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Photosensitization of photochromism of spiro-indoline-oxazines by camphorquinone

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Abstract

The thermoreversible photochromic reaction spiro-indoline-oxazine ⇌ photomerocyanine was photosensitized by triplet energy transfer using camphorquinone (E_T = 215 kJ mol^{-1}) as sensitizer and visible light excitation (λ_{exc} = 436 nm). From absorbance/time data, obtained during steady irradiation, the quantum yield of the photosensitized reaction was determined. The rate parameter for the donor–acceptor interaction was obtained from quenching measurements of the sensitizer phosphorescence and from the effect of the acceptor concentration on the reaction yield. The results obtained for six photochromes (spiro-indoline-oxazines differently substituted in the indoline and/or oxazine moiety) show that energy transfer occurs at a diffusion-controlled rate and that the limiting quantum yield of the sensitized reaction, approximately unity, is greater than the yield obtained by direct excitation of the photochrome. An upper limit to the triplet energies of the spiro-oxazines was established. Direct evidence for the triplet state was only obtained for a nitro-spiro-oxazine from low temperature phosphorescence emission of both the closed and open forms.

Keywords: Photochromism; Photosensitization; Spiro-indoline-oxazines; Camphorquinone

1. Introduction

Photosensitizers are important in several aspects of photochemistry [1]. They have been used to provide information on excited state properties and photoreaction mechanisms and to promote or select photochemical reactions. Triplet states are the best candidates for excitation energy donors. The characteristics of a good triplet sensitizer include a long triplet lifetime in solution at room temperature, a high intersystem crossing yield, long-wavelength singlet absorption and a relatively high triplet energy. Aryl ketones possessing lowest n,π^* triplet states generally fulfil these requirements. When a red shift of the excitation wavelength is desirable, diketones can be used as sensitizers [2].

In this paper, attention has been given to the photosensitization of the photochromism of spiro-indoline-oxazines (SO) by triplet–triplet energy transfer. The photochromism of SO is due to the photocleavage of the spiro bond on UV irradiation to give the open coloured photomerocyanine (PM) structure which absorbs in the visible region. Interest in photosensitization was stimulated by the prospect of extending the wavelength range to produce the coloured merocyanine form towards the visible region.

The involvement of the triplet state in the colour-forming reaction of spiranic photochromic systems has been investigated previously [3–8]. For some nitro-substituted molecules, a contribution of a triplet mechanism to the direct photoreaction was found [3,8]. Photosensitization of the reaction by triplet energy transfer was successful: in some cases the problem of evaluating the sensitization efficiency was qualitatively addressed in terms of "colourability" under fixed conditions [6,9,10]; quantum yield data for the sensitized reaction can also be found in the literature [3,7].

For some SOs, including the molecules investigated here, the molar absorption coefficients of the metastable PM and the quantum yields of the colour-forming photoreaction have been determined [11,12]. The kinetic parameters (reaction rate and activation energy) and thermodynamic quantities (equilibrium constant and enthalpy) of the thermal reaction have also been obtained [12,13]. Based on the results obtained, some general correlations between the structure of these molecules and their photochromic and thermochromic properties have been drawn.

In this work, the possibility of photosensitizing the thermoreversible SO ⇌ PM photoreaction was investigated using

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camphorquinone as sensitizer and visible light excitation. The quantum yield of the photosensitized reaction and the kinetic rate for the energy transfer process were determined. The results obtained demonstrate that photosensitization is very convenient: not only can the excitation energy be shifted to the visible, but the reaction yield also increases. The triplet reactivity of the SOs can therefore be evaluated and an upper limit to their triplet energies ($E_T \leqslant 215$ kJ mol^{-1}) can be established. No direct evidence was obtained for SO triplets, except for one of the molecules investigated, which exhibited phosphorescence emission from both the SO and PM forms in a rigid matrix at low temperature.

2. Experimental details

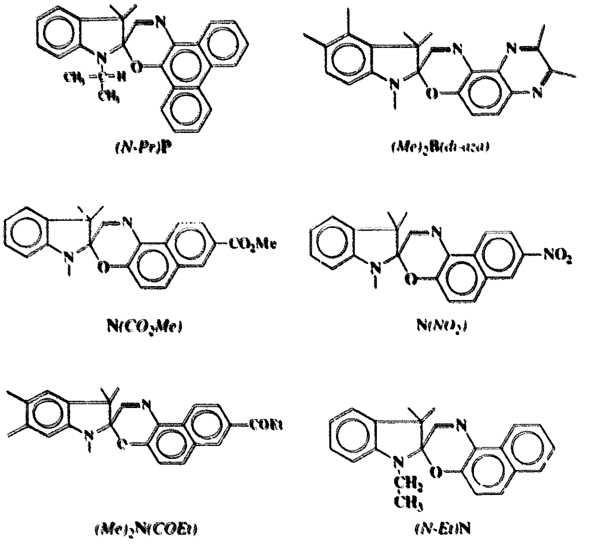
2.1. Materials

The photochromic molecules studied (supplied by Great Lakes Chemical Italia S.r.l.) were six SOs, with different aryl groups linked to the oxazine moiety (naphtho, N; phenanthro, **P**; benzo, **B**) and/or different substituents on either moiety. The structures and symbols of the molecules are shown in Scheme 1. In the symbols, the substituents on the indoline and oxazine moieties precede and follow respectively the bold letter representing the aryl group. They were prepared according to literature methods [14].

