

8. 1*H*-Phenalen-1-one: Photophysical Properties and Singlet-Oxygen Production

by Esther Oliveros, Patricia Suardi-Murasecco, Taraneh Aminian-Saghafi, and André M. Braun*

Institut de Chimie Physique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne

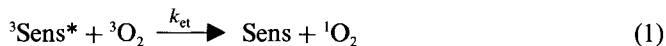
and Hans-Jürgen Hansen

Organisch-chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich

(15.XI.90)

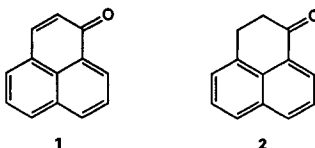
The efficiency of aromatic ketones as singlet-oxygen ($^1\text{O}_2(^1A_g)$) sensitizers can vary considerably with the electronic configuration of their lowest triplet state and the solvent used. Near-infrared measurements of the luminescence of singlet oxygen have shown that the quantum yield of singlet-oxygen production (Φ_d) by 1*H*-phenalen-1-one (**1**) is close to unity in both polar ($\Phi_d = 0.97 \pm 0.03$ in methanol) and non-polar solvents ($\Phi_d = 0.93 \pm 0.04$ in benzene). Analysis of the absorption spectra of the ground state and phosphorescence measurements show that the lowest singlet and triplet states have dominant π, π^* electronic configurations. The quantum yield of intersystem crossing (Φ_{ISC}) of **1**, determined by laser flash photolysis (partial-saturation method), is equal to unity. In comparison with other aromatic ketones, these parameters are important for the discussion of the surprisingly high Φ_{ISC} of **1** and the efficient energy transfer from its triplet state to molecular oxygen. The 1*H*-phenalen-1-one (**1**), being one of the most efficient singlet-oxygen sensitizers in both polar and non-polar media, could be used as a reference sensitizer, in particular in the area of relatively high energies of excitation.

Introduction. – Because of the relatively small energy difference between the ground state ($^3\Sigma_g^-$) and the (1A_g) excited state of molecular oxygen ($94.2 \text{ kJ} \cdot \text{mol}^{-1}$), singlet oxygen ($^1\text{O}_2(^1A_g)$) should be easily produced by energy transfer from the lowest triplet state of most sensitizers to molecular oxygen (*Eqn. 1*). However, only few sensitizers are of practical use for the generation of singlet oxygen, an activated oxidizing species which plays an important role in photo-oxidation reactions (type-II photo-oxidation) [1–7].



Several aromatic ketones have been investigated as singlet-oxygen sensitizers, their quantum yields of singlet-oxygen production (Φ_d) varying between 0.05 and 0.83 [8–12]. The value of Φ_d depends on the quantum yield of intersystem crossing (Φ_{ISC}) of the ketone and on the efficiency of energy transfer to molecular oxygen (ϕ_{et}). The large range of ϕ_{et} and Φ_d has been attributed to the quite different energy gaps between donor and acceptor molecules and to changes in the electronic configuration of the lowest triplet state of the ketones [12]. The spin statistical factor of one ninth expected for oxygen quenching to yield $^1\text{O}_2(^1A_g)$ has also been invoked in order to explain the relatively low quenching constants when compared with diffusion-controlled reactions [12–14]. The role of charge-transfer interactions has been outlined in several cases of the more polarizable $n-\pi^*$ triplet states [8] [12–15].

In this paper, we show that 1*H*-phenalen-1-one (**1**; also called perinaphthenone), a yellow dye, is one of the most efficient singlet-oxygen sensitizers found among aromatic ketones [16] and has the advantage of being soluble in polar protic and aprotic solvents, as well as in non-polar media. This ketone is photostable in benzene, hexane, and methylcyclohexane. It can react by H-abstraction in suitable deoxygenated solvents (*e.g.* propan-2-ol, EtOH) to yield a mixture of products, among them 1*H*-phenalan-1-one (= 2,3-dihydro-1*H*-phenalen-1-one; **2**) [17] [18]. However, the quantum yield of this photoreduction is very low [19].



In order to get more insight into the basic principles governing the oxygen-sensitizing ability of aromatic ketones, more should be known about the electronic configuration of their lowest triplet state, as well as about the efficiency of the formation and decay processes of this state. Following this general working principle, we have undertaken experiments to determine, by laser flash photolysis, the quantum yield of intersystem crossing (Φ_{ISC}) of **1** and the spectrophotometric parameters of its lowest triplet state. Its triplet energy (E_T) has been calculated from the phosphorescence spectrum. The quantum yield of singlet-oxygen production (Φ_A) has been determined by near-infrared luminescence measurements of singlet oxygen produced upon continuous irradiation of **1**. Depending on the solvent, rose bengal [20] [21] or 9*H*-fluoren-9-one [12] has been used as a reference sensitizer.

Methods of Analysis. – 1. *Partial-Saturation Method.* The quantum yield of intersystem crossing (Φ_{ISC}) and the molar absorption coefficient of the corresponding triplet state (ϵ_T) can be determined by laser flash photolysis experiments in oxygen-free solutions, using the partial-saturation method [22–24]. Experimentally, the dependence of the triplet-triplet absorption on the energy of the laser pulse is measured. Subsequent calculations are based on a monophotonic excitation, more often taking only into account the ground state and the triplet state (two-state model [20] [25–28]).

The variation of the observed absorbance (ΔA) due to triplet-triplet absorption upon laser excitation may be written as:

$$\Delta A = a \{1 - \exp(-bE)\} \quad (2)$$

where

$$a = (\epsilon_T - \epsilon_0) [\text{Sens}]_0 l \quad (3)$$

$$b = 2302 \epsilon_0^{\text{ex}} \Phi_{ISC} [\text{cm}^2 \cdot \text{einstein}^{-1}] \quad (4)$$

ϵ_T, ϵ_0 molar absorption coefficients of the triplet state and the ground state, respectively, at the wavelength of analysis [$\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$];

l optical path length in the direction of the monitoring beam [cm];

ϵ_0^{ex} molar absorption coefficient of the ground state at the wavelength of excitation (laser) [$\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$];

E laser photonic irradiance integrated during the pulse [$\text{einstein} \cdot \text{cm}^{-2}$];

$[\text{Sens}]_0$ initial concentration of the sensitizer [$\text{mol} \cdot \text{l}^{-1}$].

