Photochemistry of the singlet oxygen [$O_2(^1\Delta_g)$] sensitizer perinaphthenone (phenalenone) in *N*,*N*′-dimethylacetamide and 1,4-dioxane

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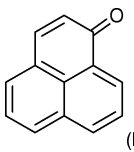
1*H*-Phenalen-1-one (perinaphthenone), an efficient singlet oxygen [$O_2(^1\Delta_g)$] sensitizer with a quantum yield of singlet oxygen production (Φ_Δ) close to unity, has been proposed as a universal standard for $O_2(^1\Delta_g)$ studies. However, data about the photochemical stability of phenalenone are limited to a few protic solvents. This parameter is of crucial interest for singlet oxygen studies under continuous irradiation over long periods of time. In this contribution, we present experimental results demonstrating that, despite low quantum yields, significant photochemical decomposition of phenalenone occurs under steady-state irradiation in air equilibrated 1,4-dioxane and *N*,*N*′-dimethylacetamide (DMA), mainly due to hydrogen abstraction from the solvent by its triplet excited state. Furthermore, singlet oxygen lifetime measurements as a function of irradiation time and comparison of the rates of decrease of the steady-state $O_2(^1\Delta_g)$ near-infrared (1270 nm) phosphorescence with those of phenalenone disappearance have led to the conclusion that at least one of the products formed during phenalenone irradiation contributes to singlet oxygen sensitization. Quantum yields of singlet oxygen production by phenalenone, determined using laser-induced optoacoustic calorimetry (LIOAC) and time-resolved near-infrared phosphorescence (TRPD), remain high in 1,4-dioxane and in DMA (0.99 ± 0.05 and 0.87 ± 0.05, respectively), confirming that this compound is a very efficient $^1O_2$ sensitizer in a large variety of solvents (the Φ_Δ value in DMA is the lowest measured so far).

Photochimie de la périnaphténone (phénalénone), un sensibilisateur de l'oxygène singulet [$O_2(^1\Delta_g)$], dans le *N*,*N*′-diméthylacétamide et le 1,4-dioxane. L'importance de la 1*H*-phénalénone-1 (ou périnaphténone) en tant que sensibilisateur de référence pour la production d'oxygène singulet [$O_2(^1\Delta_g)$] est allée croissante ces dernières années. Cependant, la stabilité photochimique de ce composé a été seulement étudiée dans un nombre limité de solvants protiques. Ce paramètre est d'une grande importance pour des études impliquant la production d'oxygène singulet sous irradiation prolongée du sensibilisateur. Dans cette contribution, nous présentons des résultats montrant qu'une décomposition photochimique partielle de la phénalénone se produit sous irradiation en continue dans le 1,4-dioxane et dans le *N*,*N*′-diméthylacetamide (DMA), principalement par suite de l'arrachement d'un atome d'hydrogène au solvant par l'état excité triplet de la cétone. De plus, la détermination des durées de vie de l'oxygène singulet en fonction du temps d'irradiation et la comparaison des vitesses de la décroissance de la production d'oxygène singulet et de la disparition de la phénalénone nous ont conduit à la conclusion qu'au moins l'un des produits formés contribue à la production d'oxygène singulet. Nous avons déterminé les rendements quantiques de production d'oxygène singulet (Φ_Δ) par la phénalénone en utilisant la combinaison de deux méthodes différentes: la calorimétrie optoacoustique induite par impulsion laser et la détection de la phosphorescence de l'oxygène singulet dans le proche infrarouge (1270 nm). Les valeurs de Φ_Δ dans le 1,4-dioxane (0.99 ± 0.05) et dans le DMA (0.87 ± 0.05) confirment que ce composé est un sensibilisateur de l'oxygène singulet très efficace dans une grande variété de solvants (la valeur dans le DMA est la plus faible mesurée jusqu'à présent).

Since the photophysical properties of 1*H*-phenalen-1-one (perinaphthenone, also called phenalenone) have been reported in 1991,[1] this aromatic ketone has gained some importance as a singlet oxygen [$O_2(^1\Delta_g)$, denoted as $^1O_2$] sensitizer in photochemistry and photobiology. Phenalenone (PN) is soluble in a large variety of solvents and its quantum yield of singlet oxygen production (Φ_Δ) is close to unity in the solvents investigated so far.[1–3] In 1994, Schmidt *et al.* proposed this compound as a universal reference singlet oxygen sensitizer.[2] However, in principle, only sensitizers possessing sufficient stability against chemical and photochemical decomposition are suitable as standards, and, to our knowledge, only very limited investigations on the photochemical stability of phenalenone have been carried out so far.[4,5]



(PN)

This ketone possesses an α,β-conjugated carbonyl group, which is mainly responsible for its photophysical and photochemical properties.[6] Depending on the electronic interaction of the carbonyl moiety with the arene groups and the substituents attached to them, the lowest singlet and triplet excited states of aromatic ketones may exhibit the characteristics of (n,π*) or (π,π*) electronic configurations.[6] Whereas triplet n,π* states undergo photochemical reactions, such as abstraction of hydrogen atoms from the solvent, electron transfer reactions, α-cleavage and other photofragmentation reactions, excited triplet states having π,π* character may undergo pericyclic reactions and show very efficient energy transfer reactions to suitable acceptor molecules, such as molecular oxygen,[7] leading to singlet oxygen sensitization.

Singlet oxygen sensitization most often proceeds according to the mechanism described below. Absorption of a photon by the sensitizer ($\lambda < 440$ nm for PN) induces a transition to the electronically excited singlet state ($^1S^*$); main deactivation processes of the singlet excited state include vibrational deactivation (internal conversion), fluorescence and intersystem crossing to the triplet excited state ($^3S^*$) [reaction (1)]. In the case of phenalenone, the quantum yield of intersystem crossing (Φ_{isc}) is close to unity in solvents investigated so far.

$$^1S^* \xrightarrow{k_{isc}} {}^3S^* \quad (1)$$

Monomolecular deactivation of the triplet state to the ground state may occur by phosphorescence and by intersystem crossing, whereas singlet oxygen is generally produced by energy transfer from the triplet excited state of the sensitizer to dissolved molecular oxygen ($^3O_2$):

$$^3S^* + {}^3O_2 \xrightarrow{k_{et}} {}^1S + {}^1O_2 \quad (2)$$

However, other reactions occurring from the triplet excited state of the sensitizer may compete with singlet oxygen sensitization, for example hydrogen abstraction from the solvent (RH):

$$^3S^* + R{-}H \xrightarrow{k_H} SH^{\cdot} + R^{\cdot} \quad (3)$$

Therefore, Φ_Δ depends on Φ_{isc} and on the efficiency of energy transfer (Φ_{et}):

$$\Phi_\Delta = \Phi_{isc}\,\Phi_{et} = \Phi_{isc}\,\frac{k_{et}[^3O_2]}{k_q[^3O_2] + \Sigma k_T} = \Phi_{isc}\,\frac{k_{et}}{k_q}\,F_{T,O_2} \quad (4)$$

where k_{et} is the rate constant for energy transfer from $^3S^*$ to $^3O_2$ [reaction (2)], k_q is the sum of the rate constants for quenching of $^3S^*$ by $^3O_2$ (equal to k_{et} if only $^1O_2$ is produced as a result of the quenching process), Σk_T is the sum of the rate constants for monomolecular and pseudo-monomolecular deactivation processes of the triplet state (radiative and nonradiative deactivation, rearrangement, reaction with the solvent, *etc.*), $F_{T,O_2}[=k_q[^3O_2]/(k_q[^3O_2] + \Sigma k_T)]$ is the fraction of triplet excited states quenched by $^3O_2$, and k_{et}/k_q is the fraction of triplet states quenched by $^3O_2$ leading to $^1O_2$ production (often denoted as S_Δ).