The solvent methylcyclohexane (MCH) was a reagent grade Carlo Erba product treated according to standard procedures.

Camphorquinone (CQ) (Aldrich product) was crystallized from cyclohexane and then sublimated in vacuo. Ferrocene (Aldrich product) was used without further purification.

The solvents used for the low temperature measurements, EPA (ethyl ether/isopentane/ethanol; 5/5/2, v/v) and EPI (ethyl ether/isopentane/ethyl iodide; 2/2/1, v/v) matrices, were reagent grade Carlo Erba (ethanol, ethyl ether, ethyl iodide) and Fluka (isopentane) products.



Scheme 1.

2.2. Equipment

Absorption spectra were recorded on a Perkin-Elmer Lambda 16 spectrophotometer or a Beckman diode array DU 7500 spectrophotometer.

Corrected emission spectra were recorded using a Spex Fluorolog-2 FL112 spectrofluorometer, controlled by a Spex DM3000F spectroscopy computer. The time-resolved unit of the spectrofluorometer was used to isolate the phosphorescence from the total luminescence spectrum and to measure the phosphorescence lifetimes and phosphorescence quenching. The accuracy in the lifetime measurements was estimated to be within 15%.

A 250 W medium pressure mercury lamp, filtered by interference filters ($\lambda = 436$ nm for the sensitized reaction and $\lambda = 366$ nm for the direct reaction), was used for excitation. The irradiation intensity, which was constant during each run, was determined using potassium ferrioxalate actinometry (typically, 10^{-6} einstein dm^{-3} s^{-1}).

2.3. Measurement conditions

2.3.1. Phosphorescence quenching measurements

Quenching measurements of the phosphorescence intensity and lifetime of CQ were performed in deaerated MCH solutions containing the sensitizer ([CQ] = 1×10^{-3} mol dm^{-3}) and varying amounts of the quencher ([SO] = 5×10^{-7} to 5×10^{-6} mol dm^{-3}). The phosphorescence intensity data were corrected for the fluorescence emission.

Measurements of photochrome ([SO] = 5×10^{-5} mol dm^{-3}) emissions were carried out in EPA and EPI rigid matrices at 77 K.

2.3.2. Photokinetic measurements

The photokinetic measurements were carried out in deaerated MCH solutions during steady irradiation. The light exposure of the sample (1 cm path length cell, 1 cm^3 of solution) was carried out in the spectrophotometer holder at right angles to the analysis light. The temperature was controlled by an Oxford Instruments cryostat. The SO concentrations ranged from 1×10^{-5} to 5×10^{-5} mol dm^{-3} and that of the sensitizer was 3×10^{-3} mol dm^{-3}, corresponding to 0.05 absorbance at the excitation wavelength. The increase in PM absorbance was followed, during stationary irradiation, at the absorption maximum (550–620 nm), where the excitation wavelengths (436 or 366 nm) do not disturb the absorbance measurement, up to photostationary state attainment. In the reaction quenching measurements by ferrocene, the excitation light intensity was corrected for the fraction of light ($\lambda = 366$ nm) absorbed by the quencher [15].

The rate parameters of the ring-closure reaction (first-order kinetics) were determined by following spectrophotometrically the disappearance of the coloured form in the visible region, after having removed the irradiation source.

3. Results and discussion

3.1. Triplet–triplet donor–acceptor interaction

CQ has all the requirements needed to be a suitable photosensitizer [16] for SO: very high (approximately unity) intersystem crossing yield, long triplet lifetime in fluid solution (approximately 200 μs) and an $S_0 \rightarrow S_1$ transition in the visible region (λ_{max} = 472 nm in MCH) where neither SO nor PM absorb. In Fig. 1, the absorption spectrum of CQ in MCH is compared with that of (N-Et)N. The triplet energy of CQ, measured in fluid solution at room temperature, is 213 kJ mol^{-1}. Moreover, CQ possesses the rare (but not uncommon for diketones) property of phosphorescing ($\Phi_P \approx 3 \times 10^{-3}$) in deaerated fluid solution at room temperature [16]. This allowed the excitation energy transfer to be followed from the effect of the acceptor concentration on the donor phosphorescence. Thus the rate constant for the interaction was determined through phosphorescence intensity quenching and lifetime shortening measurements. The total emission from CQ in deaerated MCH solution at room temperature and the phosphorescence quenching by N(CO_2Me) are shown in Fig. 2. The quenching ratios I^0/I were treated according to the Stern–Volmer (SV) equation, $I^0/I = 1 + k_q\tau^0[SO]$ (Fig. 2, inset), where I^0 and I are the emission intensities in the absence and presence of the quencher, k_q is the rate coefficient for the sensitizer–quencher interaction and τ^0 is the triplet lifetime of the sensitizer. The quenching rate parameter k_q was also determined by measurement of the donor lifetime as a function of the SO concentration using the appropriate SV equation ($\tau^0/\tau = 1 + k_q\tau^0[SO]$), where τ^0 and τ are the CQ lifetimes in the absence and presence of SO respectively. Examples of the CQ lifetime quenching by N(CO_2Me) are shown in Fig. 3. Since very similar k_q values were obtained by both methods, it can be stated that no interaction between CQ and SO occurs in the ground state. The quenching rate parameters (k_q = (2–4) × 10^9 dm^3 mol^{-1} s^{-1}), which are reported in Table 1 (column (a)), are almost diffusion controlled (k_{diff} = 10^{10} dm^3 mol^{-1} s^{-1} in MCH at 25 °C). This indicates that the interaction is exothermic and therefore the triplet states of SO acceptors are at a comparable or lower energy than CQ. As expected for a diffusion-controlled process, the molecular structure of the quencher does not appreciably affect the k_q value, since the differences detected were within experimental error.