Carmichael and Hug [22–24] have shown that the complete three-state model, which takes into account the excited singlet state, may be simplified to the two-state model (*Eqn. 2*), if the rate constant of excitation,

$$k_{\text{ex}} = 2303 \varepsilon_0^{\text{ex}} E_p(t) \quad (\text{for optically thin samples}) \quad (5)$$

where $E_p(t)$ is the laser photonic irradiance [$\text{einstein} \cdot \text{s}^{-1} \cdot \text{cm}^{-2}$],

is negligible compared to k_{ex} , sum of the monomolecular rate constants of deactivation of the singlet state.

The laser energy must be increased until partial saturation might be observed. Parameters a and b , and thus ε_T and Φ_{ISC} , can then be obtained by fitting the theoretical curve (*Eqn. 2*) with the experimental points. If bE remains relatively small and, hence, no partial saturation is reached, the exponential factor in *Eqn. 2* may be expanded in a power series, leading to a linear relation between ΔA and E ($\Delta A = a b E$). Consequently, only the product ($\Phi_{\text{ISC}} \varepsilon_T$) can be obtained from the slope (ab). This method has been described in more details in a previous publication [20].

2. Near-Infrared Luminescence Measurements of Singlet Oxygen upon Continuous Irradiation of the Sensitizer. In the absence of a physical quencher or a chemical acceptor, singlet oxygen, produced by energy transfer from the triplet state of a sensitizer to molecular oxygen (*Eqn. 1*), is deactivated in solution by collision with the solvent molecules (main decay pathway, *Eqn. 6*) and by luminescence (*Eqn. 7*).



The singlet-oxygen luminescence can be conveniently monitored at the emission maximum of 1270 nm [29] [30], under continuous irradiation of the sensitizer [31–35]. The quantum yield of this luminescence (Φ_e) is given by *Eqn. 8* in which the emitted photonic flux (P_e) can be substituted by the product of the intensity of the measured luminescence signal (S_e [mV]) and an apparatus factor (C).

$$\Phi_e = P_e/P_a = S_e C/P_a \quad (8)$$

where P_a is the photonic flux absorbed by the sensitizer.

The quantum yield of singlet-oxygen luminescence, Φ_e , is related to Φ_d by *Eqn. 9*.

$$\Phi_e = \Phi_d \phi_e = \Phi_d k_e \tau_d \quad (9)$$

where

$$\phi_e = k_e/(k_e + k_d) = k_e \tau_d \quad (10)$$

is the luminescence efficiency (if the quenching of singlet oxygen by the sensitizer (rate constant k_q^{S}) is negligible compared to the deactivation by the solvent, *i.e.* if $k_q^{\text{S}}[\text{Sens}] \ll k_d$).

k_e rate constant of singlet-oxygen luminescence ($k_e \ll k_d$ [31] [36]) [s^{-1}];

k_d rate constant of deactivation of singlet oxygen by the solvent [s^{-1}];

τ_d lifetime of singlet oxygen in the solvent used, in the absence of quencher [s].

As the singlet-oxygen luminescence is detected at 90° with respect to the axis of the beam of the incident light, the equipment-specific proportionality factor C depends on the absorbance of the solution [35]. An empirical function can be found in comparing the singlet-oxygen luminescence initiated by the same sensitizer in a given solvent at different absorbances, taking one absorbance as a reference (A^R). When the same incident photonic flux P_0 is applied, the ratio of the luminescence signals at a given absorbance A and at the absorbance A^R is given by:

$$S_e/S_e^R = (C^R/C) (\Phi_e/\Phi_e^R) (\alpha/\alpha^R) \quad (11)$$

where $\alpha = (1 - 10^{-A}) = P_d/P_0$, absorption factor.

If Φ_e , i.e. Φ_d and ϕ_e , is independent of the concentration of the sensitizer in the range of interest, a plot of $S_e/S_e^R = f(\alpha/\alpha^R)$ shows the proportionality function C^R/C characteristic of the equipment. However, Φ_d might be influenced by aggregation effects [37] and/or, as the concentration increases, the rate of quenching of singlet oxygen by the sensitizer ground state might no longer be negligible compared to the rate of deactivation by the solvent, thus decreasing the luminescence efficiency ϕ_e . In these cases, Φ_e depends on the concentration of the sensitizer, and the same plot, $S_e/S_e^R = f(\alpha/\alpha^R)$, includes the relative variation of Φ_e , and thus concentration effects on Φ_e can be demonstrated [35].

If measurements with two solutions, one containing the sensitizer under investigation and the other a reference (R), are made using identical absorbances at the wavelength(s) of excitation, hence ensuring identical absorption factors α , the factor C remains constant. Furthermore, if the same solvent (same k_e and k_d) is used in both series of experiments, the ratio of the luminescence signals, S_e/S_e^R , is related to the ratio of the incident photon flux in the two experiments and to the ratio of the quantum yields of singlet-oxygen production by the two sensitizers (if $k_d^R[\text{Sens}] \ll k_d$ for both sensitizers):

$$S_e/S_e^R = (P_0/P_0^R) (\Phi_d/\Phi_d^R) \quad (12)$$

Since Φ_d^R is known (R: reference), Φ_d may be calculated by measuring S_e^R , S_e , P_0^R , and P_0 . If the wavelength of excitation is the same for both sensitizers, Eqn. 12 simplifies to:

$$S_e/S_e^R = \Phi_d/\Phi_d^R \quad (13)$$

Results. – 1. *Absorption and Phosphorescence Spectra.* The ground-state absorption spectra of **1** have been measured in hexane, benzene, CCl_4 , and methanol (Fig. 1). The values of λ_{max} and the corresponding molar absorption coefficients ϵ_{max} are given in Table 1. On increasing the polarity of the solvent, only small modifications of the spectral parameters are observed.