If processes other than energy transfer (electron transfer and/or enhanced intersystem crossing) contribute to the quenching of $^3S^*$ by $^3O_2$, a low value of k_{et}/k_q, and hence a low value of Φ_Δ, may result, even if Φ_{isc} is close to unity. The concentration of oxygen and chemical transformation of the sensitizer during irradiation may affect singlet oxygen production. Corresponding quantum yields may be determined by a quantitative analysis of singlet oxygen.

The phenalenone triplet excited state shows very efficient energy transfer to ground state oxygen and high Φ_Δ values in some solvents,[1–3] and a dominant π,π* character may be assigned to it in these solvents.[7b] However, partial mixing with the $^3(n,\pi^*)$ state cannot be systematically excluded.[1] It has been shown that the phenalenone triplet excited state can abstract hydrogen atoms from protic solvents such as 2-propanol or ethanol in deoxygenated solutions,[4] albeit with a low quantum yield of photoreduction.[5] In this work, we have determined Φ_Δ of phenalenone (PN) in 1,4-dioxane and in *N*,*N*′-dimethylacetamide (DMA) and investigated the photochemical decomposition of PN under time-resolved and steady-state irradiation. A combination of various techniques has been used for these purposes: time-resolved and steady-state detection of the $^1O_2$ near-infrared (NIR, 1270 nm) phosphorescence (TRPD),[8] laser-induced optoacoustic calorimetry (LIOAC),[9] measurement of the content of dissolved oxygen using an optical sensing device, HPLC and GC analysis.

Experimental

Chemicals

Phenalenone (PN), 2-hydroxybenzophenone (2HBP) and quinine bisulfate (QB) were purchased from Aldrich. PN was purified as indicated in ref. 1. Spectroscopic grade *N*,*N*′-dimethylacetamide (DMA, Scharlau, Merck), ethanol (SDS) and 1,4-dioxane (Panreac, Merck) were used as solvents. DMA was purified by azeotropic distillation adding H_2O (5%) and toluene (10% per volume). Dioxane was refluxed for 1 h in the presence of sodium prior to distillation. Anthracene (Merck) was recrystallized from diethyl ether.

Fluorescence quantum yields

A Shimadzu RF540 was used to record the fluorescence spectra of diluted solutions of PN in 1,4-dioxane and DMA, of anthracene in ethanol and of quinine bisulfate in aqueous 0.1 M H_2SO_4. PN was excited at 330 nm. The quantum yields were determined from the integrated area under the corrected spectra, using optically matched solutions of anthracene in ethanol and of quinine bisulfate in aqueous 0.1 M H_2SO_4 as standards [6] and accounting for the refractive index differences between ethanol, water, DMA and dioxane. The measurements were repeated for a series of absorbances ranging from 0.015 to 0.050. Absorption spectra were registered on a Varian Cary 4E spectrophotometer.

Laser techniques for singlet oxygen analysis

Two time-resolved techniques are of particular interest for monitoring and analyzing singlet oxygen: TRPD and LIOAC. The set-ups for both techniques were described in detail elsewhere.[3] Briefly, a pulsed nitrogen laser (emission at 337 nm) was used to irradiate the samples contained in a 1 cm quartz cuvette and the concomitant luminescence (TRPD) or pressure wave (LIOAC) was detected at 90° with a germanium diode (North Coast, EOL-817P) through a long-pass silicon plate and a 1270 nm interference filter, or with a piezoelectric transducer, for the two techniques respectively. For TRPD, the solutions were equilibrated with either air or oxygen–argon mixtures ranging from 20 to 100% oxygen, while for LIOAC, they were saturated with oxygen. The output of the detector was fed to a 150 MHz LeCroy 9410 digital oscilloscope and transferred to a PC for storage and analysis. Typically 100 shots were averaged for each signal, the energy of the laser pulse not exceeding 500 and 50 μJ for TRPD and LIOAC, respectively. The principles of the two techniques are briefly described below.

Time-resolved $^1O_2$ phosphorescence detection (TRPD). Detection of the weak near-infrared (1270 nm) $^1O_2$ phosphorescence allows direct monitoring of this transient species.[8] TRPD provides a means to measure $^1O_2$ lifetimes (τ_Δ) and to determine quantum yields of $^1O_2$ production (Φ_Δ) *relative to that of a standard* $^1O_2$ *sensitizer.*[3] Relative Φ_Δ values may be calculated from the zero time (middle of the laser pulse) intensities of the $^1O_2$ phosphorescence signals, $S(0)$. $S(0)$ is related to Φ_Δ according to:

$$S(0) = Ck_e(1/n^2)\Phi_\Delta E_l(1 - 10^{-A}) \quad (5)$$

where C is a proportionality constant that includes geometric and electronic factors of the detection system, k_e is the $^1O_2$ radiative rate constant, n is the solvent refractive index, E_l the energy of the laser pulse and A the absorbance of the sensitizer solution at the excitation wavelength; the product $E_l(1 - 10^{-A})$ represents therefore the energy absorbed by the sensitizer during the pulse.

$S(0)$ is measured as a function of the laser energy for optically matched solutions of the sensitizer under study and the reference. The slopes of the straight lines obtained for the variation of $S(0)$ as a function of E_l show the same ratio as the Φ_Δ values for sensitizer and reference (after correcting for refractive index and k_e values when different solvents are used).

Laser-induced optoacoustic calorimetry (LIOAC). Using LIOAC, *absolute* Φ_Δ values may be determined from the optoacoustic wave maximum, H_m, which is recorded for sensitizer solutions and for a calorimetric reference in the same solvent. H_m is related to the incident laser energy by [3,9]

$$H_m = C'\alpha E_l(1 - 10^{-A}) \quad (6)$$

where C' is a proportionality constant that includes geometric and electronic factors of the detection system, as well as the thermoelastic properties of the solvent, and α is the fraction of absorbed energy released as prompt heat (heat integrated by the transducer, approx. 20 ns time resolution).

The calorimetric reference is assumed to release all the absorbed energy as prompt heat ($\alpha = 1$) and serves the purpose of calibrating the calorimeter. In the case of $^1O_2$ production, α is the fraction of absorbed laser energy released as heat during the formation of singlet oxygen, that is, concomitant with the decay of the sensitizer singlet and triplet states. The $^1O_2$ decay occurring on a longer time scale is not integrated by the transducer. H_m is measured as a function of the laser energy for sensitizer and calorimetric reference solutions of various absorbances. The slopes of the straight lines obtained for the variation of H_m as a function of E_l are in turn plotted *vs.* the absorption factor $(1 - 10^{-A})$. In this way, new linear relationships are obtained, the corresponding slopes showing the same ratio as the α values for sensitizer and reference. The relationship between Φ_Δ and α is given by eqn. (7).[9] Note that knowledge of the emission characteristics of the sensitizer is required.

$$\Phi_\Delta E_\Delta = (1 - \alpha)E_{exc} - \Phi_f E_f \quad (7)$$

where E_{exc} is the molar energy of the laser photons (356 kJ mol^{-1}), Φ_f and E_f(in kJ mol^{-1}) are the quantum yield and the average energy of fluorescence of the sensitizer, respectively, and E_Δ is the $O_2(^1\Delta_g)$ energy (94.2 kJ mol^{-1}).

