

Effect of the Media on the Quantum Yield of Singlet Oxygen ($O_2(^1\Delta_g)$) Production by 9H-Fluoren-9-one: Solvents and Solvent Mixtures

by Claudia G. Martínez^a), Annette Neuner^a), Cristina Martí^b), Santi Nonell^b), André M. Braun^a),
and Esther Oliveros^{*a})

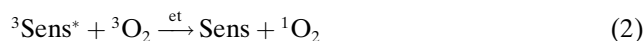
^a) Lehrstuhl für Umweltmesstechnik, Engler-Bunte-Institut, Universität Karlsruhe, D-76128 Karlsruhe

^b) Grup d'Enginyeria Molecular, Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390,
E-08017 Barcelona

We have investigated the effect of a series of 18 solvents and mixtures of solvents on the production of singlet molecular oxygen ($O_2(^1\Delta_g)$, denoted as 1O_2) by 9H-fluoren-9-one (FLU). The normalized empirical parameter E_T^N derived from $E_T(30)$ has been chosen as a measure of solvent polarity using Reichardt's betaine dyes. Quantum yields of 1O_2 production (Φ_Δ) decrease with increasing solvent polarity and protic character as a consequence of the decrease of the quantum yield of intersystem crossing (Φ_{ISC}). Values of Φ_Δ of unity have been found in alkanes. In nonprotic solvents of increasing polarity, Φ_{ISC} and, therefore, Φ_Δ decrease due to solvent-induced changes in the energy levels of singlet and triplet excited states of FLU. This compound is a poor 1O_2 sensitizer in protic solvents, because hydrogen bonding considerably increases the rate of internal conversion from the singlet excited state, thus diminishing Φ_Δ to values much lower than those in nonprotic solvents of similar polarity. In mixtures of cyclohexane and alcohols, preferential solvation of FLU by the protic solvent leads to a fast decrease of Φ_Δ upon addition of increasing amounts of the latter.

1. Introduction. – For several decades, considerable interest has been focused on singlet oxygen, the lowest electronic excited state of molecular oxygen ($O_2(^1\Delta_g)$, denoted as 1O_2 below). This activated oxygen species is relatively long-lived (with lifetimes from microseconds to tens of milliseconds, depending on the solvent) and is much more reactive than the ground triplet state (3O_2). Besides its applications in synthesis, 1O_2 is an important oxidizing intermediate involved in processes of biological, medical, and environmental significance, such as photosensitized cytotoxicity and DNA damage, cancer phototherapy, and oxidative degradation of organic materials (including oxidation of pollutants in surface waters containing humic substances; see, e.g., [1]).

Photosensitization is the most-commonly employed method for the production of 1O_2 in solution, and is also primarily responsible for its generation *in vivo* [1f]. Sensitized 1O_2 production most often involves energy transfer from the electronic excited triplet state of a sensitizer ($^3Sens^*$) to dissolved molecular oxygen (Eqns. 1 and 2).



In this case, the quantum yield of singlet oxygen production (Φ_Δ ; Eqn. 3) is proportional to the quantum yield of intersystem crossing (Φ_{ISC} ; Eqn. 1) and to the efficiency of energy transfer from $^3Sens^*$ to 3O_2 (ϕ_{et} ; Eqn. 2).

Eqns. 3–5 relate Φ_{Δ} to the rate constants of the reactions involved in $^1\text{O}_2$ production.

$$\Phi_{\Delta} = \Phi_{\text{ISC}}\phi_{\text{et}} = \Phi_{\text{ISC}} \frac{k_{\text{et}}[^3\text{O}_2]}{k_{\text{q}}[^3\text{O}_2] + \Sigma k_{\text{T}}} = \Phi_{\text{ISC}} P_{\text{O}_2}^{\text{T}} f_{\Delta}^{\text{T}} \quad (3)$$

with k_{et} : rate constant of energy transfer from $^3\text{Sens}^*$ to $^3\text{O}_2$ (*Eqn. 2*), k_{q} : total rate constant of quenching of $^3\text{Sens}^*$ by $^3\text{O}_2$ (sum of the rate constants of energy transfer, electron transfer, and enhanced intersystem crossing to the ground state), Σk_{T} : sum of the rate constants of monomolecular (radiative and nonradiative) and pseudo-monomolecular (chemical reaction, *e.g.*, with the solvent) deactivation processes of the excited triplet state. $P_{\text{O}_2}^{\text{T}}$: fraction of excited triplet states quenched by $^3\text{O}_2$ (*Eqn. 4*),

$$P_{\text{O}_2}^{\text{T}} = \frac{k_{\text{q}}[^3\text{O}_2]}{k_{\text{q}}[^3\text{O}_2] + \Sigma k_{\text{T}}} \quad (4)$$

and f_{Δ}^{T} (also denoted as S_{Δ} in the literature): fraction of excited triplet states quenched by $^3\text{O}_2$ leading to $^1\text{O}_2$ production (*Eqn. 5*).

$$f_{\Delta}^{\text{T}} = k_{\text{et}}/k_{\text{q}} \quad (5)$$

Quantum yields of $^1\text{O}_2$ production (Φ_{Δ}) not only depend on the photophysical properties of the sensitizers, but may also be considerably influenced by the experimental conditions [2], such as oxygen concentration, nature of the solvent, and temperature. These conditions may affect values of Φ_{ISC} , $P_{\text{O}_2}^{\text{T}}$, and/or f_{Δ}^{T} .

Values of Φ_{Δ} of aromatic ketones show a wide range of variation [2]. Depending on the electronic interactions of the C=O moiety with the arene groups and on the substituents, the lowest singlet and triplet excited states of these compounds may exhibit the characteristics of (n,π^*) or (π,π^*) electronic configurations [3]. Whereas triplet (n,π^*)-states undergo photochemical reactions, excited triplet states having (π,π^*)-character most often show efficient energy transfer reactions to suitable acceptor molecules, as, *e.g.*, molecular oxygen [2]. Among aromatic ketones possessing a $\text{T}_1(\pi,\pi^*)$ electronic configuration, 1*H*-phenalen-1-one (= perinaphthenone, PN) exhibits a high Φ_{Δ} value (≥ 0.90) in a large variety of polar, protic, and apolar solvents, and is, therefore, widely used as a reference $^1\text{O}_2$ sensitizer [4]. In contrast to PN, although only a few results are currently available, Φ_{Δ} of 9*H*-fluoren-9-one (FLU; a photochemically stable aromatic ketone) appears to be strongly influenced by the nature of the solvent: a Φ_{Δ} value of 0.83 was found in benzene [5a], whereas the reported values in MeOH are lower than 0.10 [4a][5b]. Recently, *Biczók et al.* [6] carried out measurements of fluorescence lifetimes (τ_{F}), fluorescence quantum yields (Φ_{F}), and triplet quantum yields (Φ_{ISC}) for fluorenone and fluorenone derivatives in protic and nonprotic solvents of varying polarity. Results for FLU showed that τ_{F} , Φ_{F} and Φ_{ISC} values are all highly solvent-dependent.