The phosphorescence of **1** appears to be very weak. The corresponding spectrum (Fig. 1) shows a 0–0 band at ca. 545 nm, which corresponds to a triplet energy (E_T) of 220

Table 1. Ground-State Absorption Data of **1**

| Solvent | λ_{max} [nm] | ϵ_{max} [$\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$] | λ_{max} [nm] | ϵ_{max} [$\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$] |
|----------------|-----------------------------|---|-----------------------------|---|
| hexane | 354 | 10150 (± 200) | 377 | 7870 (± 150) |
| CCl_4 | 354 | 9700 (± 200) | 377 | 7970 (± 150) |
| benzene | 358 | 10900 (± 200) | 378 | 9400 (± 200) |
| methanol | 360 | 11250 (± 200) | 382 | 9630 (± 200) |

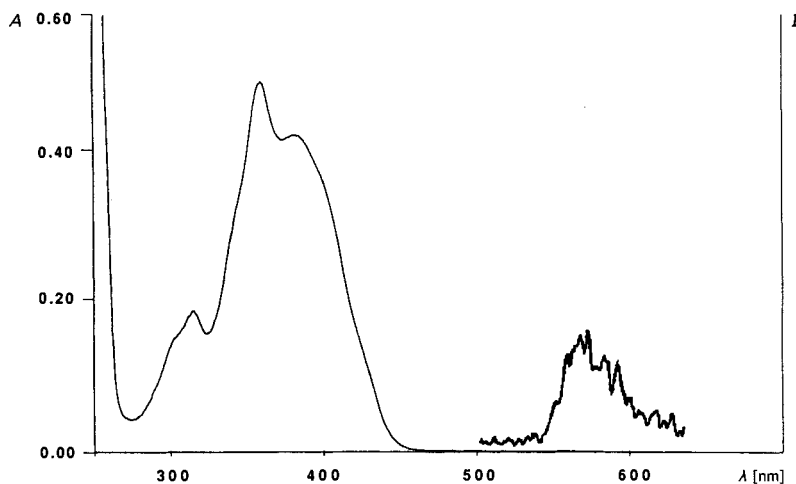


Fig. 1. Absorption spectrum of 1H-phenalen-1-one (**1**) in methanol (—, A ; $[1] = 4.3 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$) and phosphorescence spectrum in methylcyclohexane at 77 K under Ar (---, I : phosphorescence intensity in arbitrary units; $[1] = 6.1 \cdot 10^{-1} \text{ mol} \cdot \text{l}^{-1}$; $\lambda_{\text{ex}} = 225 \text{ nm}$)

(± 2) $\text{kJ} \cdot \text{mol}^{-1}$. The phosphorescence lifetime has been determined under the same conditions to be 11 ms at 77 K.

2. *Laser Flash Photolysis Experiments.* Optically thin samples of **1** at 353 nm (excitation wavelength) have been prepared in CCl_4 , in methanol and in benzene. Similar difference absorption spectra of the triplet state have been observed between 370 and 610 nm in the three solvents, using a laser pulse energy of 2 mJ. In the case of benzene solutions, Φ_{ISC} and ϵ_T have been determined by the partial-saturation method (*vide infra*), and the corrected triplet-triplet absorption spectrum has been calculated (Fig. 2). In the

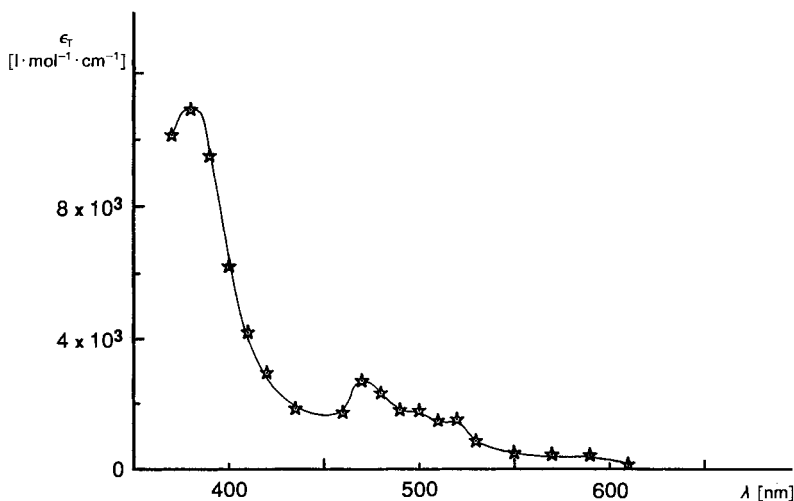


Fig. 2. Triplet-triplet absorption spectrum of 1H-phenalen-1-one (**1**) in degassed benzene, taken immediately after the laser pulse ($\lambda_{\text{ex}} = 347 \text{ nm}$, $[1] = 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; excitation energy: 2 mJ)

entire spectral range, a mono-exponential decay of the absorption signals is observed, with rate constants of $2.8 (\pm 0.3) \cdot 10^4 \text{ s}^{-1}$ ($\tau_T = 35 (\pm 4) \mu\text{s}$) in methanol and $2.6 (\pm 0.3) \cdot 10^4 \text{ s}^{-1}$ ($\tau_T = 38 (\pm 3) \mu\text{s}$) in benzene. The decay kinetics are clearly first-order for pulse energies smaller than or equal to 20 mJ.

Partial-Saturation Method. The variation of the signal at 470 nm has been measured in benzene as a function of the energy of the laser pulse up to 30 mJ (Fig. 3). Saturation is already observed for excitation energies of *ca.* 15 mJ. In order to test the validity of the two-state model, we checked if the condition $k_{ex} \ll k_s$ holds for pulse energies lower than or equal to 20 mJ. Eqn. 5 was used for the calculation of k_{ex} , determined to be $2.5 \cdot 10^8 \text{ s}^{-1}$ for a 20 mJ pulse of 16 ns duration on a surface of 0.25 cm^2 ($\epsilon_0^{ex} = 7530 \pm 60 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). No singlet lifetime is reported for **1** in the literature. As no fluorescence can be observed, we assume that this lifetime is of the same order of magnitude as the singlet lifetime of benzophenone, *i.e.* $\tau_s = 0.005 \text{ ns}$ [38], and that the condition $k_{ex} \ll k_s$ holds by a factor greater than 10^2 . A computer-assisted fit of the parameters a and b using the two-state model (Eqn. 2) yields $\Phi_{ISC} = 1.0 (\pm 0.1)$ and $\epsilon_T (470 \text{ nm}) = 2500 (\pm 200) \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for **1** in benzene.