3.2. Sensitized photoreaction

Excitation energy transfer from CQ triplet to SO triplets promotes the ring-opening reaction with the formation of the

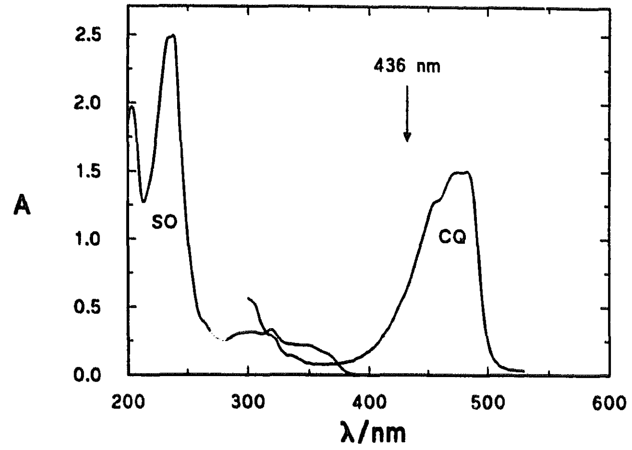


Fig. 1. Absorption spectra of (N-Et)N (2.7 × 10^{-5} mol dm^{-3}) and CQ (2.9 × 10^{-2} mol dm^{-3}) in MCH.

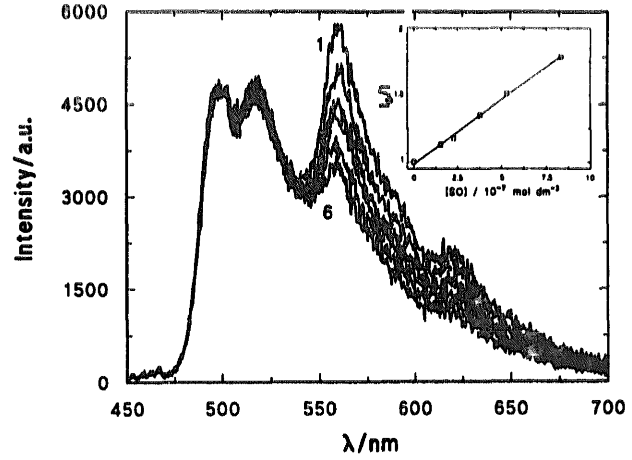


Fig. 2. Total emission of CQ in deaerated MCH solution at room temperature (spectrum 1) and CQ phosphorescence quenching by N(CO_2Me) ([N(CO_2Me)] = 2 × 10^{-7} to 9 × 10^{-7} mol dm^{-3}, spectra 2–6). Inset: quenching ratios I^0/I treated according to the SV equation.

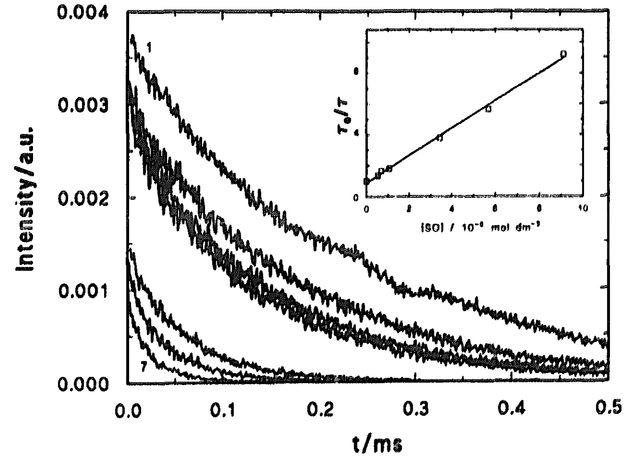


Fig. 3. Phosphorescence decay kinetics of CQ in the absence (1) and presence of N(CO_2Me) ([N(CO_2Me)] = 5 × 10^{-7} to 9 × 10^{-6} mol dm^{-3}, kinetic profiles 2–7). Inset: treatment of the data according to the SV equation.

coloured PM. Assuming that the back reaction is only thermal [11,17], the general rate law for the formation of PM is given by [7]

$$d[PM]/dt = I_{SO}\Phi_D + I_{CQ}\Phi_S - k_\Delta[PM] \qquad (1)$$

where Φ_D and Φ_S are the photochemical quantum yields of the direct and sensitized reactions, I_{SO} and I_{CQ} are the intensities of the monochromatic radiation absorbed by the spirooxazine (SO) and the sensitizer (CQ) respectively and k_Δ is the kinetic parameter of the thermal back reaction. In the absence of the sensitizer (direct photoreaction), the second term on the right-hand side is missing, while the first is missing when only the sensitizer absorbs the excitation light.