In this work, the effects of solvent polarity and proticity on $^1\text{O}_2$ production by FLU have been investigated in a series of 18 solvents. Values of Φ_{Δ} have also been determined in solvents used as components of organized systems such as micelles,

reverse micelles, and microemulsions, used as simple model media for biological membranes [7]. The variations of Φ_{Δ} in selected binary mixtures of solvents, *e.g.*, cyclohexane and alcohol, are of particular interest in this context and are reported. We have combined various techniques for the quantitative analysis of singlet oxygen: detection of the $^1\text{O}_2$ near-infrared (NIR) phosphorescence at 1270 nm under time-resolved (TRPD) or steady-state (SSPD) regimes [8], and laser-induced optoacoustic calorimetry (LIOAC) [9].

2. Results. – 2.1. *Empirical Solvent Polarity Parameters.* The normalized empirical parameter E_{T}^{N} derived from $E_{\text{T}}(30)$ [10] has been chosen as a measure of solvent polarity by using 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-yl)phenoxide (*Reichardt's* betaine dye; PBD) and its more lipophilic penta(*-tert*-butyl)-substituted derivative (LBD; *Exper. Part*). The ground and excited states of these dyes have a large difference in dipole moments, and, therefore, the $\pi - \pi^*$ transition energy is highly sensitive to solvent polarity. The $E_{\text{T}}(30)$ and E_{T}^{N} polarity parameters were determined by spectrophotometric measurements for over 360 pure solvents [10] and for 80 mixtures of different solvents [11]. Values of E_{T}^{N} for solvents used in this work are listed in *Table 1*. We have determined the E_{T}^{N} values for the two dyes dissolved in the various mixtures investigated in this work and in the pure solvents used for preparing these mixtures (*Table 2*). In solvents of low polarity and in binary mixtures containing low amounts of polar solvents, PBD aggregates and, therefore, LBD was used for obtaining reliable results. In agreement with literature data (*e.g.*, mixtures of toluene and MeOH [11a]), values of E_{T}^{N} as a function of the percent of alcohol in cyclohexane (*Fig. 1*) increase rapidly with the addition of small amounts of alcohol (up to *ca.* 20% of alcohol). This behavior results from selective solvation of the dye by the alcohol through H-bonding [10b][11a]. When the H-bonded adduct is fully formed,

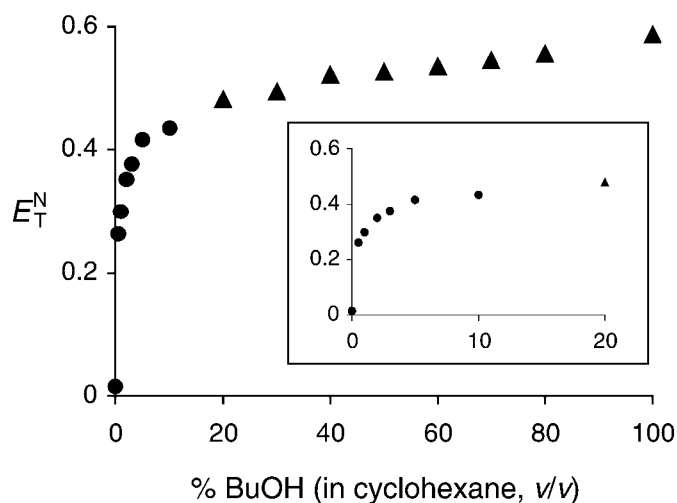


Fig. 1. Variation of E_{T}^{N} values in mixtures of cyclohexane and BuOH. E_{T}^{N} Determined with *Reichardt's* dyes: PBD (triangles); LBD (circles) (the more lipophilic dye LBD was used at lower contents of BuOH, *inset*).

Table 1. Quantum Yields of Fluorescence (Φ_F), Intersystem Crossing (Φ_{ISC}), and Singlet Oxygen Production (Φ_Δ) for FLU in Various Solvents

Solvent	E_T^N [10b]	$\Phi_F (\times 10^4)$	Φ_{ISC}	R (Φ_Δ^R) ^{a)}	Φ_Δ (SSPD) ^{b)} $\lambda_{ex} = 367$ nm (this work)	Φ_Δ (TRPD) ^{c)} $\lambda_{ex} = 337$ nm	Φ_Δ (LIOAC) ^{d)} $\lambda_{ex} = 337$ nm (this work)
Cyclohexane	0.006(2)	5–50 [12][13], 42 (this work)	1.03 [17]	PN (0.98) [4c]	1.00		1.03
Methylcyclohexane	0.006(2)	50–56 [6d]	1.00 [6d]				
Heptane	0.012(3)			PN (0.98)	1.00		
Dodecane	0.012(3)			PN (0.98)	1.00		
Hexadecane	0.012(3)			PN (0.98)	0.99		
Toluene	0.098(8)	97–98 [6e][14]	0.88 [6e], 0.68 [14]	PN (0.93)	0.88		
Benzene	0.111	100–130 [13][12b][15]	0.93 [15][17][5a]	PN (0.93) [4a]	0.83	0.82, 0.83 [5a]	
Et ₂ O	0.117	49 [6d]	0.96 [6d]				
1,4-Dioxane	0.164	58–100 [6d][16], 70 (this work)	0.96 [6d]	PN (0.99) [4d]	0.92	0.93 (this work)	0.94
THF	0.207	64 [6d]	0.87 [6d]				
Propylene oxide	0.281			PN (0.95)	0.87		
<i>N,N</i> -Diethylacetamide	0.330			PN (0.87)	0.72		
Acetone	0.355	200–300 [12b][15][6d][17], 310 (this work)	0.77 [6d][15][17]	PN (1.02) (this work, LIOAC)	0.79		0.82
<i>N,N</i> -Dimethylacetamide	0.377	230 (this work)		PN (0.87) [4d]	0.64	0.63 (this work)	0.66
MeCN	0.460	250–340 [16][15][6d][14], 390 (this work)	0.34 [14], 0.46 [6d], 0.48 [15]	PN (0.98) [4b]	0.42		
<i>Alcohols</i>							
2,4-Dimethylpentan-3-ol	0.290			PN (0.97)	0.17		
Octan-1-ol	0.537	25 [6d]	0.14 [6d]				
Pentan-1-ol	0.586	22 [6d]	0.11 [6d]				
<i>i</i> -PrOH	0.546	27–30 [12][13]		RB (0.76) [18]	0.06		
BuOH	0.586	45 (this work)		PN (1.00) (this work, LIOAC), RB (0.73) [19]	0.08		
BuOD	0.586	9–15 [16][6d]		<i>Idem</i> BuOH	0.06		
EtOH	0.654	7 [16]	0.06 [6d]				
MeOH	0.762		0.02–0.07 [5b]	PN (0.97) [4a]; RB (0.76) [19]			
CD ₃ OD	0.762			PN (0.97) [4a]; RB (0.76) [19]	0.02 [4a]		

^{a)} R: Reference sensitizer for SSPD and TRPD; PN: phenalene, RB: rose Bengal. ^{b)} Steady-state ¹O₂ phosphorescence detection (SSPD); standard deviation $\pm 5\%$.

^{c)} Time-resolved ¹O₂ phosphorescence detection (TRPD); standard deviation: $\pm 8\%$. ^{d)} Light-induced optoacoustic calorimetry; standard deviation: $\pm 8\%$.