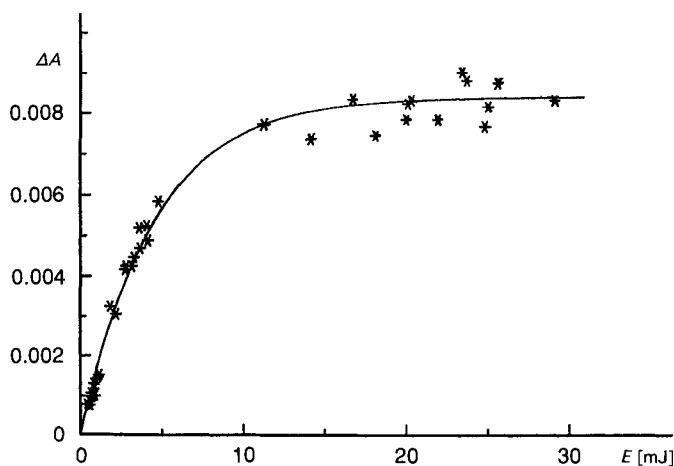


Fig. 3. Experimental points of the variation of the transient absorbance at 470 nm of 1H-phenalen-1-one (**1**) in benzene vs. the energy of the laser pulse (E , mJ) and corresponding calculated curve for the two-state model ($[1] = 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $\lambda_{ex} = 347 \text{ nm}$)

3. *Near-Infrared Luminescence of Singlet Oxygen Upon Continuous Irradiation.* The luminescence signals of singlet oxygen produced by **1**, by rose bengal as a reference sensitizer in CD_3OD , and by 9H-fluoren-9-one as a reference in C_6H_6 and C_6D_6 , were measured at 1270 nm. The excitation wavelengths were 367 nm in the case of **1** and of 9H-fluoren-9-one and 547 nm for rose bengal. Values of 0.76 and 0.825 were used for the quantum yields of singlet-oxygen production (Φ_s^R) by rose bengal in methanol [39–41] and by 9H-fluoren-9-one in benzene [12], respectively.

In the case of rose bengal, Φ_s and ϕ_e , and hence Φ_e , are independent of the concentration of the sensitizer (the rate constant of quenching of singlet oxygen by rose bengal is smaller than $6 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [42]), and a plot of $S_e/S_e^R = f(\alpha/\alpha^R)$ shows the standard proportionality function C^R/C (Eqn. 11, $\Phi_e/\Phi_e^R = 1$) [35]. Similar plots are found for

1*H*-phenalen-1-one or 9*H*-fluoren-9-one as sensitizers; as they can be superimposed to the one found for rose bengal (Fig. 4), we can deduce that the Φ_e of these ketones are also independent of their concentration in the range investigated. Consequently, Φ_A of **1** in benzene solutions can be calculated using Eqn. 13, as the wavelength of excitation and, hence, the incident photonic flux are identical for the reference (9*H*-fluoren-9-one) and the sample. In the case of methanol, Eqn. 12 must be used. The incident radiant flux F_0

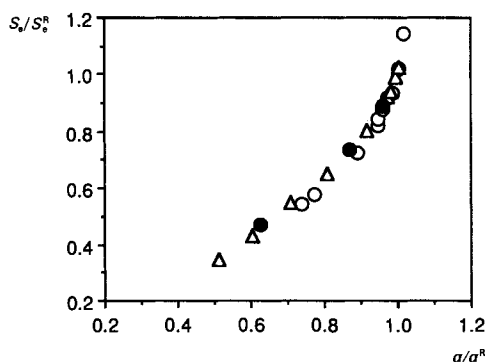


Fig. 4. Plot of $S_e/S_e^R = f(\alpha/\alpha^R)$ for rose bengal (Δ), 1*H*-phenalen-1-one (**1**; \bullet), and 9*H*-fluoren-9-one (\circ); (see Eqn. 11 and text)

Table 2. Quantum Yields of Singlet-Oxygen Production by 1*H*-Phenalen-1-one (**1**; Φ_A) in Benzene and Methanol

| Solvent | Reference | S_e/S_e^{Ra} | F_0^R/F_0 ($\lambda_{ex}^R, \lambda_{ex}$) | Φ_A^R | Φ_A^a |
|----------|---------------------------|----------------|--|-------------------------|-----------------|
| C_6D_6 | 9 <i>H</i> -fluoren-9-one | 1.14 | 1 (367, 367) | 0.825 [12] ^b | 0.94 ± 0.04 |
| C_6H_6 | 9 <i>H</i> -fluoren-9-one | 1.08 | 1 (367, 367) | 0.825 [12] ^b | 0.93 ± 0.04 |
| CD_3OD | rose bengal | 2.00 | 0.43 ^b (547, 367) | 0.76 [39–41] | 0.97 ± 0.04 |

^a) Average of at least three independent measurements. Experiments using different absorbances (typically 1.7 and 1.2) lead to the same result within experimental error.

^b) Mean value obtained from measurements in C_6H_6 by time-resolved thermal lensing (0.82) and time-resolved phosphorescence detection (0.83) [12].

Table 3. Quantum Yields of Singlet-Oxygen Production (Φ_A) by 9*H*-Fluoren-9-one and 2-Acetonaphthone in Benzene and Methanol

| Sensitizer | Solvent | Reference | S_e/S_e^{Ra} | F_0^R/F_0 ($\lambda_{ex}^R, \lambda_{ex}$) | Φ_A^R | Φ_A^a |
|---------------------------|----------|---------------------------|----------------|--|-------------------------|-------------------|
| 9 <i>H</i> -Fluoren-9-one | CD_3OD | rose bengal | 0.04 | 0.49 ^a (547, 367) | 0.76 [39–41] | 0.02 ± 0.01^c |
| 2-Acetonaphthone | C_6H_6 | 9 <i>H</i> -fluoren-9-one | 0.153 | 5.28 ^a (367, 336) | 0.825 [12] ^b | 0.73 ± 0.04^d |
| | CD_3OD | rose bengal | 0.28 | 2.29 ^a (547, 336) | 0.76 [39–41] | 0.79 ± 0.04 |

^a) Average of at least three independent measurements. Experiments using different absorbances (typically 1.7 and 1.2) lead to the same result within experimental error.