Singlet oxygen phosphorescence measurements under continuous irradiation

The equipment for the continuous monochromatic excitation of the sensitizer for the measurements of the $^1O_2$ phosphorescence at 1270 nm has been previously described in detail.[1,8d,10] Solutions of PN in DMA and 1,4-dioxane were placed in 1 × 1 cm fluorescence cells (volume: 4.5 cm^3; solution volume: 3.5 cm^3). Most experiments were carried out with an initial absorbance at the excitation wavelength (367 nm) of 1.24 ± 0.02. Solutions were irradiated using a 1000 W Xe–Hg arc and a monochromator (6 nm bandwidth). The incident radiant power on the sample cell was measured by actinometry using Aberchrome 540 as a chemical actinometer[11] and regularly checked with a thermopile (Laser Instrumentation, model 154). It varied between 5.5–6.4 ± 0.2 mW, corresponding to an incident photonic rate (P_0) of 1.69–1.96 (±0.15) × 10^{-8} einstein s^{-1} (1 einstein = 1 mol of photons). The solutions were magnetically stirred during irradiation. The temperature was 25 °C. The $^1O_2$ luminescence signals were registered over several minutes. Control experiments in the absence of dissolved oxygen confirmed that fluorescence emission from PN does not extend into the NIR region. Absorption spectra were registered on a Shimadzu UV-260 spectrophotometer. The molar absorption coefficients of PN were determined to be: ε(DMA, 367 nm) = 8500 ± 50 L mol^{-1} cm^{-1}, ε(1,4-dioxane, 367 nm) = 8860 ± 50 L mol^{-1} cm^{-1}.

Quantitative analysis of phenalenone

PN depletion was monitored by HPLC and GC analysis. Irradiation experiments were performed on the same optical bench and under the same experimental conditions as used for the $^1O_2$ phosphorescence measurements under continuous irradiation (*vide supra*). An HP Series II 1090 liquid chromatograph, equipped with a diode array detector (DAD) and a LiChrospher-100 RP 18 column and precolumn, was used for quantitative HPLC analysis [eluent: mixture of acetonitrile and an aqueous solution of 0.10 mol L^{-1} $(C_2H_5)_3N$ acidified to pH 7 with H_3PO_4 (25 : 75 v/v)]. The quantitative GC analysis was performed using an HP 5980 Series II gas chromatograph equipped with an HP 7673 automatic sampler. An FID detector or an HP 5965B ID IR detector in combination with an HP 5971A MSD quadrupole mass spectrometer was employed. The column was an HP-INNOWAX (length = 30 m, diameter = 3.2 mm, film thickness = 0.5 mm). For the analysis, 3.5 cm^3 of PN solutions in DMA and in dioxane were irradiated for 5–45 min, in 5 min steps. A new solution was used for each irradiation time and analyzed by spectrophotometry and by chromatography. Confirmation of the nature of the products formed was achieved using standard libraries (EPA/IR library 599963-10003 (1990) HP-document HP599963B and Wiley PBM library (1992) HP-document HPG1035A, HP Analytical Division, Waldbronn, Germany.

Optical sensor system for the quantitative determination of dissolved oxygen

An optical sensor system for the quantitative determination of dissolved oxygen was provided by Hewlett Packard and adapted for its use in nonaqueous media.[12] The sensor (outer diameter 0.36 mm) contains a polymer-supported ruthenium(II)-polypyridyl complex {$[Ru(dpp)_3]^{2+}$: ruthenium(II)-tris(2,3-bis(2′-pyridyl)pyrazine)}, which serves as a luminophore. The luminescence lifetime of the polymer-supported luminophore is characteristic for the oxygen content inside the sensor head. A polymer membrane permits the diffusion of dissolved oxygen from the bulk solution into the sensor head and *vice versa.* A pulsed light-emitting electrode is used for the excitation of $[Ru(dpp)_3]^{2+}$ at 455 nm and the luminescence from the complex is monitored at 636 nm in a time-resolved mode in the microsecond range. Data acquisition and calculation of oxygen concentration, taking into account calibration curves at given temperatures, were made with an HP workstation linked *via* an A/D interface.[13] The cells (volume 4.5 cm^3) were entirely filled with liquid and sealed before irradiation. In DMA and 1,4-dioxane, the response time of the oxygen sensor was 6 ± 2 min (maximum

time needed to stabilize the sensor signal when changing from deaerated to oxygen-saturated solutions). The experimental conditions as well as the setup employed were identical to those used for the quantitative determination of $^1O_2$ under continuous irradiation (except for the volume of solution in the cell).

Results and discussion

Absorption and fluorescence characteristics

Fig. 1 shows the absorption and emission spectra of PN in DMA and dioxane. The fluorescence quantum yield has been calculated to be $\Phi_f = 0.008$ for PN in DMA (Table 1). We could not detect fluorescence from PN in dioxane, thus $\Phi_f < 10^{-3}$ in this case. Assuming that the thermal deactivation processes (internal conversion) are negligible for rigid aromatic ketones such as PN,[6] the very low values of Φ_f for PN in dioxane and DMA indicate that the quantum yields of intersystem crossing (Φ_{ISC}) of PN in these solvents are very close to unity, as already observed in other solvents where no fluorescence could be detected.[1]

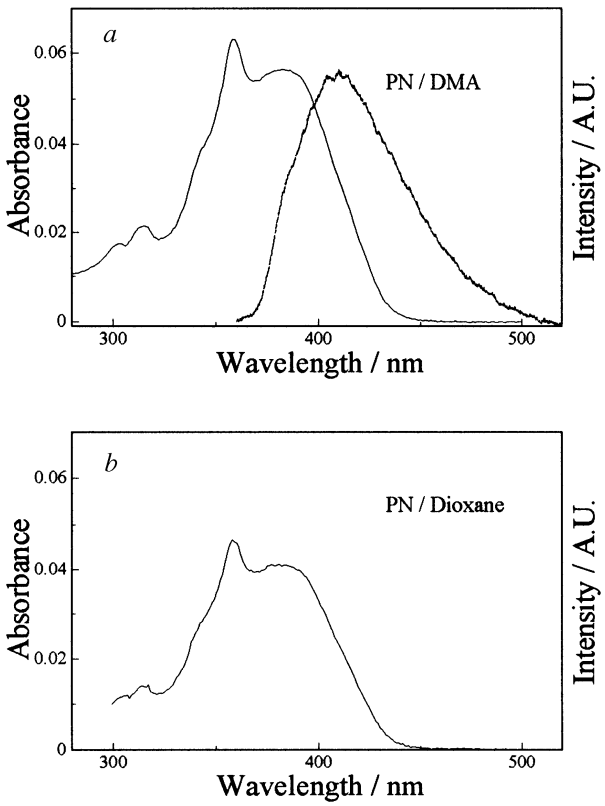


Fig. 1 (*a*) Absorption (left) and fluorescence (right) spectra of phenalenone (PN) in *N*,*N*′-dimethylacetamide (DMA). (*b*) Absorption spectrum of PN in 1,4-dioxane.