The kinetic equation of the colour-forming reaction is particularly simple for the donor–acceptor systems under investigation, since the excitation light (λ = 436 nm) is absorbed by CQ only (Fig. 1). It is therefore constant over the entire colour-forming process up to the photostationary state; thus the introduction of a photokinetic factor [11,18] is unnecessary. In terms of the PM absorbance (A_{PM}), the kinetic equation is

$$dA_{PM}/dt = \epsilon_{PM}I_{CQ}\Phi_S - k_\Delta A_{PM} \qquad (2)$$

where ϵ_{PM} is the molar extinction coefficient of PM and I_{CQ} can be expressed as a function of the total incident light I_0 (einstein dm^{-3} s^{-1}) and the CQ absorbance at the excitation wavelength A_{CQ}, which is constant for the entire process ($I_{CQ} = I_0[1-\exp(-2.3A_{CQ})]$). Because of the constancy of the term $\epsilon_{PM}I_{CQ}\Phi_S$, Eq. (2) can be easily integrated in a closed form. By separating the variables, A_{PM} can be expressed as a function of time by

$$A_{PM} = \frac{\epsilon_{PM}I_{CQ}\Phi_S}{k_\Delta}(1-e^{-k_\Delta t}) = A_{PM}^{\infty}(1-e^{-k_\Delta t}) \qquad (3)$$

where $\epsilon_{PM}I_{CQ}\Phi_S/k_\Delta$ corresponds to the limiting PM absorbance A_{PM}^{∞} at the photostationary state when the rate of the forward photosensitized reaction is outweighed by the rate of the thermal back reaction. The PM absorbance (A_{PM}), followed at the absorption maximum (550–590 nm) during steady irradiation of the sensitizer, fits this mono-exponential function (Eq. (3)) well, as shown in Fig. 4 (top curve) for N(CO_2Me). By this fitting procedure, the k_Δ value was obtained with good accuracy (correlation coefficient, greater than 0.98).

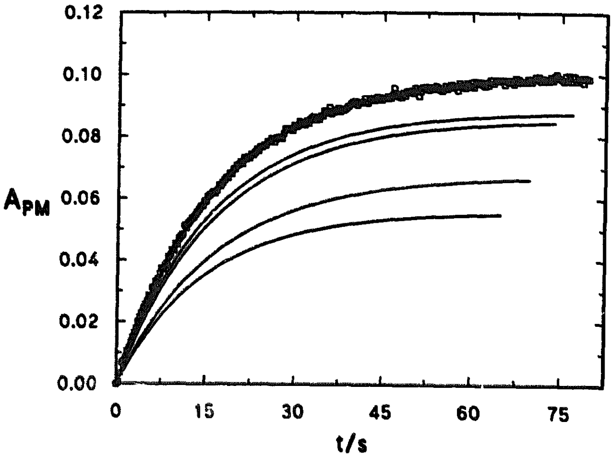


Fig. 4. CQ photosensitized colour-forming kinetics of N(CO_2Me) during steady irradiation (λ_{exc} = 436 nm). Full lines represent best fits of the experimental points (shown in the top curve).

As expected, a decrease in the SO concentration leads to a decrease in the limiting absorbance value at the photostationary state (Fig. 4), because of the reduced number of donor–acceptor collisions. At each SO concentration, the quantum yield was evaluated from Eq. (2), which represents a linear relationship between the colour-forming rate (dA_{PM}/dt) and A_{PM}, by extrapolating the colour-forming rate at zero time

$$\Phi_S = \frac{(dA_{PM}/dt)_{t\to 0}}{\epsilon_{PM}I_0[1-\exp(-2.3A_{CQ})]} \qquad (4)$$

To calculate Φ_S, previously determined ϵ_{PM} values [12] were used. The graphical treatment of the data for several SO concentrations is shown in Fig. 5. The slopes of the linear plots gave k_Δ values. Alternatively, the Φ_S values were determined from the pre-exponential term of Eq. (3), by measuring the limiting PM absorbance at the photostationary state. The Φ_S values obtained by the two methods agree within experimental uncertainty (± 10%). The k_Δ values determined as the slopes of the straight lines of Eq. (2) (corresponding to those derived from the fitting procedure) were generally higher than those determined after having switched off the irradiating lamp, and generally decreased with increas-

Table 1

Kinetic parameters (correlation coefficients) for triplet–triplet energy transfer from ^{3}CQ to SOs and/or PMs obtained by: (a) CQ phosphorescence lifetime shortening (room temperature); (b) quenching of sensitized reaction quantum yield (280 K); (c) intercept of plots from Eq. (8); (d) slope to intercept ratio of plots from Eq. (8)