^b) Mean value obtained from measurements in C_6H_6 by time-resolved thermal lensing (0.82) and time-resolved phosphorescence detection (0.83) [12].

^c) Result in agreement with literature value [9].

^d) Result in agreement with literature value obtained from measurements by time-resolved thermal lensing (0.73) and time-resolved phosphorescence detection (0.71) [12].

(mW) at $\lambda_{\text{ex}} = 367$ nm (**1** and 9*H*-fluoren-9-one) and F_0^{R} at $\lambda_{\text{ex}}^{\text{R}} = 547$ nm (rose bengal) were measured with a thermopile and Φ_{A} calculated using Eqn. 14:

$$\Phi_{\text{A}}/\Phi_{\text{A}}^{\text{R}} = (S_{\text{e}}/S_{\text{e}}^{\text{R}}) (F_0^{\text{R}}/F_0) (\lambda_{\text{ex}}^{\text{R}}/\lambda_{\text{ex}}) \quad (14)$$

For comparison, the quantum yields of singlet-oxygen production by 2-acetonaphthone (= methyl naphthalen-2-yl ketone) have been determined in benzene (C₆H₆; reference: 9*H*-fluoren-9-one) and methanol (CD₃OD; reference: rose bengal). As the molar absorption coefficient of this compound is very low at 367 nm, a λ_{ex} of 336 nm has been used and Φ_{A} calculated using Eqn. 14. The results are summarized in Tables 2 and 3.

Discussion. – With quantum yields of intersystem crossing and of singlet-oxygen production close to unity, 1*H*-phenalen-1-one is a particularly efficient singlet-oxygen sensitizer. Φ_{A} is almost independent of the solvent, as shown by the results in methanol and in benzene (Table 2). This conclusion is further supported by the value of Φ_{A} of 0.95 (± 0.08) determined in CCl₄ by other authors [43]. For this latter experiments, tetramethylethylene was used as a singlet-oxygen acceptor, and the quantum yield of photo-oxidation (hydroperoxide formation due to the ene reaction) as a function of the acceptor concentration was determined.

Depending on the electronic interaction of the carbonyl moiety with the arene groups and the substituents attached to them, the lowest singlet and triplet states of aromatic ketones may exhibit the characteristics of n,π^* or π,π^* electronic configuration. The energetic ordering within the two manifolds may, however, also depend on the solvent. In the case of **1**, the S₀–S₁ absorption shows a molar absorption coefficient in the typical range of a π – π^* transition ($\epsilon > 1000$ l·mol⁻¹·cm⁻¹). Only a slight solvent effect is observed (Table 1), with a small bathochromic shift in methanol, indicating that a dominant π – π^* transition is involved.

The triplet state of **1** is reported to abstract a H-atom from propan-2-ol or EtOH in deoxygenated solutions [17–19]; this result and the relative short lifetime of the phosphorescence measured at 77 K (*ca.* 11 ms) would be in favour of an n,π^* configuration of the lowest triplet state [44]. However, the quantum yield of photoreduction is very low [19], and the phosphorescence spectrum does not show the typical vibrational progression usually found for the carbonyl moiety of triplet states of n,π^* configuration [45]. A possible explanation for these observations is that ³(n,π^*) and ³(π,π^*) configurations are close in energy and partially mixed, the latter being the lower one, as found in many α,β -unsaturated alicyclic and aromatic ketones [46–48].

Intersystem crossing to the triplet state is very efficient ($\Phi_{\text{ISC}} \approx 1$). Maximum efficiency of this process asks for a rate constant (k_{ISC}) of the order of, or greater than 10⁸ s⁻¹ [49]. In the case of **1**, the energy difference between the lowest singlet and triplet states determined from the absorption and phosphorescence spectra is *ca.* 70 kJ·mol⁻¹ (E_{S} = 288 (± 5) kJ·mol⁻¹ (hexane), E_{T} = 220 (± 2) kJ·mol⁻¹ (methylcyclohexane)). Considering this relatively large energy gap between S₁ and T₁ and the rigidity of the molecule, an efficient intersystem crossing between the π,π^* states is unlikely. Most probably, intersystem crossing occurs between the S₁ (π,π^*) state and the ³(n,π^*) state (assumed to be T₂), the energy of which must be lower than that of S₁. The apparent very fast intersystem crossing in **1** can then be explained by the strong spin-orbit coupling between these two states of different electronic configuration [50]. S₁(π,π^*)–T₂(n,π^*) transitions

have already been observed in other aromatic ketones [49], *e.g.* in 9-acetoanthracene, for which an energy difference ΔE between S_1 and T_2 of *ca.* 20 kJ \cdot mol $^{-1}$ and a k_{ISC} of *ca.* 10 10 s $^{-1}$ have been reported [49].

Since an increase of solvent polarity destabilizes $^3(n, \pi^*)$ states [51] but shows a tendency to lower the energies of $^3(\pi, \pi^*)$ states, no change of the energetic ordering within the triplet manifold of **1** is expected when the solvent is changed from benzene to methanol. In fact, H-abstraction in deoxygenated alcoholic solutions is very inefficient [17–19] [52], and our experiments in methanol confirm these findings, the quenching of the triplet state of **1** by molecular oxygen being much faster than a competing H-abstraction leading to products of an intermediate ketyl radical. The low reactivity of naphthyl ketones for H-abstractions has long been associated with an energetic ordering of the triplet states placing a π, π^* state well below the corresponding n, π^* state. Under these conditions, H-abstraction requires mixing by equilibration between the two triplet states, its extent depending on the energy gap between these states [48].

Higher solvent polarity will increase the energy gap between $T_1(\pi, \pi^*)$ and $T_2(n, \pi^*)$ states. However, the energy of the $T_2(n, \pi^*)$ state of **1** in methanol must still be lower than that of the $S_1(\pi, \pi^*)$ state, because the unit efficiency of intersystem crossing remains unchanged as the polarity of the solvent is increased.