Time-resolved phosphorescence detection (TRPD) of singlet oxygen

Singlet oxygen phosphorescence detection provided evidence for $^1O_2$ production by PN in 1,4-dioxane and *N*,*N*′-dimethylacetamide. Singlet oxygen lifetimes (τ_Δ) have been measured by the time-resolved technique (TRPD). The decays observed in DMA and 1,4-dioxane could be fitted with single exponential functions and, within experimental error, the $^1O_2$ lifetimes remained constant in the range of concentrations used in both solvents (PN concentration ranging from 10^{-5} to 1.3×10^{-4} mol L^{-1}) . Therefore, $^1O_2$ quenching by PN itself is negligible under these conditions and the measured τ_Δ is equal to the inverse of the pseudo-first-order rate constant of $^1O_2$ deactivation by the corresponding solvent [k_d, reaction (8)]. Values of 10.2(±0.2) and 25.7(±0.5) μs have been derived for τ_Δ in DMA and 1,4-dioxane, respectively.

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \qquad (8)$$

In both solvents, the intensities of the $^1O_2$ phosphorescence signals extrapolated to zero time [*S*(0), see experimental] were independent of oxygen concentration, as deduced from experiments in which the solutions were saturated with oxygen–argon mixtures containing 20% to 100% oxygen. Therefore, the oxygen concentration in air-equilibrated solutions is high enough that all PN triplet excited states are quenched by oxygen and the corresponding Φ_Δ for PN do not depend on the oxygen concentration in the range investigated [eqn. (4)]. No changes in the absorption spectra of PN could be observed after irradiation with laser pulses of low energy as used in this work for TRPD.

Quantum yield of singlet oxygen production in 1,4-dioxane

Since LIOAC allows *absolute* Φ_Δ values to be determined, no standard $^1O_2$ sensitizer is needed, contrary to TRPD. The optoacoustic waves produced upon irradiation of optically matched solutions of PN and the calorimetric reference (2-hydroxybenzophenone, 2HBP) with laser pulses of the same energy ($\lambda_{ex} = 337$ nm) are shown in the inset of Fig. 2. They show the same shape and distinct amplitudes, indicating that the heat release dynamics may be described satisfactorily by the sum of a "fast" component (prompt heat), which accounts for all processes occurring within the time resolution of the transducer (*ca.* 20 ns), and of a "slow" component, which accounts for those processes outside the time window of the experiment (*ca.* 5 μs) and therefore do not contribute to the signal.[14] The formation of $^1O_2$ under the present conditions falls into the first category, while its decay definitely belongs to the second one. It is therefore legitimate to use the amplitudes of these waves as a measure of the prompt heat released.

Table 1 Quantum yields of fluorescence (Φ_f), singlet oxygen production (Φ_Δ), PN decomposition [$\Phi(-PN)$] and triplet oxygen consumption [$\Phi(-{}^3O_2)$] determined for phenalenone (PN) in DMA and 1,4-dioxane

	Method	DMA	1,4-dioxane
E_f/kJ mol^{-1}	—	289	—
Φ_f	—	0.008	$<10^{-3}$
Φ_Δ	LIOAC	0.87 ± 0.05	0.99 ± 0.05
$\Phi(-PN)$	HPLC, GC	$(2.1 \pm 0.2) \times 10^{-2}$	$(1.3 \pm 0.1) \times 10^{-2}$
$\Phi(-{}^3O_2)^a$	Oxygen optical sensor	$(4.6 \pm 0.6) \times 10^{-2}$	$(3.4 \pm 0.4) \times 10^{-2}$
$\Phi(-PN)^b$	HPLC, GC	$(2.0 \pm 0.2) \times 10^{-2}$	$(1.3 \pm 0.1) \times 10^{-2}$
$\Phi(-{}^3O_2)^{b,c}$	Oxygen optical sensor	1.02 ± 0.20	1.05 ± 0.20

[a] $d[^3O_2]/dt = (0.19 \pm 0.01) \times 10^{-6}$ mol L^{-1} s^{-1} in DMA and $(0.14 \pm 0.01) \times 10^{-6}$ mol L^{-1} s^{-1} in dioxane. [b] With furfuryl alcohol, [FFA] = 10^{-2} mol L^{-1}. [c] Estimation of Φ_Δ: $-d[^3O_2]/dt = (4.2 \pm 0.4) \times 10^{-6}$ mol L^{-1} s^{-1} in DMA and $(4.3 \pm 0.4) \times 10^{-6}$ mol L^{-1} s^{-1} in dioxane.

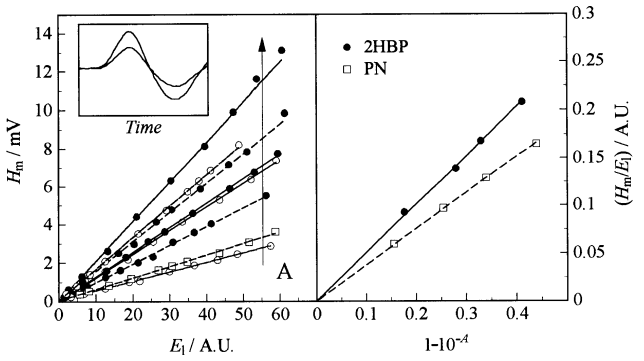


Fig. 2 Maximum amplitude of the optoacoustic wave (H_m) as a function of the laser pulse energy (E_l) for phenalenone (PN) and 2-hydroxybenzophenone (2HBP) solutions of increasing absorbance (*left*) and dependence of the slopes of the straight lines thus obtained on the absorption factor (*right*). *Inset*: Typical optoacoustic waves for the two compounds (λ_{ex} = 337 nm, solvent: oxygen-saturated 1,4-dioxane).

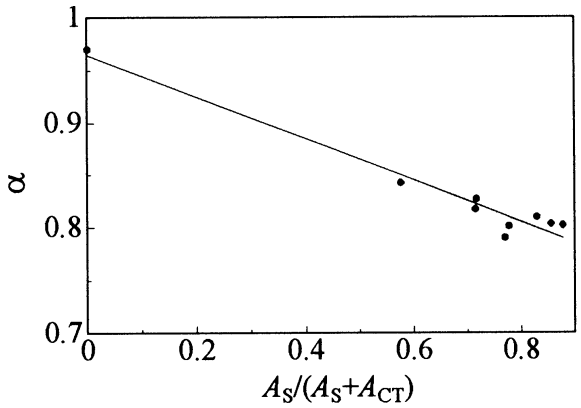


Fig. 3 Dependence of the fraction of absorbed laser energy released as prompt heat (α) on the relative absorbance of the sensitizer PN [$A_S/(A_S + A_{CT})$] in oxygen-saturated DMA solutions (in this solvent, an additional solvent-oxygen charge transfer band competes for light absorption with an absorbance A_{CT}).

The measurement of the signal maximum amplitude (H_m) at several laser energies and sample absorbances for sensitizer and calorimetric reference leads to the value of α (fraction of absorbed energy released as prompt heat), as described in the experimental section [eqn. (6)] and shown in Fig. 2. Knowing α, a Φ_Δ value of 0.99 ± 0.05 for PN in 1,4-dioxane (Table 1) has been readily calculated using eqn. (7).