SO	k_q (10^9 dm^3 mol^{-1} s^{-1})			
	(a)	(b)	(c)	(d)
(N-Et)N	3.8 (0.985)	2.2 (0.998)		
(N-Pr)F	3.0 (0.992)	3.9 (0.980)		
N(CO_2Me)	3.9 (0.998)	2.5 (0.998)	6.9 (0.997)	1.2
$(Me)_2$B(di-aza)	2.3 (0.984)	2.4 (0.981)	3.9 (0.999)	1.4
N(NO_2)	3.4 (0.984)	3.4 (0.987)	3.1 (0.993)	1.4
$(Me)_2$N(COEt)	3.5 (0.992)	1.5 (0.999)	4.4 (0.997)	0.7

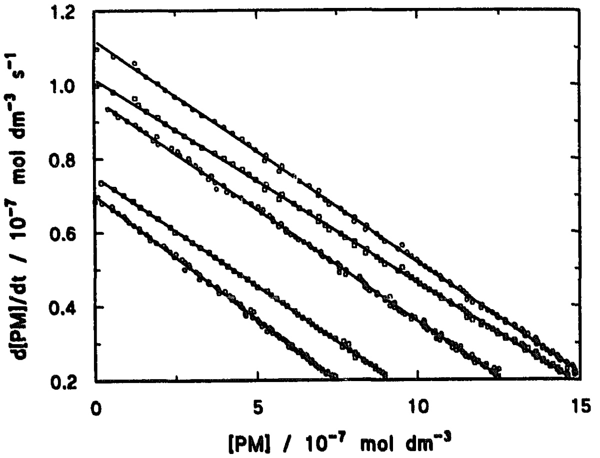


Fig. 5. Colour-forming kinetic data of Fig. 4 treated according to Eq. (2).

Table 2
Concentration effects on the photosensitized reaction yield, Φ_S and bleaching rate parameter k_Δ for $(Me_2)B$(di-aza) determined at 280 K under different conditions: (a) steady irradiation in the presence of the sensitizer; (b) after switching off the irradiating lamp in the presence of the sensitizer; (c) in the absence of the sensitizer

[$(Me)_2B$(di-aza)] (10^{-5} mol dm^{-3})	Φ_S	k_Δ (s^{-1})		
		(a)	(b)	(c)
1.47	0.57	0.026	0.0084	
2.45	0.67	0.021	0.0095	
3.92	0.70	0.017	0.0088	0.0086
6.37	0.80	0.017	0.010	

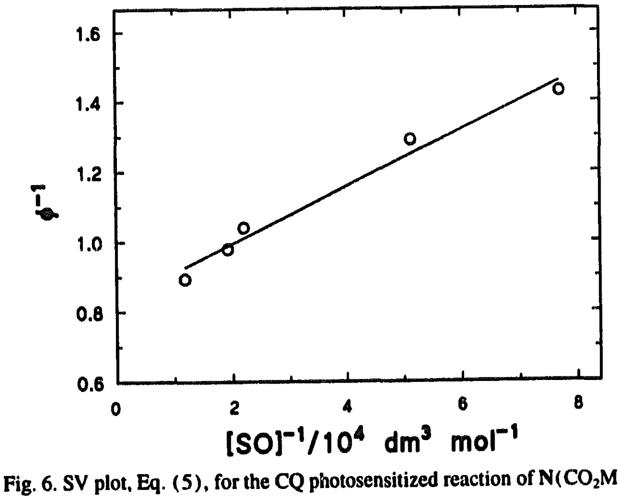


Fig. 6. SV plot, Eq. (5), for the CQ photosensitized reaction of $N(CO_2Me)$.

ing SO concentration. The effect of concentration on Φ_S and k_Δ is shown in Table 2 for one of the molecules investigated, $(Me)_2B$(di-aza).

The quantum yield data, obtained at different SO concentrations, fit the SV equation

$$\frac{1}{\Phi_S}=\frac{1}{\Phi_S^{\mathrm{lim}}}\left(1+\frac{1}{K_{SV}[SO]}\right) \tag{5}$$

for photosensitized reactions well, which allowed Φ_S^{lim}, i.e. the value corresponding to complete energy transfer from the CQ triplet to SO, to be extrapolated as the intercept, and the SV constant, K_{SV} ($=k_q\tau^0$), as the intercept to slope ratio. An example of the SV linear trend (Eq. (5)) is shown in Fig. 6. As can be seen from Table 1, the k_q values obtained are in good agreement with those derived from phosphorescence quenching measurements. This clearly indicates that the energy transfer process is responsible for both the phosphorescence quenching and reaction sensitization. The Φ_S^{lim} values, determined in deaerated MCH solutions at 280 K, are compared with the direct reaction quantum yields (Φ_D [12]) in Table 3, where the k_Δ values determined at the same temperature are also reported. As can be seen from Table 3, the Φ_S^{lim} values are fairly high and are greater than Φ_D. It can be considered that the limiting sensitized quantum yield is unity for all the molecules investigated; Φ_S^{lim} values larger than unity, found in some cases, are due to measurement uncertainties.

The effect on the bleaching parameter of the presence of CQ and its dependence on SO concentration (Table 2) can be attributed to interaction of the metastable PM with either the CQ ground state or CQ triplet state. Interaction with ^3CQ is operative only on irradiation, whereas interaction with the ground state sensitizer can be isolated by measuring, in the dark, the decolouration of previously irradiated solutions in the presence and absence of CQ. Since the differences between the rate constants measured under the two conditions (absence or presence of CQ) are within the measurement uncertainty (±10%), the PM–CQ interaction, if any, cannot be detected experimentally.