Among aromatic compounds investigated as singlet-oxygen sensitizers, *Redmond* and *Braslavsky* [12] could show a qualitative differentiation between n, π^* and π, π^* sensitizers, the latter having higher S_d values (0.9 ± 0.1) than the former (0.30 ± 0.05). S_d has been defined as the fraction of sensitizer triplet states which, among those being quenched by molecular oxygen, produce $^1\text{O}_2(^1A_g)$, thus

$$S_d = k_{\text{et}}/k_t \quad (15)$$

k_{et} rate constant of Eqn. 1;

k_t rate constant of total quenching of sensitizer triplet states by molecular oxygen (energy transfer, electron transfer, deactivation leading to the ground states of both sensitizer and molecular oxygen).

S_d is linked to Φ_d by Eqn. 16.

$$\Phi_d = \Phi_{\text{ISC}} \phi_{\text{et}} = \Phi_{\text{ISC}} \frac{k_{\text{et}}[^3\text{O}_2]}{k_t[^3\text{O}_2] + k_T} = \Phi_{\text{ISC}} \frac{k_t[^3\text{O}_2]}{k_t[^3\text{O}_2] + k_T} \frac{k_{\text{et}}}{k_t} = \Phi_{\text{ISC}} S_Q S_d \quad (16)$$

k_T sum of the monomolecular and pseudo-monomolecular rate constants of the sensitizer triplet decay processes in the absence of oxygen;

S_Q ratio of the sum of triplet sensitizer decay rates involving molecular oxygen over the total decay rate. S_Q is about unity if $k_T \ll k_t [^3\text{O}_2]$ as it is the case for the compounds studied in this paper (long-lived sensitizer triplet states and low concentrations of sensitizer, thus ensuring negligible triplet-triplet annihilation and ground-state self-quenching).

In the case of 1*H*-phenalen-1-one (**1**), Φ_d and thus S_d values are high, in benzene ($\Phi_d = S_d = 0.93 \pm 0.04$) as well as in methanol ($\Phi_d = 0.97 \pm 0.3$, *Table 2*), and, following the classification of triplet states according to their S_d value, **1** must be definitely among the most efficient singlet-oxygen sensitizers of π, π^* configuration.

For an evaluation of the general validity of a direct relation between the electronic configuration of the lowest triplet state of a sensitizer and its efficiency of singlet-oxygen

production, more data from similar experiments with a series of sensitizers in polar media are needed. In fact, data reported in [12] concern only sensitizers and energy-transfer parameters in benzene solution. A few results of experiments in polar solvents may be mentioned.

E.g., acetophenone exhibits a lowest triplet state of dominant n,π^* configuration in apolar solvents [53] [54], yielding a Φ_d and an S_d of only 0.33 [12], but strong mixing of n,π^* and π,π^* electronic configurations is observed in triplet-triplet absorption spectra taken in polar solvents, and a Φ_d of *ca.* 0.6 is found in methanol [9]. Assuming S_Q to be unity in both cases, the increase of Φ_d and, hence, of S_d with solvent polarity would then be clearly linked to the participation of the $^3(\pi,\pi^*)$ state in singlet-oxygen production.

For 1*H*-phenalen-1-one (**1**), which exhibits a $T_1(\pi,\pi^*)$ state in polar and apolar media, a slightly higher S_d value is observed in methanol (*Table 2*), probably due to the higher energy gap between the $T_2(n,\pi^*)$ and $T_1(\pi,\pi^*)$ states in polar media.

Similar results are obtained for 2-acetonaphthone, a π,π^* singlet-oxygen sensitizer with a triplet energy comparable to that of **1** ($E_T = 248 \text{ kJ} \cdot \text{mol}^{-1}$ [55]). Our experiments yield Φ_d values of 0.79 ± 0.04 in methanol and of 0.73 ± 0.04 (0.71–0.73 [12]) in benzene (*Table 3*). As in the case of **1**, the quantum yield of singlet-oxygen production in methanol is slightly higher. S_Q being unity, these results lead to a S_d of 2-acetonaphthone in benzene of 0.87 [12], as its Φ_{ISC} , measured in the same solvent, is 0.84 [56].

The 9*H*-fluoren-9-one has approximately the same triplet energy as 1*H*-phenalen-1-one (**1**) [55] and also exhibits π,π^* electronic configuration of its T_1 state in both apolar and polar environment [57–59]. Its S_d in benzene was determined to be 0.88 ($\Phi_d = 0.82$ –0.83) [12]. However, already *Gollnick et al.* found a Φ_d of only 0.02–0.07 in methanol [39]. Our luminescence measurements (*Table 3*) confirm these earlier results obtained by chemical trapping of singlet oxygen.

At first sight and following the line of argumentation given above, this very low value of Φ_d is rather surprising. However, isomerization experiments using 9*H*-fluoren-9-one as a sensitizer [56] [60], photoreduction [61], and singlet lifetime (fluorescence) measurements [57] indicate that the intersystem crossing rate in 9*H*-fluoren-9-one decreases markedly with increasing solvent polarity. This has been explained by an inversion of the energetic ordering of the S_1 and T_2 states. In fact, intersystem crossing is very fast in apolar media where $T_2(n,\pi^*)$ lies below $S_1(\pi,\pi^*)$, and Φ_{ISC} has a value of 0.93 in benzene and 1.0 in cyclohexane [56] [60]. In polar solvents, the energy of $S_1(\pi,\pi^*)$ is lowered, and $T_2(n,\pi^*)$ is destabilized placing it above the $S_1(\pi,\pi^*)$ state, thus leading to a low intersystem crossing rate. Φ_{ISC} has not been quantified in methanol, however, a value of 0.77 was obtained in acetone [60], and it has been shown by photoreduction and sensitized isomerization experiments that the efficiencies of these reactions in propan-2-ol drop to *ca.* 12% of those measured in cyclohexane. We may then deduce that the low Φ_d measured in methanol is due to the inefficient intersystem crossing in this solvent, whereas the value of S_d may be not (or only slightly) affected by the solvent.

The high efficiency of singlet-oxygen production of 1*H*-phenalen-1-one (**1**) in both polar and apolar solutions designs this compound as a reference sensitized, in particular in the area of relative high energies of excitation.