Quantum yield of singlet oxygen production in DMA

The optoacoustic determination of Φ_Δ in DMA is complicated by the fact that this solvent forms a contact complex with oxygen that absorbs substantially at 337 nm (the absorbance is 0.007 for an optical pathlength of 1 cm under air and increases up to 0.042 under oxygen). Moreover, irradiation of the corresponding charge transfer (CT) absorption band produces $^1O_2$, as unequivocally demonstrated by its phosphorescence at 1270 nm. From TRPD [eqn. (5)] comparing the signals for oxygen-saturated DMA and an optically matched solution of PN in cyclohexane (solvents for which the refractive indices, and hence the $^1O_2$ radiative rate constants, are similar)[15], we estimate that the CT complex sensitizes $^1O_2$ with a $\Phi_{\Delta,CT}$ of 0.13. This behavior is similar to that reported for several other solvents.[16] The presence of this additional chromophore in the system implies that the measured α value is actually a linear combination of the α values of the two individual chromophores:

$$\alpha = \frac{A_S \alpha_S + A_{CT} \alpha_{CT}}{A_S + A_{CT}} \quad (9)$$

where "S" stands for the sensitizer (PN) or for the calorimetric reference (2HBP), and "CT" stands for the DMA–oxygen complex.

A value of 0.97 is obtained for α_{CT}, by applying eqn. (7) to the CT complex in oxygen-saturated DMA. Eqn. (9) may be more conveniently rewritten as:

$$\alpha = \alpha_{CT} + (\alpha_S - \alpha_{CT}) \frac{A_S}{A_S + A_{CT}} \quad (10)$$

suggesting that a plot of α *vs.* $A_S/(A_S + A_{CT})$ should be linear and its slope could be used to calculate α_S for PN, and subsequently the Φ_Δ value through eqn. (7). We have determined the values of α, as $(H_m/H_{m,ref})\alpha_{ref}$, using several oxygen-saturated optically matched solutions of PN and of 2HBP. Values of α_{ref} have been calculated for each 2HBP solution using eqn. (9). Fig. 3 shows the linear plot obtained in agreement with eqn. (10). The scattering of some points is relatively large due to the rather small correction introduced by the absorption of the CT complex. In Fig. 3, we have drawn the straight lines through the intercept value of α_{CT} = 0.97 obtained more precisely by TRPD as indicated above. The Φ_Δ value obtained in this way is 0.87 ± 0.05, lower than in 1,4-dioxane (0.99 ± 0.05) (Table 1) and in most commonly employed solvents.[1–3] Assuming that Φ_{ISC} for PN is unity in dioxane ($\Phi_f < 10^{-3}$) and close to unity in DMA (Φ_f = 0.008), one can estimate an upper limit ($\Phi_{ISC} - \Phi_\Delta$) for the quantum yield of the chemical reactions from the PN triplet state (such as hydrogen abstraction from the solvent) of about 0.13 in DMA, whereas the corresponding value in 1,4-dioxane should be much lower (0.01).

Phenalenone decomposition under continuous irradiation

Contrary to the time-resolved experiments reported in the previous sections, PN undergoes a photochemical transformation under continuous irradiation at 367 nm, as shown by the changes in the absorption spectra (Fig. 4). Two isobestic points appear at 338 ± 2 and 431 ± 2 nm in DMA and at 332 ± 2 and 430 ± 2 nm in 1,4-dioxane.

Combined HPLC and GC measurements of the PN concentration as a function of irradiation time have been performed. The combination of both analytical methods minimized the experimental error. The quantum yields for PN disappearance [$\Phi(-PN)$] have been calculated from the initial rate of PN disappearance and the incident photon rate measured by actinometry (see experimental section). Values of (2.1 ± 0.2) × 10^{-2} and (1.3 ± 0.1) × 10^{-2} have been obtained for $\Phi(-PN)$ in DMA and in 1,4-dioxane, respectively (Table 1). Although these values are relatively small, they lead to an important decrease of the absorbance observed at 367 nm in DMA and 1,4-dioxane during 45 min of irradiation (Fig. 4). The decrease of the PN relative concentration ($[PN]_t/[PN]_0$) and of the relative absorbance at 367 nm (A_t/A_0) are shown in Fig. 5. In 1,4-dioxane, the decrease of the absorbance at 367 nm matches the decrease of the PN concentration until about 20 min of irradiation. At longer irradiation times, PN disappearance is faster than the absorbance decrease, showing that PN decomposition products absorb, albeit not to a large extent, at 367 nm. In the case of DMA, inner filter effects by PN decomposition products are more pronounced and are significant at an early stage of the irradiation (Fig. 5).

Since PN is inert towards singlet oxygen, the most probable mechanistic hypothesis to explain PN disappearance is that hydrogen abstraction from the solvent by the PN triplet excited state competes with $^1O_2$ production. This hypothesis is supported by control experiments showing that PN disappearance was faster in the absence than in the presence of oxygen. Furthermore, phenalanone (PA), resulting from the photoreduction of PN, has been identified as the main reac-

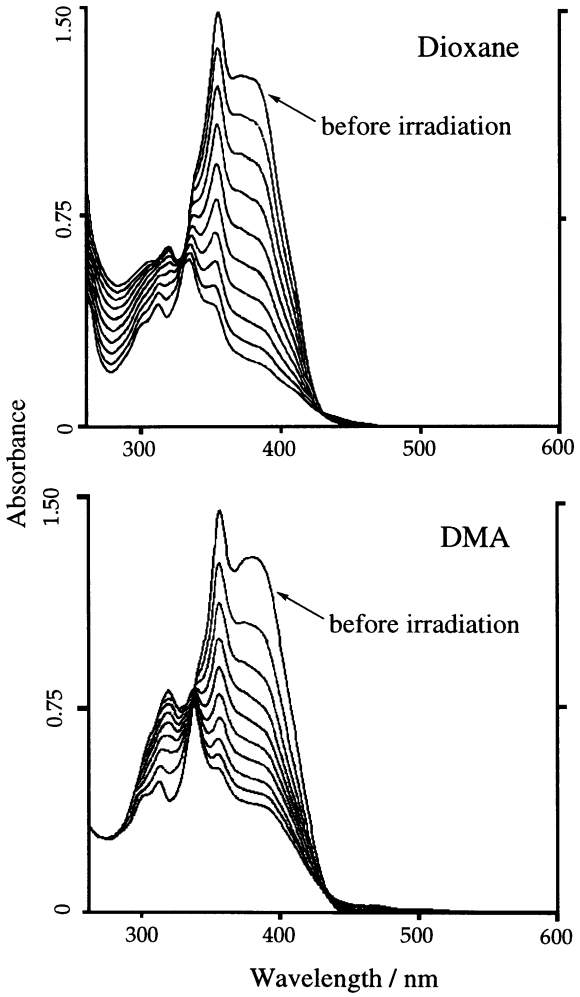


Fig. 4 Decrease of the UV/VIS absorbance under continuous irradiation of phenalenone (PN) solutions at 367 nm (solvents: air-equilibrated DMA and 1,4-dioxane, absorption spectra registered before irradiation and every 5 min up to 45 min of irradiation are represented).