Considering the interaction ^3CQ+PM, which is present on irradiation, the expression for the experimental rate value (k_Δ(a), i.e. column (a) in Table 2) is given by

$$k_\Delta(a)=k'_q[^3CQ]+k_\Delta(b) \tag{6}$$

where k'_q represents the bimolecular rate parameter (^3CQ+PM interaction). By applying the photostationary state approximation to ^3CQ, Eq. (7) is obtained

$$k_\Delta(a)=I_{CQ}k'_q\tau^0/(1+k_q\tau^0[SO]+k'_q\tau^0[PM])+k_\Delta(b) \tag{7}$$

where k_Δ(b) represents the monomolecular bleaching parameter obtained in the dark and k_q and k'_q are the rate parameters

Table 3
Limiting yields (Φ_S^{lim}) for the SO ↔ PM reaction photosensitized by camphorquinone in MCH, compared with the quantum yield of the direct photoreaction (Φ_D), and bleaching rate parameters (k_Δ) at 280 K (values averaged over four SO concentrations)

SO	Φ_S^{lim}	Φ_D	k_Δ (s^{-1})
(N-Et)N	1.2	0.46	0.037
(N-Pr)F	0.8	0.51	0.029
$N(CO_2Me)$	1.3	0.35	0.068
$(Me)_2B$(di-aza)	0.87	0.17	0.009
$N(NO_2)$	0.94	1.10	0.012
$(Me)_2N$(COEt)	0.91	0.14	0.013

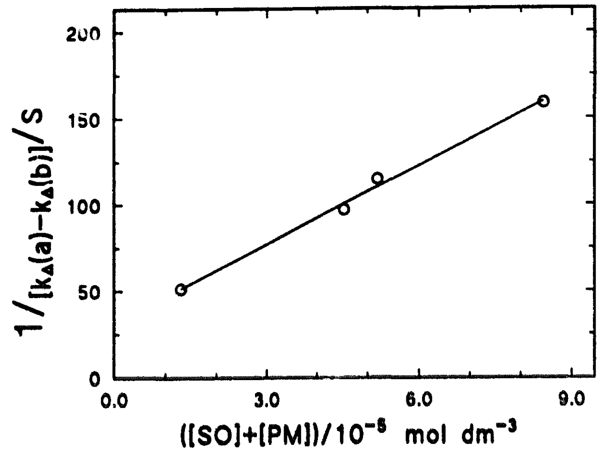


Fig. 7. Kinetic data of N(CO_2Me) treated according to Eq. (8).

for ^3CQ quenching by SO (see Table 1) and PM respectively. Considering that the PM triplet energy is surely lower than the CQ triplet energy, a diffusion-controlled rate can be expected for their interaction. Thus by rearranging Eq. (7) and considering the approximation ($k'_q - k_q \approx 0$), Eq. (8) is obtained

$$
\begin{aligned}
1/[k_\Delta(a) - k_\Delta(b)]& \\
&= (1/I_{CQ}k'_q\tau^0)(1 + k_q\tau^0[SO] + k'_q\tau^0[PM]) \\
&= (1/I_{CQ}k'_q\tau^0)[1 + k_q\tau^0(c_0 - [PM]) + k'_q\tau^0[PM]] \\
&= (1/I_{CQ}k'_q\tau^0)[1 + k_q\tau^0 c_0 + (k'_q - k_q)\tau^0[PM]] \\
&\approx (1/I_{CQ}k'_q\tau^0)(1 + k_q\tau^0 c_0) \qquad (8)
\end{aligned}
$$

If the assumptions are correct, a straight line should be obtained by plotting $1/[k_\Delta(a) - k_\Delta(b)]$ against the initial SO concentration c_0, and the k'_q value, given by the intercept (reciprocal intercept divided by $I_{CQ}\tau^0$), should approach the k_q value obtained from the slope to intercept ratio. As shown in Fig. 7 for N(CO_2Me), the linearity is very good (correlation coefficient, greater than 0.99); this occurs with four of the molecules investigated, but linearity could not be detected with (N-Pr)F and (N-Et)N. The quenching rate parameters obtained are compared in Table 3. Their similarity and closeness to the diffusion-controlled value confirm that the assumptions are reasonable.

3.3. *Phosphorescence emission measurements at 77 K*

Due to efficient competition from the opening reaction in the singlet state, fluorescence emission from the SOs is generally very weak or completely undetectable. Fluorescence from the PMs has been observed at low temperature (220 K) [19] and in a rigid matrix at 77 K [20]. Little information can be found in the literature on the phosphorescence emission of SOs and PMs. Phosphorescence emissions have been reported for some nitro-spiropyrans [21] and nitro-spirooxazines [22].