This work is part of the projects No. 2-5.253 and 20-26 145.89 of the *Swiss National Science Foundation*. The authors thank Dr. U. Spittel for the phosphorescence measurements. They are also grateful to Prof. M. Grätzel, EPFL, for providing the laser equipment and to Dr. P. P. Infelta, EPFL, for the necessary computer programs. The authors are particularly grateful to A. Oliveros, INSA Lyon, who, during his stay at the EPFL, wrote the software allowing data acquisition and treatment for the near-infrared luminescence equipment.

Experimental. – *General.* The 1*H*-phenalen-1-one (**1**) was dissolved in CH_2Cl_2 (*Fluka, puriss.*) and purified by chromatography on prep. TLC silica gel plates (*Merck*) and by subsequent recrystallization from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 2:1. Methylcyclohexane (*Merck, Uvasol*, fluor. grade), hexane (*Merck, Uvasol*), CCl_4 (*Fluka, puriss.*), methanol (*Fluka, puriss.*), and benzene (*Fluka, puriss.*) were used as solvents, and 2-acetonaphthone was purchased from *Aldrich-Chemie* and used without further purification. A selected sample of rose bengal (*Fluka*) showing the same spectroscopic and photophysical characteristics as a sample of pure rose bengal (Prof. K. Leismann) [19] and 9*H*-fluoren-9-one (*Fluka, puriss.*) were used as reference sensitizers in MeOH and in benzene, resp. Ground-state absorption spectra were recorded on *UV-260-Shimadzu* and *Perkin-Elmer-Lambda-9* spectrophotometers.

Phosphorescence Measurements. A $6.1 \cdot 10^{-5}$ M soln. of **1** in methylcyclohexane was prepared. Samples were purged with Ar for 1 h and cooled to 77 K with liq. N_2 . Phosphorescence spectra were recorded on a *Perkin-Elmer-LS5* fluorimeter connected to a data station. The phosphorescence lifetimes were determined using a *PRA* time-correlated single-photon counting apparatus.

Laser Flash Photolysis Experiments. Solns. of **1** ($2.5(\pm 0.2) \cdot 10^{-5}$ mol \cdot l $^{-1}$) were degassed in 1-cm sample cells by at least three freeze-thaw cycles using a diffusion pump (*Pfeiffer TPH11Q*, $2 \cdot 10^{-6}$ Torr). A ruby laser (*JK Laser Systems 2000*) with a frequency doubler ($\lambda_{\text{ex}} = 347$ nm) and with a pulse width of ca. 16 ns was used as excitation source. The energy of the laser pulse was measured by a fast photodiode (*ITT F-4014*), calibrated with a joulemeter (*Laser Instruments Ltd.*, series 14 [62]). The irradiated surface on the sample cell was 0.25 cm 2 . In a cross-beam geometry, the monitoring light of a Xe lamp (*Oriel*, 450 W) was filtered adequately before and after the sample cell and then analyzed with a photomultiplier (*Hamamatsu R928*) coupled to a monochromator (*Bausch & Lomb*, blaze 500 nm). The signals were amplified by a *Tektronix 7A13* and recorded on a digital oscilloscope (*Tektronix 7D20*) which in turn was controlled by a *HP-87* computer.

Near-Infrared Luminescence of Singlet Oxygen. The sensitizers were dissolved in CD_3OD , C_6D_6 (> 99.5%; Dr. Glaser) or C_6H_6 (absorbances of ca. 1.7, and of 0.3 to 1.8 for control of concentration effects (*Fig. 4*)). Equivalent 1-cm fluorescence cells were used for the experiments. For each experiment, series of measurements alternating between reference and sample were carried out. The results are the average of at least two series of measurements. For each measurement, the cell was placed on an optical bench and irradiated with a Xe/Hg lamp (1 kW, *Osram, Müller*), through a H_2O filter (10 cm) and a monochromator (*ISA Jobin-Yvon B204*, 6-nm band width). The luminescence of singlet oxygen was collected at 90°, using a mirror, chopped at a frequency of 11 Hz, and measured by a Ge-detector (*Judson*) cooled to -78° and connected to a preamplifier (30 dB) and to a lock-in amplified (*EG&G, Princeton Applied Research 5101*). Signals were recorded on a graphic plotter connected to the lock-in amplifier, and on a digital multimeter (*HP 3478A*) controlled by a *HP 200* computer. The incident radiant flux (mW) were measured without cell using a thermopile (*Laser instrumentation*, model 154).

REFERENCES

- [1] H. Kautsky, H. De Bruijn, *Naturwissenschaften* **1931**, *19*, 1043.
- [2] A. U. Khan, M. Kasha, *J. Chem. Phys.* **1963**, *39*, 2105.
- [3] C. S. Foote, S. Wexler, *J. Am. Chem. Soc.* **1964**, *86*, 3878.
- [4] G. Ohloff, *Pure Appl. Chem.* **1975**, *43*, 481.
- [5] H. H. Wasserman, J. L. Ives, *Tetrahedron* **1981**, *37*, 1825.
- [6] 'Singlet O_2 ', Ed. A. A. Frimer, CRC Press, Boca Raton, 1985, Vol. I-IV.
- [7] A. M. Braun, M.-T. Maurette, E. Oliveros, 'Technologie Photochimique', Presses Polytechniques Romandes, Lausanne, 1986, Chapt. 11, p. 429–481.
- [8] S. K. Chattopadhyay, C. V. Kumar, P. K. Das, *J. Photochem.* **1985**, *30*, 81.