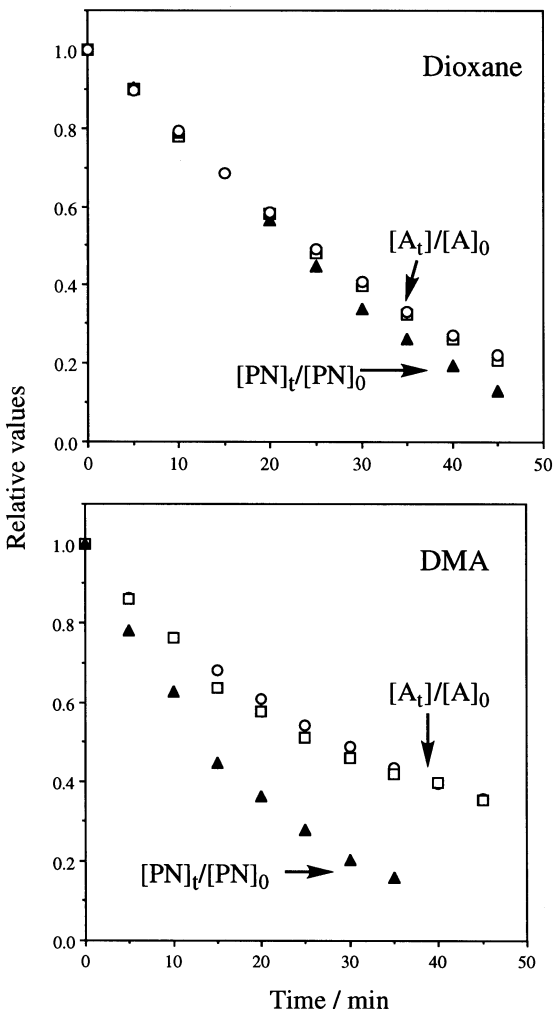


Fig. 5 Decrease of the relative phenalenone concentration ($[PN]_t/[PN]_0$, full triangles) and of the relative absorbance at 367 nm (A_t/A_0, circles: same solution irradiated during 45 min; squares: solutions used for HPLC analysis) under continuous irradiation of air-equilibrated DMA and 1,4-dioxane solutions ($\lambda_{ex} = 367$ nm, $A_0 = 1.24$).

tion product in both dioxane and DMA. In the case of DMA, hydrogen abstraction may involve the formation of a charge transfer complex between the triplet excited state of the ketone and the amino group, increasing the reaction rate and the efficiency of photoreduction.[6,17]

Evolution of singlet oxygen production under continuous irradiation

Under continuous excitation of PN at 367 nm, the PN sensitized $^1O_2$ production also decreases with time in both air-equilibrated DMA and 1,4-dioxane (Fig. 6). Monochromatic irradiation of PN at 367 nm for 45 min led to a regular decrease of the $^1O_2$ NIR signal in DMA to approximately 37% of the initial signal. In 1,4-dioxane, the signal remained relatively stable during the first 15–20 min of irradiation (during this time, the decrease of the absorbance at 367 nm matches the decrease of the PN concentration, Fig. 5), then the $^1O_2$ signal decreased to about 43% of the initial signal after 45 min of irradiation. The $^1O_2$ NIR emission also decreased under continuous excitation of PN in several other solvents, such as ethanol, 2-propanol and ethylene glycol, but not in carbon tetrachloride or benzene.

Under continuous irradiation of a stable singlet oxygen sensitizer (S) and in the absence of $^1O_2$ acceptors or quenchers, the concentration of excited species, including $^1O_2$, may be considered as constant [steady-state approximation, eqn. (11)], and the steady-state $^1O_2$ concentration can be calculated according to eqn. (12):

$$\frac{d[^1O_2]}{dt} = \frac{d[^3S^*]}{dt} = \frac{d[^1S^*]}{dt} = 0 \qquad (11)$$

$$[^1O_2] = P_a \Phi_\Delta \tau_\Delta = P_0(1 - 10^{-A})\Phi_\Delta \tau_\Delta \qquad (12)$$

where P_a is the rate of photons absorbed by the sensitizer (PN) and P_0 the incident photon rate (expressed in einstein $L^{-1}\,s^{-1}$).

Under the conditions used in the case of PN in DMA, the steady-state $^1O_2$ concentration should be 3.7×10^{-11} mol L^{-1} [$P_0(367\ nm) = 4.4 \times 10^{-6}$ einstein $L^{-1}\ s^{-1}$, $A(367\ nm) = 1.24$, $\Phi_\Delta = 0.87$, $\tau_\Delta = 1.02 \times 10^{-5}$ s] at the beginning of the irradiation time. However, PN undergoes partial reaction under continuous irradiation (Figs. 4 and 5) and $^1O_2$ production decreases (Fig. 6). Within experimental error, we measured a constant τ_Δ value by TRPD, independent of the irradiation time. Therefore, it may be concluded that the products of PN reaction are not $^1O_2$ quenchers. Under the assumption that these products do not interact with the PN triplet excited state (constant Φ_Δ for PN) and that they are not $^1O_2$ sensitizers, the $^1O_2$ concentration decreases over time due to the decrease of the PN concentration and to inner filter effects of the products:

$$\frac{[^1O_2]_t}{[^1O_2]_0} = \frac{A_{t,PN}}{A_t}\frac{(1 - 10^{-A_t})}{(1 - 10^{-A_0})} \qquad (13)$$

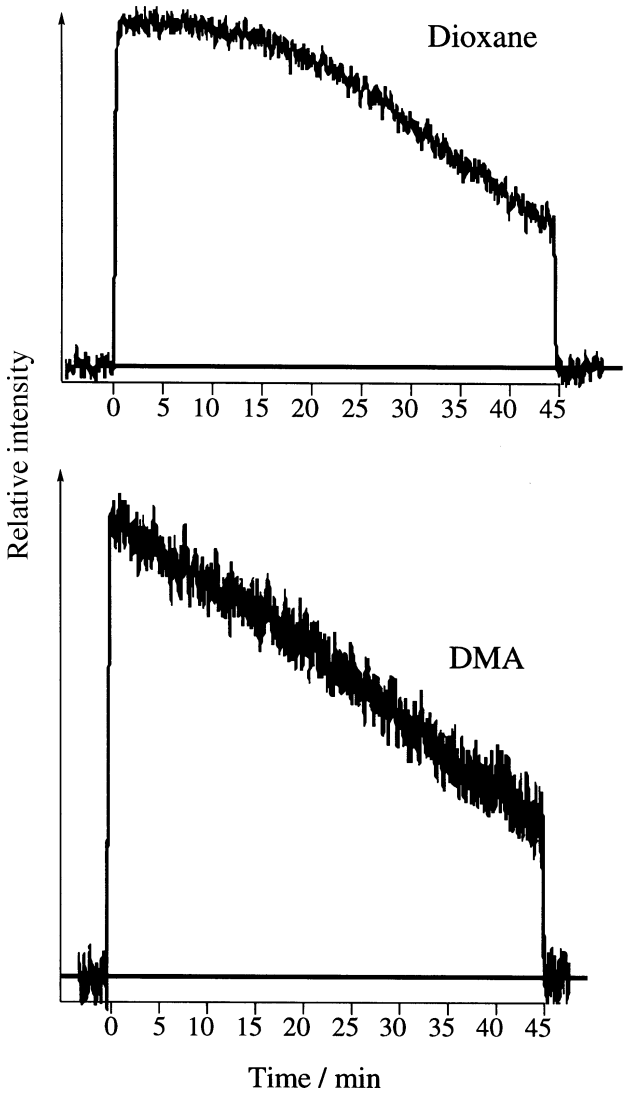


Fig. 6 Singlet oxygen NIR phosphorescence signals under continuous irradiation of phenalenone (PN) solutions at 367 nm (time zero corresponds to the beginning of the irradiation; signals have been recorded at different sensitivities in DMA and dioxane).