Table 2. *Quantum Yields of Singlet Oxygen Production (Φ_{Δ}) by FLU in Mixtures of Cyclohexane and Alcohol (BuOH or 2,4-dimethylpentan-3-ol (DMP)) and in MeCN Containing Traces of H_2O*

Mixtures	E_T^N (This work)	Φ_{Δ} (SSPD) ^{a)} $\lambda_{ex} = 367$ nm	Φ_{Δ} (LIOAC) ^{b)} $\lambda_{ex} = 337$ nm
% BuOH in cyclohexane (v/v)			
0	0.006(2)	1.00 ^{c)}	1.03
1	0.299	0.83 ^{c)}	
2	0.352	0.75 ^{c)}	
3	0.377	0.68 ^{c)}	
5	0.417	0.58 ^{c)}	0.51
10	0.435	0.45 ^{c)}	0.48
15	0.463	0.37 ^{c)}	0.38
20	0.482	0.31 ^{d)}	0.32
25	0.492	0.26 ^{d)}	0.29
30	0.494	0.23 ^{d)}	
40	0.522	0.18 ^{d)}	
50	0.527	0.15 ^{d)}	
60	0.536	0.13 ^{d)}	
70	0.546	0.11 ^{d)}	
80	0.556	0.10 ^{d)}	
100% BuOH	0.587	0.08 ^{d)}	
% DMP in cyclohexane (v/v)			
0	0.006(2)	1.00 ^{c)}	
5	0.202	0.81 ^{c)}	
15	0.225	0.61 ^{c)}	
25	0.249	0.44 ^{c)}	
100% DMP	0.319	0.17 ^{c)}	
% H_2O in MeCN (v/v)			
0	0.465	0.42 ^{c)}	
0.08	0.485	0.39 ^{c)}	
0.40	0.512	0.25 ^{c)}	

^{a)} Standard deviation: $\pm 5\%$ and $\pm 8\%$ with PN and RB as reference sensitizers, respectively. ^{b)} Standard deviation: $\pm 8\%$. ^{c)} Reference sensitizer: PN ($\Phi_{\Delta} = 0.98$). ^{d)} Reference sensitizers: PN ($\Phi_{\Delta} = 0.98 - 0.99$); RB ($\Phi_{\Delta} = 0.73$).

further addition of alcohol leads to a slower increase of E_T^N due to nonspecific solvation effects.

2.2. *Absorption and Fluorescence Characteristics of 9H-Fluoren-9-one.* The absorption spectrum of FLU is affected by solvent polarity. In agreement with literature results [12], relatively small bathochromic shifts were observed for all the absorption bands when changing from an apolar to a polar solvent. The effect on the absorption band in the longest wavelength range (380–450 nm) is shown in Fig. 2 for cyclohexane and BuOH.

Solvent polarity has a much larger effect on the fluorescence wavelength $\lambda_{max,F}$. A large bathochromic shift was observed from apolar solvents (cyclohexane, $\lambda_{max,F} = 450$ nm) to protic solvents (BuOH, $\lambda_{max,F} = 562$ nm). In nonprotic solvents, the red shift increases moderately with polarity (1,4-dioxane, $\lambda_{max,F} = 499$ nm; acetone, $\lambda_{max,F} = 498$ nm; MeCN, $\lambda_{max,F} = 513$ nm). Fluorescence quantum yields (Φ_F) are low [6d], ranging from 5×10^{-4} to 3×10^{-2} in the solvents investigated in this work (Table 1).

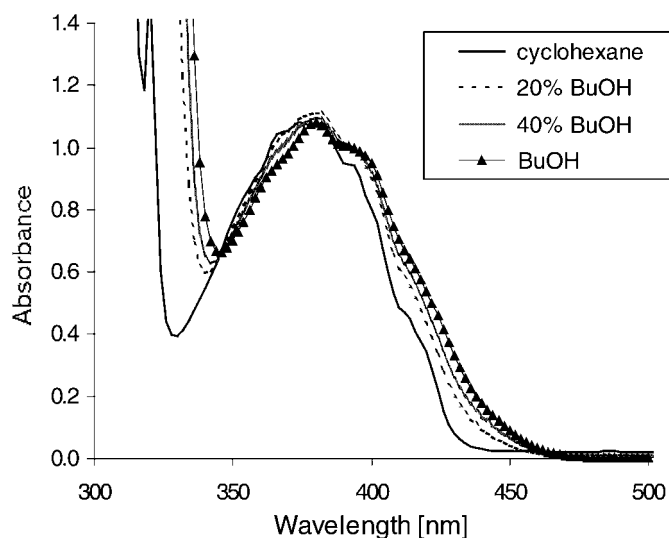


Fig. 2. Absorption spectra of fluorenone (FLU) in cyclohexane, BuOH, and in mixtures of the two solvents ([FLU] ca. $4 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$; $\epsilon_{367} = 230 \pm 81 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and $280 \pm 81 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, in BuOH and cyclohexane, respectively).

Values of Φ_{F} not previously reported were determined if needed for Φ_{Δ} determinations by optoacoustic calorimetry (*Exper. Part, Eqn. 6*).

2.3. *Determination of the Quantum Yields of Singlet Oxygen Production by 9H-Fluoren-9-one: Laser-Induced Optoacoustic Calorimetry (LIOAC)*. This method provides a means to determine absolute Φ_{Δ} values and is, therefore, convenient for solvents (and solvent mixtures) for which no reference $^1\text{O}_2$ sensitizer is available. Values of Φ_{Δ} may be determined from the amplitude of the first maximum of the optoacoustic wave (H_{m}) (*Exper. Part*). In this work, H_{m} was recorded as a function of the laser energy for oxygen-saturated FLU solutions of various absorbances, as well as for the calorimetric reference (2-hydroxybenzophenone, 2HBP). 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 *Exper. Part* and shown in *Fig. 3* for FLU in 1,4-dioxane. Knowing α , the fluorescence quantum yield, and the fluorescence energy, Φ_{Δ} values may be calculated with *Eqn. 6* (*Exper. Part*; see, e.g., [4c][4d][9]).

Values of Φ_{Δ} of $1.03(\pm 0.08)$, $0.94(\pm 0.07)$, $0.82(\pm 0.06)$, and $0.66(\pm 0.04)$ were obtained in cyclohexane, 1,4-dioxane, acetone, and *N,N'*-dimethylacetamide (DMA), respectively, by the maximum-amplitude technique. This method was also used to determine Φ_{Δ} of PN (reference sensitizer for $^1\text{O}_2$ phosphorescence measurements) in acetone and BuOH. Values of ca. 1.0 were obtained in both solvents (*Table 1*).

Absolute values of Φ_{Δ} were also determined by LIOAC for FLU in air-saturated mixtures of cyclohexane and BuOH. In this case, the deconvolution method was used for the analysis of the optoacoustic waves (*Exper. Part*) [4c][9]. Results are listed in *Table 2*. Within experimental error, these values and those obtained by steady-state NIR phosphorescence (*Sect. 2.4*) are in good agreement.

