sinta, G. Barclay, J. Cameron, J. Am. Chem. Soc. 117 (1995) 3848.
[13] H. Hwang, D.-J. Jang, K.-H. Chae, J. Photochem. Photobiol. A.: Chem. 126 (1999) 37.
[14] A.J. McCarroll, J.C. Walton, Chem. Comm. (2000) 351.
[15] A.J. McCarroll, J.C. Walton, J. Chem. Soc. Perkin Trans. 2 (2000) 2399.
[16] H. Sakuragi, S.I. Ishikawa, T. Nishimura, M. Yoshida, N. Inamoto, K. Tokumaru, Bull. Chem. Soc. Jpn. 49 (1976) 1949.
[17] M. Yoshida, H. Sakuragi, T. Nishimura, S.-I. Ishikawa, K. Tokumaru, Chem. Lett. (1975) 1125.
[18] H. Sakuragi, M. Yoshida, H. Kinoshita, K. Utena, K. Tokumaru, M. Hoshino, Tetrahedron Lett. 18 (1978) 1529.
[19] A. Padwa, F. Albrecht, J. Am. Chem. Soc. 94 (1972) 1000.
[20] X. Allonas, J. Lalevée, J.-P. Fouassier, H. Tachi, M. Shirai, M. Tsunooka, Chem. Lett. (2000) 1090.
[21] K. Sandros, Acta Chem. Scand. 18 (1964) 2355.
[22] W.G. Herkstroeter, D.P. Specht, S. Farid, J. Photochem. 21 (1983) 325.
[23] C.M. Brennan, R.A. Caldwell, J.E. Elbert, D.J. Unett, J. Am. Chem. Soc. 116 (1994) 3460.
[24] M.K. Davies, A.A. Gorman, I. Hamblett, D.J. Unett, J. Photochem. Photobiol. A.: Chem. 88 (1995) 5.
[25] R.D. Levine, J. Phys. Chem. 83 (1979) 159.
[26] V. Balzani, F. Bolletta, F. Scandola, J. Am. Chem. Soc. 102 (1980) 2152.
[27] J. Lalevée, X. Allonas, F. Louërat, J.P. Fouassier, H. Tachi, A. Izumitani, M. Shirai, M. Tsunooka, Phys. Chem. Chem. Phys. 3 (2001) 2721.
[28] K. Sandros, Acta Chem. Scand. 27 (1973) 3021.
[29] J. Andraos, G.G. Barclay, D.R. Medeiros, M.V. Baldovi, J.C. Scaiano, R. Sinta, Chem. Mater. 10 (1998) 1694.
[30] J. Wang, T. Tateno, H. Sakuragi, K. Tokumaru, J. Photochem. Photobiol. A.: Chem. 92 (1995) 53.
[31] D.E. Falvey, G.B. Schuster, J. Am. Chem. Soc. 108 (1986) 7419.