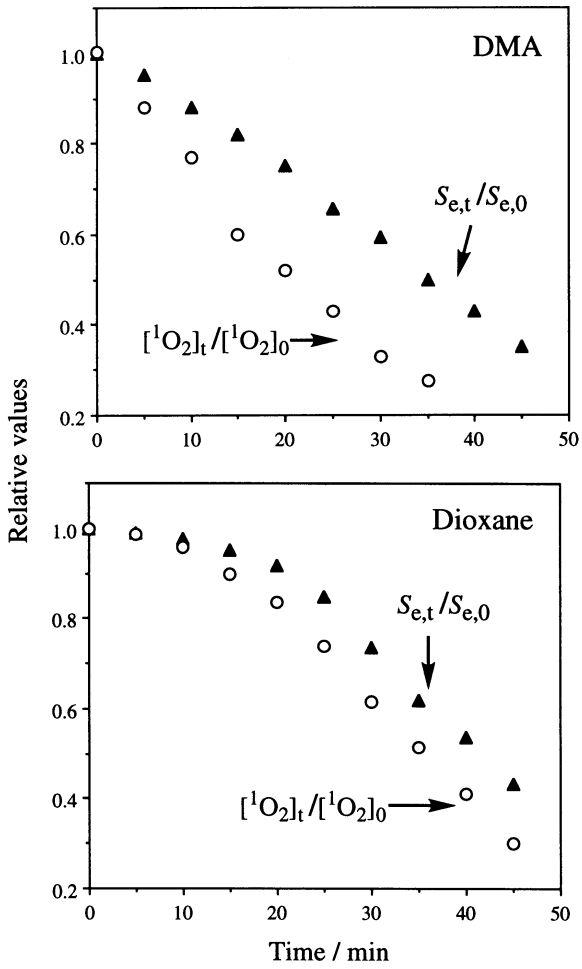


Fig. 7 Relative singlet oxygen NIR phosphorescence signal ($S_{e,t}/S_{e,0}$, full triangles) and relative concentration of singlet oxygen calculated according to eqn. (13) ($[^1O_2]_t/[^1O_2]_0$, open circles) as a function of the irradiation time of phenalenone (PN) solutions (solvents: DMA and 1,4-dioxane, $\lambda_{ex} = 367$ nm, $A_0 = 1.24$).

where A_0 and A_t are the global absorbances at the beginning of the irradiation and at time t, respectively, and $A_{t,\,PN}$ is the PN absorbance at time t ($A_{0,\,PN} = A_0$).

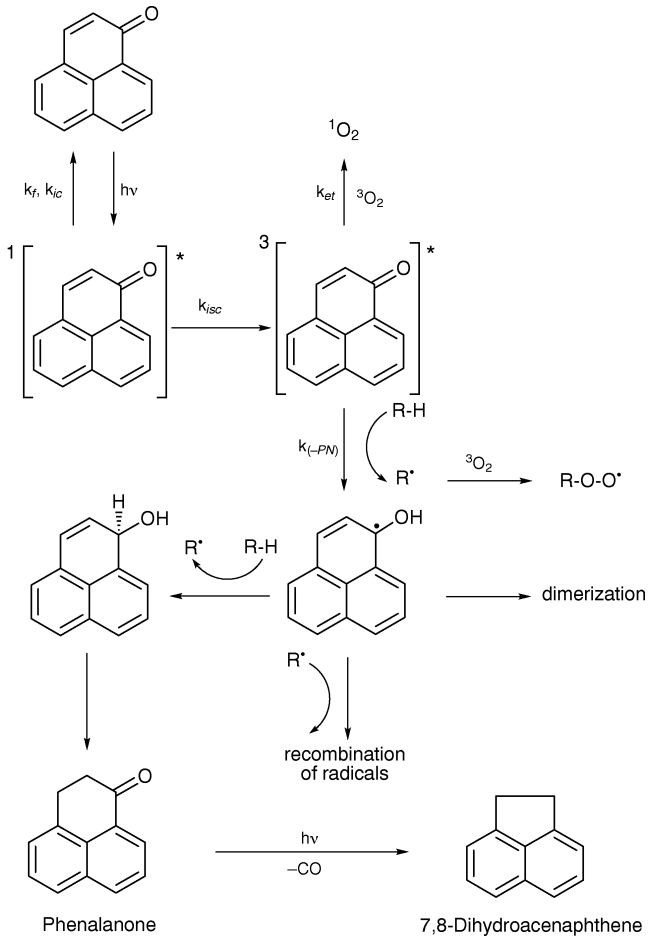
As indicated in the previous section, the concentration of PN has been monitored by HPLC and GC. Therefore, the values of $[^1O_2]_t/[^1O_2]_0$ as a function of the irradiation time may be calculated using eqn. (13) and compared to the relative decrease of the experimental $^1O_2$ NIR signal ($S_{e,\,t}/S_{e,\,0}$, Fig. 7). As can be seen in Fig. 7, the $^1O_2$ production under continuous irradiation decreases more slowly than predicted assuming that PN reaction products act only as inner filters [eqn. (13)]. (The small correction due to the nonlinear response of the detector as a function of the absorption factor[8d] would slightly increase the difference). Therefore, it may be concluded that at least one of the PN reaction products is also a $^1O_2$ sensitizer. The $^1O_2$ production decrease under irradiation is a consequence of the lower absorbance(s) of the sensitizing product(s) at 367 nm compared to PN (and eventually of a lower Φ_Δ of the products). The overall effect is even more pronounced in DMA, due to the bathochromic shift of the product(s) absorption in changing from dioxane to DMA.

It should be noted that two compounds, which might be singlet oxygen sensitizers, phenalanone and, in lower amounts, 7,8-dihydroacenaphthene, have been identified among the reaction products in both DMA and dioxane by GC-MS/FTIR. A possible mechanism for the formation of these products is shown in Scheme 1. The PN excited triplet state may abstract a hydrogen atom from both solvents (DMA and 1,4-dioxane), yielding the PN ketyl radical. Abstraction of a second hydrogen atom from the solvent by the ketyl radical would lead to the formation of phenalenol and by a subsequent allylic hydrogen shift to phenalanone (*via* its enol form). Phenalanone may react further by α-cleavage to yield 7,8-dihydroacenaphthene. Note that a series of higher masses in the range between 200 and 500 are found in the GC-MS analysis, indicating that dimers or oligomers of phenalenone, as well as products resulting from the addition of solvent molecules to phenalenone and the intermediates mentioned above, may be formed.