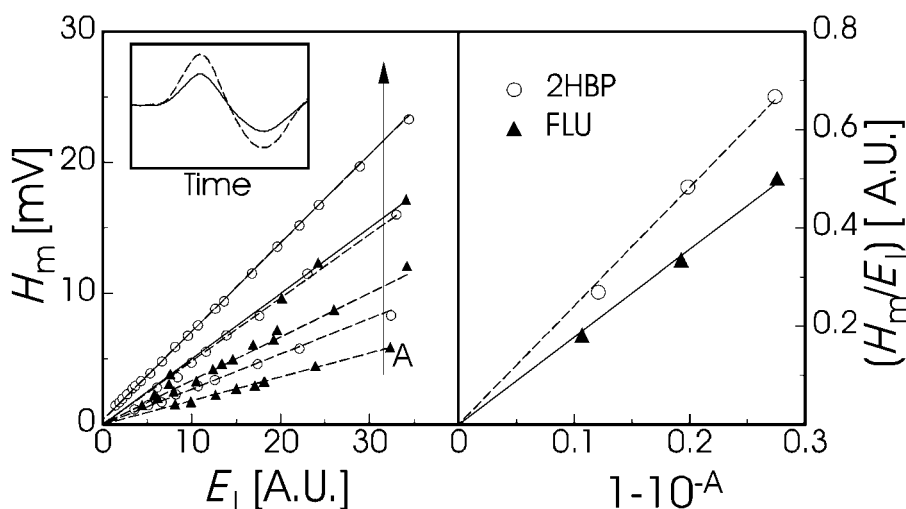


Fig. 3. Maximum amplitude of the optoacoustic wave (H_m) as a function of the energy of the laser pulse (E_l) for fluorenone (FLU) and 2-hydroxybenzophenone (2HBP) solutions of increasing absorbance (left) and dependence of the slopes of the straight lines thus obtained on the absorption factor (right). Inset: typical optoacoustic waves for the two compounds ($\lambda_{ex} = 337$ nm, solvent: oxygen-saturated 1,4-dioxane).

2.4. Determination of the Quantum Yields of Singlet Oxygen Production by 9H-Fluoren-9-one: Phosphorescence Measurements. Albeit weak, 1O_2 NIR phosphorescence provides a convenient method for the direct monitoring of this species under steady-state or time-resolved regimes [8]. The 1O_2 phosphorescence decay traces observed in the various solvents by time-resolved detection (TRPD) could be fitted with single exponential functions from which 1O_2 lifetimes (τ_Δ) could be derived (for a typical decay trace, see Fig. 4, Inset). Within experimental error, the value of τ_Δ in a given solvent remained constant in the range of FLU concentrations used for TRPD (3×10^{-4} to 3×10^{-3} mol \cdot l $^{-1}$), and no differences were observed between FLU and PN or RB solutions. Therefore, no significant 1O_2 quenching by FLU occurs under the experimental conditions used.

Quantum-yield determinations based on the detection of the 1O_2 luminescence involve relative measurements and require the use of reference sensitizers of known Φ_Δ (Exper. Part). In this work, rose bengal (RB) and phenalenone (PN) were employed. In the time-resolved regime, Φ_Δ values were determined by measuring the zero-time intensity ($S(0)$) of the decay signal as a function of the laser energy for sensitizer and reference solutions of various absorbances (Fig. 4). Values of Φ_Δ of $0.93 (\pm 0.04)$ and $0.63 (\pm 0.03)$ were obtained in 1,4-dioxane and DMA, respectively, in good agreement with LIOAC measurements (Table 1).

Stable 1O_2 phosphorescence signals were obtained in all solvents and solvent mixtures under continuous irradiation of FLU at 367 nm, and most of the Φ_Δ determinations were carried out by this method (steady-state phosphorescence detection, SSPD). When PN was used as a reference sensitizer, FLU and PN were irradiated at the same wavelength. In this case, the ratio of the Φ_Δ values of the two compounds ($\Phi_\Delta/\Phi_\Delta^R$) was equal to the ratio of the luminescence signals S_Δ/S_Δ^R ,

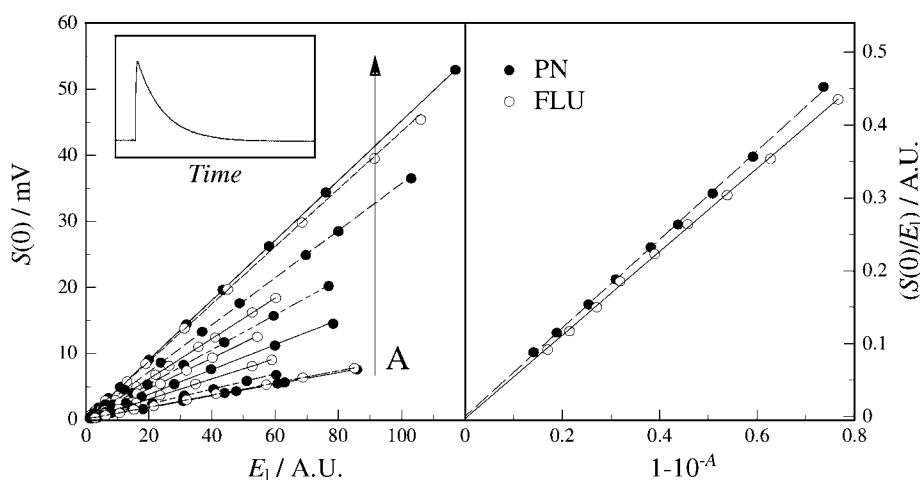


Fig. 4. Zero-time intensity of the phosphorescence signal of singlet oxygen ($S(0)$) as a function of the energy of the laser pulse (E_1) for fluorenone (FLU) and phenalenone (PN) in 1,4-dioxane solutions of increasing absorbance (left) and dependence of the slopes of the straight lines thus obtained on the absorption factor (right). Inset: typical singlet-oxygen transient phosphorescence at 1270 nm ($\lambda_{\text{ex}} = 337$ nm).

minimizing experimental error on Φ_{Δ} of FLU (Eqn. 7). When RB was used as a reference, corrections for the different incident photonic rates at 367 and 547 nm (λ_{ex} for RB) had to be introduced (*Exper. Part*). Results are summarized in Table 1.

In mixtures of a nonpolar solvent with alcohols, values of Φ_{Δ} for FLU show a fast decrease with increasing amounts of the protic solvent (Table 2, and Fig. 5, a). Addition of small amounts of BuOH to cyclohexane led to a fast drop of Φ_{Δ} : from 1.00 in pure cyclohexane to 0.58, when 5% of BuOH was added, and to values lower than 0.20, when the alcohol percentage exceeded 30% (Table 2 and Fig. 5, a). A similar behavior was observed in mixtures of cyclohexane and the less polar alcohol 2,4-dimethylpentan-3-ol (DMP). Consistent with the lower polarity of DMP ($E_{\text{T}}^{\text{N}} = 0.290$) compared to BuOH ($E_{\text{T}}^{\text{N}} = 0.586$), values of Φ_{Δ} are higher than in cyclohexane/BuOH mixtures with the same alcohol contents (Fig. 5, a).

2.5. Solvent Polarity and Quantum Yields of Singlet-Oxygen Production by Fluorenone. Fig. 6 shows the variations of Φ_{Δ} as a function of the empirical solvent polarity parameter E_{T}^{N} for pure solvents (Sect. 2.1). Values of Φ_{Δ} decrease with increasing solvent polarity and show a wide range of variation, from 1.00 (± 0.05) in alkanes (cyclohexane, dodecane, hexadecane) to values lower than 0.15 in protic solvents. Intermediate Φ_{Δ} values have been obtained in nonprotic polar solvents such as acetone, DMA, or MeCN. It is noteworthy that the Φ_{Δ} value for DMP lies out of the trend shown by all solvents.