In order to observe triplet state emission, SOs were analysed in a rigid EPA matrix at 77 K. Under these conditions, for N(NO_2) only, the phosphorescence emission of the closed form was detected. The well-structured spectrum obtained is illustrated in Fig. 8 (λ_{exc} = 366 nm, 1 ms delay time) together with the corresponding excitation spectrum (λ_{em} = 543 nm) which reproduces the SO absorption well. The emission is assigned to phosphorescence because of its lifetime (5–6 ms) and spectral position (triplet energy, 220 kJ mol^{-1}). Surprisingly, this energy is slightly higher than that of the CQ sensitizer measured under the same conditions (215 kJ mol^{-1}); it was expected to be somewhat lower to account for the diffusion-controlled quenching rate. However, solvent relaxation at higher temperature (which is very low for CQ [16]) can affect the donor and acceptor triplet energies differently, thus favouring the energy transfer from CQ to SO at room temperature.

For the other photochromes, only the fluorescence of the photochemically produced PMs could be detected. Attempts to populate the SO triplet state by CQ (5×10^{-3} mol dm^{-3}) sensitization in an EPA matrix at low temperature in order to observe the phosphorescence emission, or to induce intersystem crossing by the external heavy atom effect (EPI matrix), failed. Only with N(NO_2) was the phosphorescence emission of the open form observed in an EPI matrix. For this PM, while only fluorescence could be detected in an EPA matrix, a relatively long-lived (τ = 10.3 μs) emission appeared in both the absence (λ_{exc} = 600 nm) and presence (λ_{exc} = 470 nm) of CQ in an EPI matrix. In the latter case, the emission was sensitized by CQ, since PM does not absorb the excitation light: sensitization occurred by a trivial process (re-absorption by PM of the CQ emission), since the CQ lifetime remained unchanged (τ^0 = 1.6 ms at 77 K). Because of the bathochromic shift of the photochrome emission with respect to fluorescence and its lifetime, it was assigned to the π,π^* triplet state of PM. The phosphorescence emission of N(NO_2) in EPI, together with its fluorescence and fluorescence excitation spectra in EPA, is shown in Fig. 9. In this molecule, the PM triplet state is populated by intersystem crossing and the radiative probability is enhanced by the

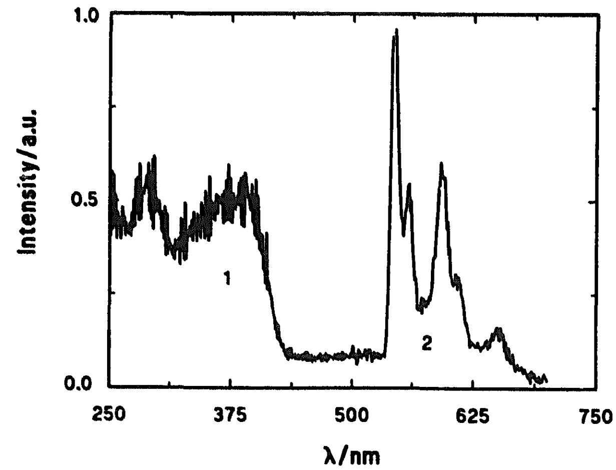


Fig. 8. Phosphorescence excitation (1) and phosphorescence emission (2) spectra of the closed form of N(NO_2) in an EPA matrix at 77 K.

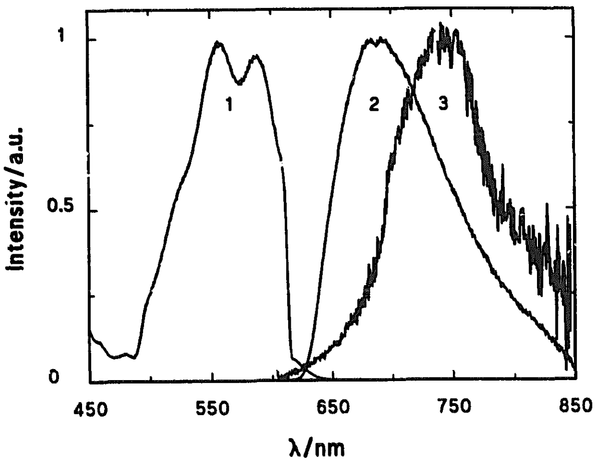


Fig. 9. Fluorescence excitation (1) and fluorescence emission (2) spectra in an EPA matrix and phosphorescence emission spectrum (3) of the open form of $N(NO_2)$ in an EPI matrix at 77 K.

external heavy atom effect; for the other molecules, the external heavy atom is unable to induce intersystem crossing and therefore phosphorescence was not observed.

3.4. Photoreaction quenching

Photosensitization measurements clearly show that the opening reaction occurs easily from the triplet state, while Φ_D values, lower than Φ_S, may be due to either non-unity intersystem crossing (triplet mechanism or mixed mechanism) or to completely inefficient intersystem crossing (pure singlet mechanism). The search for the triplet emission described above seems to indicate that only for the nitro derivative is a triplet mechanism reliable. To obtain further evidence about the excited state responsible for the ring-opening process, photoreaction yield measurements were carried out in the presence of a low energy triplet quencher, ferrocene ($E_T = 163$ kJ mol^{-1}). Using ferrocene concentrations in the range 10^{-4}–10^{-2} mol dm^{-3} and directly exciting SO with 366 nm light, photoreaction quenching was hardly detectable and only with the nitro derivative. Treating the quantum yield data of the quenched and unquenched reaction according to the appropriate SV equation was unreliable, due to the small quenching ratio measured even with the highest quencher concentrations attainable (10^{-2} mol dm^{-3}). By assuming diffusion-controlled quenching by ferrocene, the triplet lifetime of $N(NO_2)$ in fluid solution could be quoted approximately on the nanosecond time scale. The same order of magnitude has recently been determined from laser flash photolysis measurements [23].