Consumption of molecular oxygen during continuous excitation of phenalenone in the absence and in the presence of a singlet oxygen acceptor

The evolution of the concentration of molecular oxygen ($^3O_2$) dissolved in DMA and 1,4-dioxane under continuous excitation of PN has been determined using an optical oxygen sensor in a sealed quartz cell (see experimental section). The experimental conditions matched those of the $^1O_2$ luminescence measurements under steady-state irradiation.

When PN was irradiated in air-equilibrated DMA and 1,4-dioxane solutions, consumption of dissolved oxygen (Fig. 8) was observed in parallel to PN depletion. The quantum yields, determined from the pseudo-zero-order decrease of the $^3O_2$



Scheme 1 Chemical reactions originating from the triplet excited state of phenalenone (^{3}PN*) in the presence of molecular oxygen.

concentration during 30 min (Fig. 8) and the incident photon rate measured by actinometry, are low compared to Φ_Δ values [$\Phi(-{}^3O_2)$ of $(4.6 \pm 0.6) \times 10^{-2}$ and $(3.4 \pm 0.4) \times 10^{-2}$ in DMA and dioxane, respectively, Table 1], but they are about twice the quantum yields of PN disappearance in both solvents. If hydrogen abstraction from the solvent (RH) by the PN triplet excited state is the main process leading to phenalenone disappearance, radical species derived from PN (ketyl radical) and from the solvent (R˙) should be formed (Scheme 1) and may be trapped by molecular oxygen.[18] Therefore, the

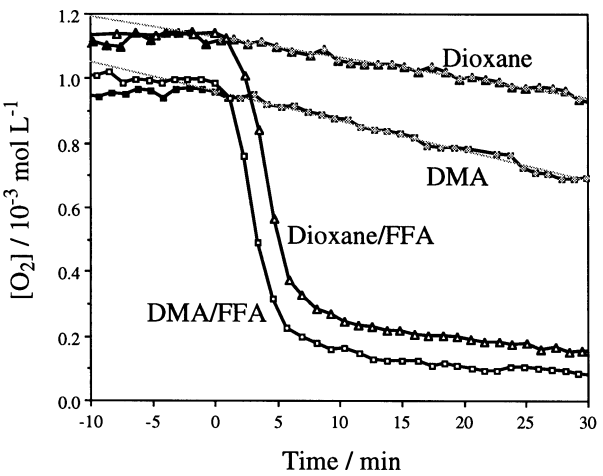


Fig. 8 Evolution of the concentration of dissolved oxygen measured with an oxygen optical sensor in air-equilibrated phenalenone (PN) solutions: in DMA; in DMA with furfuryl alcohol (FFA); in 1-4-dioxane and in 1-4-dioxane with FFA ($[PN]_0 = 1.40 \times 10^{-4}$mol L^{-1}, $[FFA]_0 = 10^{-2}$ mol L^{-1}).

overall process leads to PN depletion and oxygen consumption, and the molar ratio of PN and $^3O_2$ consumed depends on the relative efficiencies of the various reaction paths.

The concentration of dissolved $^3O_2$ has also been measured in the presence of a very efficient $^1O_2$ acceptor, furfuryl alcohol (FFA)[19] (Fig. 8 and Table 1) as control experiments. FFA reacts with $^1O_2$ by a Diels–Alder type 1,4-addition to form an unstable endoperoxide.[19b] The rate constant of the chemical reaction is on the order of 2–3 $\times 10^7$ L mol^{-1} s^{-1} in methanol[19b] and of 10^8 L mol^{-1} s^{-1} in water.[19c,d,f] Therefore, at high enough concentrations of FFA, oxygen consumption may be considered to be almost exclusively due to $^1O_2$ trapping by FFA, and, since the rate constant of $^1O_2$ physical quenching by FFA is negligible compared to that of the chemical reaction,[19] $^1O_2$ deactivation by the solvent [reaction (8)] and chemical reaction with FFA [reaction (14)] are the only reactions to be retained.

$$^1O_2 + \text{FFA} \xrightarrow{k_r} [\text{FFAO}_2] \longrightarrow \text{products} \quad (14)$$

The quantum yield of $^3O_2$ disappearance may then be written as:

$$\Phi(-{}^3O_2) = -\frac{\mathrm{d}[{}^3O_2]}{P_a\,\mathrm{d}t} = \Phi_\Delta \frac{k_r[\text{FFA}]}{(k_d + k_r[\text{FFA}])} \quad (15)$$

where P_a is the rate of photons absorbed by the sensitizer (PN) (in einstein L^{-1} s^{-1}) and k_r is the bimolecular rate constant of the chemical reaction between $^1O_2$ and FFA (in L mol^{-1} s^{-1}).

Values of k_r in DMA or 1,4-dioxane are not known. However, at an early reaction stage (less than 10% of FFA depletion) and under conditions where k_d is negligible compared to the product $k_r \cdot [\text{FFA}]_0$ (*i.e.*, about 10 times lower), the quantum yield of oxygen consumption $\Phi(-{}^3O_2)$ should be independent of the FFA concentration and represent the value of Φ_Δ. We have verified that $\Phi(-{}^3O_2)$ is indeed independent of the initial FFA concentration above 10^{-2} mol L^{-1}. Knowing the values of k_d in DMA and dioxane determined by TRPD (9.8×10^4 and 3.9×10^4 s^{-1}, respectively), we estimate lower limits for the rate constants of the chemical reaction of $^1O_2$ with FFA to be approximately 10^8 L mol^{-1} s^{-1} in DMA and 4×10^7 L mol^{-1} s^{-1} in dioxane, close to the values in water and methanol. Experimental errors are rather high for measurements of dissolved $^3O_2$ in the presence of FFA, due to the high reactivity of the latter with singlet oxygen. Moreover, the values obtained for Φ_Δ [measured as $\Phi(-{}^3O_2)$] in the two solvents (Fig. 8 and Table 1) are about unity, larger than those measured by LIOAC; this result might be explained by competing H abstraction from FFA by the PN triplet excited state leading to formation of radicals and, thus, increased oxygen consumption. Within experimental error, quantum yields of PN disappearance in the presence and in the absence of FFA are identical, as would be expected if there is no interaction between FFA and PN.

Conclusions

The quantum yields of singlet oxygen production (Φ_Δ) by phenalenone (PN) in 1,4-dioxane and in *N*,*N*′-dimethylacetamide (DMA), determined by near-IR emission and optoacoustic calorimetry (LIOAC), are high (0.99 and 0.87, respectively), confirming that this compound is a very efficient $^1O_2$ sensitizer in a large variety of solvents (the Φ_Δ value in DMA is the lowest measured so far). However, although PN is stable under time-resolved irradiation with laser pulses of very low energy, it decomposes under steady-state irradiation, in air-equilibrated 1,4-dioxane and DMA, mainly due to hydrogen abstraction from the solvent by its triplet excited state. Subsequently, significant decreases of the PN concentration and of the $^1O_2$ luminescence signal occur during irradiation, despite

the low values of the corresponding quantum yields, 1.3×10^{-2} and 2.3×10^{-2}, respectively. Therefore, the use of PN as a reference $^1O_2$ sensitizer under continuous irradiation is limited, since, depending on the choice of the solvent and on the experimental conditions, results of experiments involving $^1O_2$ sensitization by PN might be misinterpreted if potential photochemical decomposition of PN is not taken into account.

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