Fig. 5, b, shows that the variation of Φ_{Δ} of FLU in mixtures as a function of the polarity parameter E_{T}^{N} follows a similar pattern for cyclohexane/BuOH and cyclohexane/DMP mixtures. However, in the latter, Φ_{Δ} drops at much lower polarities, *i.e.*, at $E_{\text{T}}^{\text{N}} \approx 0.23$. Although FLU is not H₂O-soluble, the effect of traces of H₂O on Φ_{Δ} has been studied with MeCN as a solvent. A fast decrease of Φ_{Δ} was observed: Φ_{Δ} dropped from 0.42 to 0.25 upon addition of only 0.4% of H₂O (Table 2). This notwithstanding,

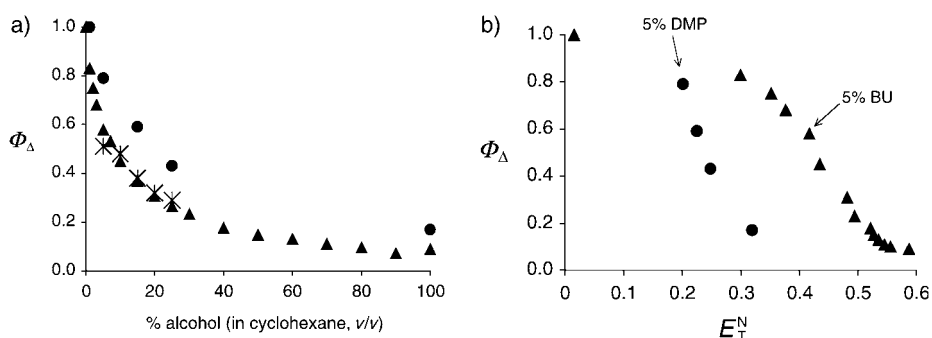


Fig. 5. Quantum yields of singlet-oxygen production (Φ_{Δ}) by FLU in mixtures of cyclohexane and alcohols: a) as a function of the percentage of alcohol in cyclohexane; b) as a function of E_T^N (2,4-dimethylpentan-3-ol (DMP): dots; BuOH (BU): triangles (SSPD), stars (LIOAC) in Fig. 5,a)

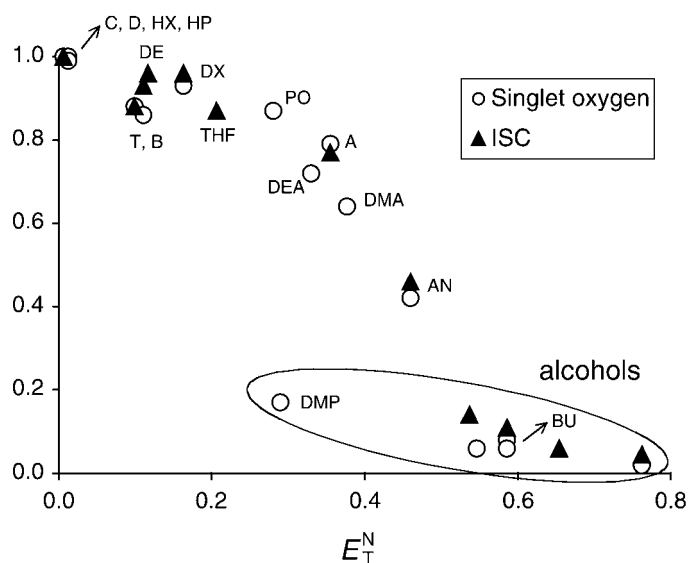


Fig. 6. Quantum yields of intersystem crossing (Φ_{ISC} : triangles) and singlet-oxygen production (Φ_{Δ} : circles) for FLU in solvents of varying polarity (E_T^N). C: cyclohexane, D: dodecane, HX: hexadecane, HP: heptane, B: benzene, T: toluene, DE: Et₂O, DX: 1,4-dioxane, THF: tetrahydrofuran, PO: propylene oxide, A: acetone, DMA: *N,N*-dimethylacetamide, DEA: *N,N*-diethylacetamide, AN: MeCN, DMP: 2,4-dimethylpentan-3-ol, BU: BuOH.

the behavior is very similar for both cyclohexane/BuOH and MeCN/H₂O mixtures: when E_T^N increases from *ca.* 0.46 to *ca.* 0.51, Φ_{Δ} decreases from 0.38 to 0.21 in the former case, and from 0.42 to 0.25 in the latter case.

Discussion. – The fluorescence quantum yields (Φ_F) of FLU in the solvents investigated in this work are low (Table I), in agreement with literature data obtained in a variety of solvents [6] ($\Phi_F \leq 3 \times 10^{-2}$). Therefore, the deactivation of the singlet

excited state (S_1) of FLU is dominated by radiationless processes, *i.e.*, intersystem crossing to the triplet state (ISC) and internal conversion to the ground-state (IC). Depending on the solvent characteristics, large differences in triplet quantum yields (Φ_{ISC}) have been reported [6c][6d].

Nonprotic Solvents. Deactivation of S_1 to the triplet state appears to be the dominant pathway in apolar solvents. In this case, the rate constant of intersystem crossing (k_{ISC}) is much larger than the rate constant of internal conversion (k_{IC}), and Φ_{ISC} is close to unity ($\Phi_{ISC}=1.00$ in methylcyclohexane [6d][15]). In nonprotic solvents, values of k_{ISC} and Φ_{ISC} decrease with increasing solvent polarity [6c][6d]: for example, $\Phi_{ISC}=0.93, 0.77, 0.34-0.48$ for benzene ($E_T^N=0.111$), acetone ($E_T^N=0.355$), and MeCN ($E_T^N=0.460$), respectively (Table 1). These results may be explained qualitatively by the effects of solvent polarity on the energetic ordering of singlet and triplet excited states of FLU [20]: *i*) in polar solvents, S_1 has a dominant (π, π^*) configuration, and the $T_2(n, \pi^*)$ state has a higher energy than S_1 ; therefore, intersystem crossing to the triplet manifold is not favored (the lower-lying T_1 state having (π, π^*) configuration), and internal conversion is dominant; *ii*) in nonpolar solvents, the (n, π^*) states are stabilized relative to the ground state, and the $T_2(n, \pi^*)$ lies below the singlet (π, π^*) state; in this case, intersystem crossing becomes favorable between $S_1(\pi, \pi^*)$ and $T_2(n, \pi^*)$ [20b], or between $S_1(n, \pi^*)$ and $T_1(\pi, \pi^*)$ [20a].

As can be seen in Fig. 6, within experimental error, the variation of Φ_Δ in non-protic solvents follows that of Φ_{ISC} . FLU sensitizes 1O_2 with a Φ_Δ of unity in alkanes (heptane, dodecane, hexadecane, cyclohexane), and Φ_Δ decreases with increasing medium polarity. Therefore, values of both $P_{O_2}^T$ and f_Δ^T for FLU are close to unity in these solvents (Eqns. 3–5). This is a consequence of *i*) the long lifetime of the triplet excited state of FLU (*e.g.*, 0.1, 0.5, and 1.0 ms in MeCN, methylcyclohexane, and benzene, resp.) [13][21], which allows quenching of all FLU triplet states by molecular oxygen ($P_{O_2}^T \approx 1$), and *ii*) a triplet quenching mechanism largely dominated by energy transfer ($f_\Delta^T \approx 1$). It should be noted that two very different values have been published for Φ_{ISC} of FLU in toluene (0.88 [6e] and 0.68 [14]). Since we determined a value of Φ_Δ of 0.88 in this solvent, a Φ_{ISC} of 0.68 appears definitely too low.