- [9] K. Gollnick, T. Franken, G. Schade, G. Dörnhöfer, *Ann. New York Acad. Sci.* **1970**, 171, 89.
- [10] A. A. Gorman, I. Hamblett, M. A. J. Rodgers, *J. Am. Chem. Soc.* **1984**, 106, 4679.
- [11] A. A. Gorman, I. Hamblett, C. Lambert, A. L. Prescott, M. A. J. Rodgers, H. M. Spence, *J. Am. Chem. Soc.* **1987**, 109, 3091.
- [12] R. W. Redmond, S. E. Braslavsky, *Chem. Phys. Lett.* **1988**, 148, 523.
- [13] H. Ishida, H. Tsubomura, *J. Photochem.* **1974**, 2, 285.
- [14] A. Garner, F. Wilkinson, *Chem. Phys. Lett.* **1977**, 45, 432, and ref. cit. therein.
- [15] O. L. J. Gijzeman, F. Kaufman, *J. Chem. Soc., Faraday Trans. 2* **1973**, 69, 721.
- [16] E. Oliveros, P. Suardi-Murasecco, A. M. Braun, XIIIth IUPAC Symposium on Photochemistry, Warwick, 1990, p. P168.
- [17] H. Köller, G. P. Rabold, K. Weiss, T. K. Mukherjee, *Proc. Chem. Soc.* **1964**, 332.
- [18] G. P. Rabold, K. H. Bar-Eli, E. Reid, K. Weiss, *J. Chem. Phys.* **1965**, 42, 2438.
- [19] N. A. Kuznetsova, A. V. Reznichenko, V. N. Kokin, O. L. Kaliya, *Zh. Org. Khim.* **1982**, 18, 620.
- [20] P. Murasecco-Suardi, E. Gassmann, A. M. Braun, E. Oliveros, *Helv. Chim. Acta* **1987**, 70, 1760.
- [21] J. J. M. Lamberts, D. C. Neckers, *Tetrahedron* **1985**, 41, 2183.
- [22] G. L. Hug, I. Carmichael, *J. Photochem.* **1985**, 31, 179.
- [23] I. Carmichael, G. L. Hug, *J. Phys. Chem.* **1985**, 89, 4036.
- [24] I. Carmichael, G. L. Hug, *J. Phys. Chem. Ref. Data* **1986**, 15, 1–250.
- [25] U. Lachisch, A. Schafferman, G. Stein, *J. Chem. Phys.* **1976**, 64, 4205.
- [26] R. Bensasson, C. R. Goldschmidt, E. J. Land, T. G. Truscott, *Photochem. Photobiol.* **1978**, 28, 277.
- [27] U. Lachisch, P. P. Infelta, M. Grätzel, *Chem. Phys. Lett.* **1979**, 62, 317.
- [28] P. Jacques, A. M. Braun, *Helv. Chim. Acta* **1981**, 64, 1800.
- [29] A. A. Krasnovsky, Jr., *Photochem. Photobiol.* **1979**, 29, 29.
- [30] A. Brombery, C. Foote, *J. Phys. Chem.* **1989**, 93, 3968.
- [31] A. A. Krasnovsky, Jr., *Chem. Phys. Lett.* **1981**, 81, 443.
- [32] R. D. Hall, G. R. Buettner, A. G. Motten, C. F. Chignell, *Photochem. Photobiol.* **1987**, 46, 295.
- [33] P. Murasecco-Suardi, E. Oliveros, A. M. Braun, H.-J. Hansen, *Helv. Chim. Acta* **1988**, 71, 1005.
- [34] S. Croux, M.-T. Maurette, M. Hocquaux, A. Ananides, A. M. Braun, E. Oliveros, *New J. Chem.* **1990**, 14, 161.
- [35] A. M. Braun, E. Oliveros, *Pure Appl. Chem.* **1990**, 62, 1467.
- [36] R. Schmidt, E. Afshari, *J. Phys. Chem.* **1990**, 94, 4377.
- [37] E.g. P. Murasecco, E. Oliveros, A. M. Braun, P. Monnier, *Photobiochem. Photobiophys.* **1985**, 9, 193.
- [38] S. L. Murov, 'Handbook of Photochemistry', Ed. M. Dekker, New York, 1973.
- [39] K. Gollnick, G. O. Schenck, *Pure Appl. Chem.* **1964**, 9, 507.
- [40] E. Gandin, J. Lion, A. van de Vorst, *Photochem. Photobiol.* **1983**, 37, 271.
- [41] E. Gassmann, A. M. Braun, unpublished results.
- [42] C. Tanielan, L. Golder, *Photochem. Photobiol.* **1981**, 34, 411.
- [43] D. E. Nicodem, R. S. da Silva, M. M. da Silva, personal communication.
- [44] N. Kanamaru, M. T. Long, E. C. Lim, *Chem. Phys. Lett.* **1974**, 26, 1.
- [45] D. R. Kearns, W. A. Case, *J. Am. Chem. Soc.* **1966**, 88, 5087.
- [46] K. Schaffner, XXIIIrd IUPAC Congress, Boston, Butterworths, London, 1973, Vol. 1, p. 405–417.
- [47] T. Matsumoto, M. Sato, S. Hirayama, *Chem. Phys. Lett.* **1972**, 13, 13.
- [48] P. J. Wagner, A. E. Kempainen, H. N. Schott, *J. Am. Chem. Soc.* **1973**, 95, 5604.
- [49] N. J. Turro, 'Modern Molecular Photochemistry', Benjamin Cummings, Menlo Park, CA, 1978, p. 186.
- [50] S. K. Lower, M. A. El-Sayed, *Chem. Rev.* **1966**, 66, 199.
- [51] A. Beckett, G. Porter, *Trans. Faraday Soc.* **1963**, 59, 2051.
- [52] K. Schaffner, personal communication.
- [53] Ref. [49], p. 381.
- [54] H. Lutz, E. Breheret, L. Lindquist, *J. Phys. Chem.* **1973**, 77, 1758.
- [55] W. G. Herkstroeter, A. A. Lamola, G. S. Hammond, *J. Am. Chem. Soc.* **1964**, 86, 4537.
- [56] A. A. Lamola, G. S. Hammond, *J. Chem. Phys.* **1965**, 43, 2129.
- [57] L. A. Singer, *Tetrahedron Lett.* **1969**, 923.
- [58] T. Kobayashi, S. Nagakura, *Chem. Phys. Lett.* **1976**, 43, 429.
- [59] G. Buemi, C. Gandolfo, F. Zuccarello, A. Raudino, E. Ciliberto, *J. Mol. Struct.* **1981**, 86, 1.
- [60] R. A. Caldwell, R. P. Gajewski, *J. Am. Chem. Soc.* **1971**, 93, 532.
- [61] J. B. Guttenplan, S. G. Cohen, *Tetrahedron Lett.* **1969**, 2125.
- [62] H. Dürr, G. Dörr, K. Zengerle, E. Mayer, J.-M. Curchod, A. M. Braun, *Now. J. Chim.* **1985**, 9, 717.