Protic Solvents. As already mentioned (Sect. 2.5), FLU is a very poor 1O_2 sensitizer in alcohols (Table 1). The low values of Φ_{ISC} in protic solvents (alcohols, phenols [6c][6d]) explain this result. In these solvents, k_{IC} was found to be much larger than k_{ISC} , a result of H-bonding interactions between FLU and the solvent. The latter quenches the S_1 state of FLU at rates that roughly follow its H-bonding power [6b–d]. A striking example of the importance of this process for 1O_2 production is the case of DMP (Fig. 6). The E_T^N polarity parameter of this solvent is comparable to that of propylene oxide (Table 1); however, Φ_Δ of FLU in the latter solvent (0.87) is *ca.* 6 times higher than in DMP (0.17). The important effect of H-bonding on Φ_{ISC} explains why DMP lies outside the general trend in Fig. 6. Note that, although H-bonding is the main factor controlling values of Φ_{ISC} (and, therefore, of Φ_Δ) in protic solvents, the effect of the alcohol polarity (nonspecific interactions) is still noticeable: a decreasing trend is observed for both Φ_{ISC} and Φ_Δ , when E_T^N increases.

Mixtures. In mixtures of cyclohexane and alcohols, as expected, preferential solvation of FLU by the alcohol through H-bonding is clearly demonstrated by the fast decrease of Φ_Δ upon alcohol addition (Fig. 5). The lower polarity of DMP compared to

BuOH leads to a slower decrease of Φ_{Δ} as a function of the alcohol percentage in cyclohexane/DMP mixtures (Fig. 5, a). When alcohol was added to cyclohexane, addition of 5% of BuOH and 15% of DMP were needed, respectively, for observing the same decrease of Φ_{Δ} , consistent with the lower polarity of the latter (Fig. 5, a). However, for the same E_{T}^{N} , Φ_{Δ} values of FLU are lower in cyclohexane/DMP than in cyclohexane/BuOH mixtures. Since, for a given E_{T}^{N} value, the DMP mixtures contain more alcohol, this result reflects an additional specific effect of the alcohol, most likely its H-bonding ability resulting in preferential solvation of FLU. The same holds true for the MeCN/H₂O mixtures. FLU is not H₂O-soluble but is efficiently solvated by H₂O, as shown by the 40% decrease of Φ_{Δ} by addition of 0.4% of H₂O in MeCN (Table 2). When alcohol was added to cyclohexane, addition of 5% of BuOH and 15% of DMP were needed for observing the same decrease of Φ_{Δ} . In summary, when a protic solvent is added to a nonprotic one, the variation of Φ_{Δ} follows a similar pattern in all cases, the importance of the Φ_{Δ} decrease depending on the nature of the protic solvent.

In conclusion, values of Φ_{Δ} of FLU are very sensitive to the nature of the microenvironment and show regular trends in their variation as a function of the medium polarity and proticity. Therefore, singlet-oxygen production by FLU might be used as a probe of the sensitizer microenvironment in more complex systems such as micellar media and microemulsions [7].

The authors are particularly thankful to *Heinrich J. Reese* for his valuable technical assistance in solvent purification. *C. G. M.* gratefully acknowledges the *Deutsche Forschungsgemeinschaft (DFG)* for a fellowship (Graduiertenkolleg Nr. 366).

Experimental Part

Chemicals. 9H-fluoren-9-one (*Fluka, puriss.*) was purified by recrystallization from EtOH, and 1H-phenalen-1-one (perinaphthenone, *Merck*) as indicated in [4a]. Rose bengal (*Aldrich, 97%*) was purified with two different chromatographic columns: silica gel 60 (CH₂Cl₂/MeOH 9:1) and *Sephadex G25* (5 × 10⁻⁴ M NH₄OH in aq. soln.). Anthracene (*Merck*) used as fluorescence standard was recrystallized from Et₂O. 2-Hydroxybenzophenone (optoacoustic reference) was purchased from *Aldrich*. The *Reichardt's* dye, 2,6-diphenyl-4-(2,4,6-triphenylpyridin-1-yl)phenoxide (PBD) was obtained from *Fluka*, whereas the more lipophilic penta(*tert*-butyl)-substituted betaine dye (LBD) was kindly provided by Prof. *C. Reichardt* (Universitaet Marburg, Germany). All solvents (benzene, BuOH, hexadecane, dodecane (*Aldrich*), BuOD (*Ciba-Geigy*), MeCN (*Baker*), toluene (*Riedel-de-Haen*), heptane (*Fluka*), acetone, 1,2-propylene oxide, MeOH, cyclohexane, *N,N'*-dimethylacetamide, *N,N'*-diethylacetamide (*Merck*), *i*-PrOH (*Rotipuran*), Et₂O (*Roth*)) were of the highest purity available and used without further treatment, except for 2,4-dimethylpentan-3-ol (distilled under normal pressure), 1,4-dioxane (refluxed for 1 h in the presence of Na prior to distillation), *N,N'*-dimethylacetamide and *N,N'*-diethylacetamide (purified by azeotropic distillation adding H₂O (5% (v/v)), and toluene (10% (v/v))). Deuterated solvents (D₂O and CD₃OD) with an isotopic enrichment of 99.9% were supplied by *Euriso-Top Groupe, CEA*, France. H₂O was of triply distilled quality (*USF Purelab*). All solns. were air-equilibrated, unless otherwise indicated. Experiments were performed at r.t. (22 ± 1°).

Preparation of Mixtures. Mixtures of alcohol and cyclohexane were prepared by mixing selected exact volumes of each solvent (the percentages of alcohol indicated in the figures correspond to the volume-% before mixing). The two mixtures of MeCN and H₂O were prepared by adding 20 and 100 µl of H₂O to 25 ml of MeCN, resp.

Empirical Solvent-Polarity Parameters $E_{\text{T}}(30)$ and E_{T}^{N} . The $E_{\text{T}}(30)$ polarity parameter is defined as the excitation energy (kcal · mol⁻¹) of the solvatochromic indicator 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridin-1-yl)phenoxide (PBD) in a particular solvent [10]. This parameter can be calculated from the wavelength of the maximum of the absorption band (λ_{max}) corresponding to the intramolecular $\pi - \pi^*$ transition of charge-transfer character (absorption band at longest wavelength). A high $E_{\text{T}}(30)$ value corresponds to a high solvent polarity.

Since PBD is not soluble in aliphatic hydrocarbons, the more lipophilic penta-(*tert*-butyl)-substituted betaine dye (LBD) had to be used as a secondary standard [10]. $E_T(30)$ values may be normalized to E_N^N values by reference to tetramethylsilane (TMS; $E_N^N = 0$) as extreme apolar and H_2O ($E_N^N = 1$) as extreme polar reference solvents in order to avoid the dimension $\text{kcal} \cdot \text{mol}^{-1}$ [10].

Absorption and Fluorescence Measurements. Absorption spectra were recorded on a Shimadzu UV-260 or a Varian Cary 4E spectrophotometer. A Shimadzu RF 540 instrument was used to record fluorescence spectra of FLU in various solvents and of anthracene in EtOH as a reference [22]. FLU was excited at 337 nm. The quantum yields were determined from the integrated area under the corrected spectra, with optically matched solutions [3], and accounting for the refractive-index differences between solvents. The measurements were repeated for a series of absorbances ranging from 0.015 to 0.050.

Reference 1O_2 Sensitizers. Rose bengal (RB) and 1*H*-phenalen-1-one (PN) were used as reference sensitizers. RB is not soluble in apolar solvents and has practically identical Φ_Δ values in H_2O (0.75) and in MeOH (0.76) [19][23]. PN is soluble in a variety of solvents and has a Φ_Δ close to unity (e.g., 0.93, 0.97, and 0.98 in benzene, MeOH, and cyclohexane, resp.) [4]. Despite its high Φ_Δ , PN has been shown to be relatively unstable in some solvents [4d]. In this case, values of the 1O_2 luminescence signals in steady-state experiments were measured at the very beginning of each irradiation period. Moreover, PN solns. were discarded after use and replaced with fresh ones.

Laser Techniques for Singlet-Oxygen Analysis. Two time-resolved techniques are of particular interest for monitoring and analyzing singlet oxygen: time-resolved 1O_2 phosphorescence detection (TRPD) and laser-induced optoacoustic calorimetry (LIOAC). The set-ups for both techniques were described in detail in [4c, d][24]. For TRPD and LIOAC in solvent mixtures, the solns. were equilibrated with air, while for LIOAC in neat solvents, they were saturated with O_2 . Typically, 20 to 100 shots were averaged for each signal, the energy of the laser pulse not exceeding 500 and 50 μJ for TRPD and LIOAC, resp. The principles of the techniques are presented very briefly below.

Laser-Induced Optoacoustic Calorimetry (LIOAC). The heat released in radiationless processes causes a small solvent expansion, which, in turn, induces a pressure wave. In LIOAC, a piezoelectric transducer measures the intensity of the pressure wave in a time-resolved manner, thus providing both thermodynamic and kinetic information on these processes. When the shapes of the optoacoustic waves are identical for the sample and a photocalorimetric reference is used, i.e., a substance that releases all absorbed light energy within the time resolution of the detector, 2-hydroxybenzophenone in our case, absolute Φ_Δ values may be determined from the optoacoustic wave maximum (H_m) as [4c, d][9]:

$$\Phi_\Delta E_\Delta = (1 - \alpha) E_{\text{exc}} - \Phi_F E_F \quad (6)$$

where E_{exc} is the molar energy of the laser photons ($355.2 \text{ kJ einstein}^{-1}$, α is the fraction of absorbed energy released as prompt heat (heat integrated by the transducer, ca. 20 ns time resolution), Φ_F and E_F ($\text{kJ} \cdot \text{einstein}^{-1}$) are the quantum yield and the average energy of fluorescence of the sensitizer, resp., and E_Δ is the $O_2(^1\Delta_g)$ energy ($94.2 \text{ kJ} \cdot \text{mol}^{-1}$).

The value of α (Eqn. 6) is determined by recording H_m as a function of the laser energy for O_2 -saturated sensitizer solns. of various absorbances and for a calorimetric reference. The slopes of the straight lines obtained for the variation of H_m as a function of E_i are 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. Values of Φ_Δ for FLU were determined by this method in cyclohexane ($\alpha = 0.71$, $\lambda_{\text{max},F} = 450 \text{ nm}$), 1,4-dioxane ($\alpha = 0.75$, $\lambda_{\text{max},F} = 499 \text{ nm}$), and acetone ($\alpha = 0.75$, $\lambda_{\text{max},F} = 498 \text{ nm}$) (Table I), as well as for PN (reference) in acetone ($\alpha = 0.71$) and BuOH ($\alpha = 0.72$) (fluorescence negligible).

The optoacoustic determination of Φ_Δ in DMA was complicated by the fact that this solvent forms a contact complex with O_2 , which absorbs substantially at 337 nm (absorbance 0.042 under O_2), and irradiation of the corresponding charge-transfer absorption band produces 1O_2 with a $\Phi_{\Delta,CT}$ of 0.13 [4d]. In this case, the α value measured experimentally had to be corrected for the α value of the complex, as indicated in [4d] for PN.

The deconvolution method was used for the analysis of the optoacoustic waves in air-saturated mixtures of cyclohexane and BuOH. In solvent mixtures, O_2 bubbling was avoided to prevent variations in the solvent composition due to differential vaporization. In the resulting air-saturated solns., triplet quenching by O_2 occurred typically in the hundreds of ns time scale, which resulted in clear shifts of the optoacoustic waves compared to those of the calorimetric reference. Under these conditions, the optoacoustic amplitudes can no longer be compared, and the deconvolution method of analysis must be used instead [9]. The software Sound Analysis from *Quantum Northwest* was used to this end with the kinetic model described previously [4c].

Time-Resolved Phosphorescence Detection (TRPD). Detection of the weak near-IR (1270 nm) $^1\text{O}_2$ phosphorescence allows direct monitoring of this transient species (see, e.g., [8]). TRPD provides a means to measure $^1\text{O}_2$ lifetimes (τ_Δ) and to determine quantum yields of $^1\text{O}_2$ production (Φ_Δ) relative to that of a standard $^1\text{O}_2$ sensitizer. Relative Φ_Δ values may be calculated from the zero time (middle of the laser pulse) intensities of the $^1\text{O}_2$ phosphorescence signals, $S(0)$. $S(0)$ is measured as a function of the laser energy (E_l) for optically-matched solns. 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 when measured in the same solvent and at the same excitation wavelength.

Steady-State $^1\text{O}_2$ Phosphorescence Measurements (SSPD). The home-built equipment used for monitoring the $^1\text{O}_2$ luminescence at 1270 nm upon continuous excitation of the sensitizer has been already described in detail in [4a][25]. Values of Φ_Δ for FLU in the various media were determined relative to a reference sensitizer (R) of known Φ_Δ . Air-equilibrated solns. were used. Experiments were carried out with absorbance values of 0.5 and 1.5 at the wavelengths of excitation (367 nm for FLU). The luminescence signals (S_e) were recorded alternatively for solutions of FLU and R during at least 3 min (stable signals). The baseline was also recorded for 3 min before and after each irradiation period. The experimental results are the average of, at least, two different series of measurements. Under the conditions used (same solvent for FLU and R, matched absorbances at the wavelength(s) of excitation, $^1\text{O}_2$ quenching by FLU and R negligible compared with $^1\text{O}_2$ deactivation by the medium), Φ_Δ of FLU may be calculated with Eqn. 7 (see, e.g., [4a, d][26]).

$$\frac{S_e}{S_e^R} = \frac{\Phi_\Delta P_0}{\Phi_\Delta^R P_0^R} \quad (7)$$

where S_e and S_e^R are the $^1\text{O}_2$ luminescence signals for FLU and R, and P_0 and P_0^R are the incident photonic rates at the wavelength of excitation of FLU and R, resp.

The ratio P_0/P_0^R was determined from the incident radiant powers (in W) measured with a thermopile (*Laser Instrumentation*, model 154). Typical values of incident radiant powers varied from 6 (± 0.2) to 6.8 (± 0.2) mW at 367 nm (irradiation wavelength for FLU and PN), and from 3.0 (± 0.1) to 3.4 (± 0.1) mW at 547 nm (irradiation wavelength for RB). When the sensitizer under study and R are irradiated at the same wavelength, the ratio S_e/S_e^R is equal to the ratio of the Φ_Δ of the sensitizers ($\Phi_\Delta/\Phi_\Delta^R$).

REFERENCES

- [1] a) 'Singlet O_2 ', Ed. A. A. Frimer, CRC Press, Boca Raton, 1985, Vol. I–IV; b) A. M. Braun, M.-T. Maurette, E. Oliveros, 'Photochemical Technology', D. F. Ollis and N. Serpone Transl., John Wiley and Sons, New York, 1991, Chapt. 10; c) T. J. Dougherty, *Photochem. Photobiol.* **1993**, *58*, 895; d) H. Sies, C. F. Menck, *Mutation Res.* **1992**, *275*, 367; e) J. M. O'Brien, R. J. Singh, J. B. Feix, B. Kalyanaraman, *Photochem. Photobiol.* **1991**, *54*, 851; f) E. Cadenas, *Annu. Rev. Biochem.* **1989**, *58*, 79; g) A. M. Braun, F. H. Frimmel, J. Hoigné, *Int. J. Environ. Anal. Chem.* **1986**, *27*, 137.
- [2] a) F. Wilkinson, W. P. Helman, A. B. Ross, *J. Phys. Chem., Ref. Data* **1993**, *22*, 113; b) A. P. Darmanyan, C. S. Foote, *J. Phys. Chem.* **1993**, *97*, 4573; c) A. P. Darmanyan, C. S. Foote, *J. Phys. Chem.* **1993**, *97*, 5032.
- [3] N. J. Turro, 'Modern Molecular Photochemistry', University Science Books, Mill Valley, CA, 1991.
- [4] a) E. Oliveros, P. Suardi-Murasecco, T. Arminian-Saghafi, A. M. Braun, H.-J. Hansen, *Helv. Chim. Acta* **1991**, *74*, 79; b) R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, *J. Photochem. Photobiol. A: Chem.* **1994**, *79*, 11; c) C. Martí, O. Jürgens, O. Cuenca, M. Casals, S. Nonell, *J. Photochem. Photobiol., A: Chem.* **1996**, *97*, 11; d) E. Oliveros, S. H. Bossmann, G. Heit, G. Troescher, A. Neuner, C. Martínez, A. M. Braun, C. Martí, S. Nonell, *New J. Chem.* **1999**, *23*, 85.
- [5] a) R. W. Redmond, S. E. Braslavsky, *Chem. Phys. Lett.* **1988**, *148*, 523; b) K. Gollnick, G. O. Schenck, *Pure Appl. Chem.* **1964**, *9*, 507.
- [6] a) L. Biczók, T. Bérces, T. Yatsushashi, H. Tachibana, H. Inoue, *Phys. Chem. Chem. Phys.* **2001**, *3*, 980; b) L. Biczók, T. Bérces, H. Inoue, *J. Phys. Chem. A* **1999**, *103*, 3837; c) L. Biczók, T. Bérces, H. Linschitz, *J. Am. Chem. Soc.* **1997**, *119*, 11071; d) L. Biczók, L. Jicsinszky, H. Linschitz, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *18*, 237, and ref. cit. therein, e) L. Biczók, T. Bérces, *J. Phys. Chem.* **1988**, *92*, 3842.
- [7] C. G. Martínez, A. M. Braun, E. Oliveros, *Helv. Chim. Acta*, in preparation.
- [8] a) A. U. Khan, *Chem. Phys. Lett.* **1980**, *72*, 112; b) A. A. Krasnovsky Jr., *Chem. Phys. Lett.* **1981**, *81*, 443; c) M. A. J. Rodgers, *J. Am. Chem. Soc.* **1983**, *105*, 6201; d) A. M. Braun, E. Oliveros, *Pure Appl. Chem.* **1990**, *62*, 1467; e) S. Croux, M.-T. Maurette, M. Hocquaux, A. Ananides, A. M. Braun, E. Oliveros, *New J.*

- Chem.* **1990**, *14*, 161; f) E. Oliveros, F. Besançon, M. Boneva, B. Kräutler, A. M. Braun, *J. Photochem. Photobiol., B: Biol.* **1995**, *29*, 37; g) S. Nonell, S. E. Braslavsky, in 'Methods in Enzymology, Singlet Oxygen, UV-A, and Ozone', **2000**, 319, 37.
- [9] a) S. E. Braslavsky, G. E. Heibel, *Chem. Rev.* **1992**, *92*, 1381; b) J. E. Rudzki, J. L. Goodmann, K. S. Peters, *J. Am. Chem. Soc.* **1985**, *107*, 7849; c) J. Rudzki-Small, L. J. Libertini, E. W. Small, *Biophys. Chem.* **1992**, *42*, 29.
- [10] a) C. Reichardt, 'Solvents and Solvent Effects in Organic Chemistry', VCH, Weinheim, 2nd edn., 1988; b) C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319; c) Y. Marcus, The properties of solvents, Wiley, Chichester-Weinheim, 1998.
- [11] a) P. M. Mancini, A. Teranzani, M. Gasparri, L. Vottero, *J. Phys. Org. Chem.* **1995**, *8*, 617; b) K. Herodes, I. Leito, I. Koppel, M. Rosés, *J. Phys. Org. Chem.* **1999**, *12*, 109, and refs. cit. therein.
- [12] a) S. Arathi Rani, J. Sobhanadri, T. A. Prasada Rao, *J. Photochem. Photobiol., A: Chem.* **1996**, *94*, 1; b) T. Fujii, M. Sano, S. Mishima, H. Hiratsuka, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1833.
- [13] L. A. Singer, *Tetrahedron Lett.* **1969**, *12*, 923.
- [14] R. S. Murphy, C. P. Moorlag, W. H. Green, C. Bohne, *J. Photochem. Photobiol. A: Chem.* **1997**, *110*, 123.
- [15] L. J. Andrews, A. Deroulede, H. Linschitz *J. Phys. Chem.* **1978**, *82*, 2304.
- [16] L. M. Ilharco, A. R. Garcia, J. Lopes da Silva, M. João Lemos, L. F. Vieira Ferreira, *Langmuir* **1997**, *13*, 3787.
- [17] R. A. Caldwell, R. P. Gajewski, *J. Am. Chem. Soc.* **1971**, *93*, 532.
- [18] D. Schmidt, E. Afshari, *J. Phys. Chem.* **1990**, *94*, 4377.
- [19] D. C. J. Neckers, *J. Photochem. Photobiol., A: Chem.* **1989**, *47*, 1.
- [20] a) T. Kobayashi, S. Nagakura, *Chem. Phys. Lett.* **1976**, *43*, 429; b) E. A. Gastilovich, N. V. Korol'kova, G. A. Val'kova, *Russian J. Phys. Chem.* **1991**, *65*, 1527.
- [21] L. Biczóck, Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest, Hungary, personal communication.
- [22] D. F. Eaton, *Pure Appl. Chem.* **1988**, *60*, 1107.
- [23] P. Murasecco-Suardi, E. Gassmann, A. M. Braun, E. Oliveros, *Helv. Chim. Acta* **1987**, *70*, 1760.
- [24] L. A. Martinez, A. M. Braun, E. Oliveros, *J. Photochem. Photobiol., B: Biol.* **1998**, *45*, 103, and refs. cit. therein.
- [25] E. Oliveros, P. Murasecco-Suardi, A. M. Braun, H. J. Hansen, in 'Carotenoids, Methods in Enzymology, Part A, Chemistry, Separation, Quantitation and Antioxidation', Ed. L. Parker, Academic Press, San Diego, CA, 1992, pp. 420–429.
- [26] T. Aminian-Saghafi, G. Nasini, T. Caronna, A. M. Braun, E. Oliveros, *Helv. Chim. Acta* **1992**, *75*, 531.

Received September 12, 2000