4. Conclusions

The results of this work show that photosensitization by CQ of the colour-forming reaction in the SO ⇌ PM systems is very efficient, regardless of the photochrome structure. The quantum yield of the photosensitized process increases, compared with the direct photoreaction quantum yield, and tends to unity. Thus colourability increases. Since the photosensitized reaction occurs exclusively via the triplet state, while the direct photoreaction occurs by a singlet mechanism (except for the nitro derivative), it can be stated that SO triplets possess a one-way deactivation to PM, while a certain percentage (50%–80%) of singlet excited states back relax to SO. For $N(NO_2)$, the exceptionally high Φ_D value also supports a triplet reaction mechanism on direct excitation.

In addition, photosensitization with CQ extends the λ range for producing the coloured merocyanine form towards the visible, which is important from an application point of view.

However, the presence of the sensitizer also promotes additional reactions which, increasing the apparent bleaching rate constant, tend to lower the colourability. This effect was undetectable for (N-Et)N and (N-Pr)F. Moreover, the interaction of triplet CQ with PM may also decrease the durability of the photochrome. Degradation on photosensitization of the photochromism of some spiro-oxazines by using greater concentrations of both the donor and acceptor and pulsed excitation has already been reported in the literature [9]. Under our experimental conditions, this inconvenience, which has previously been revealed using other sensitizers (biacetyl, benzophenone) [7], was not detected with CQ, but may possibly occur after several irradiation cycles.

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References

[1] Th. Förster, *Discuss. Faraday Soc.*, *27* (1959) 7; J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970; F. Wilkinson, *Adv. Photochem.*, *3* (1964) 601; N.J. Turro, *Pure Appl. Chem.*, *49* (1977) 405; A.A. Lamola, *Energy Transfer and Organic Photochemistry*, Interscience, New York, 1969; R.G. Bennett and R. Kellogg, *Progr. React. Kinetics*, *4* (1966) 215; S. Speiser, *J. Photochem.*, *22* (1983) 195; N.J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978.

[2] M.B. Rubin, *Top. Curr. Chem.*, *13* (1969) 251; M.B. Monroe, *Adv. Photochem.*, *8* (1971) 77.

[3] H. Bach and J.G. Calvert, *J. Am. Chem. Soc.*, *92* (1970) 2608.

[4] P. Appriou, R. Guglielmetti and F. Garnier, *J. Photochem.*, *8* (1978) 145.

[5] M. Sakuragi, K. Aoki, T. Tamaki and K. Ichimura, *Bull. Chem. Soc. Jpn.*, *63* (1990) 74.

[6] D. Eloy, P. Escaffre, R. Gautron and P. Jardon, *J. Chim. Phys.*, *89* (1992) 897.

[7] G. Favaro, V. Malatesta, U. Mazzucato, G. Ottavi and A. Romani, *J. Mol. Cryst. Liq. Cryst.*, *246* (1994) 299.

[8] A. Kellmann, F. Tfibel, E. Pottier, R. Guglielmetti, A. Samat and M. Rajzmann, *J. Photochem. Photobiol. A: Chem.*, *76* (1993) 77.

[9] D. Eloy, P. Escaffre, R. Gautron and P. Jardon, *Bull. Soc. Chim. Belg.*, *101* (1992) 779.

[10] A. Samat, J. Kister, F. Garnier, J. Metzger and R. Guglielmetti, *Bull. Soc. Chim. Fr.*, (1975) 2627.

[11] G. Favaro, V. Malatesta, U. Mazzucato, G. Ottavi and A. Romani, *J. Photochem. Photobiol. A: Chem.*, *87* (1995) 235.

[12] G. Favaro, V. Malatesta, U. Mazzucato, C. Miliani and G. Ottavi, *Proc. Ind. Acad. Sci.*, *107* (1995) 659.

[13] G. Favaro, F. Masetti, U. Mazzucato, G. Ottavi, P. Allegrini and V. Malatesta, *J. Chem. Soc., Faraday Trans.*, *90* (1994) 333.

[14] N.Y.C. Chu, in H. Dürr and H. Bouas-Laurent (eds.), *Photochromism*, Elsevier, Amsterdam, 1990, p. 493.

[15] G. Favaro, F. Masetti and A. Ramadori, *J. Photochem.*, *10* (1979) 349.

[16] A. Romani, G. Favaro and F. Masetti, *J. Lumin.*, *63* (1995) 183.

[17] F. Wilkinson, J. Hobley and M. Naftaly, *J. Chem. Soc., Faraday Trans.*, *88* (1992) 1511.

[18] A. Bar and G. Gauglitz, *J. Photochem. Photobiol. A: Chem.*, *46* (1989) 15; B. Borderie, D. Lavabre, J.C. Micheau and J.P. Laplante, *J. Phys. Chem.*, *96* (1992) 2953; G. Gauglitz and E. Scheerer, *J. Photochem. Photobiol. A: Chem.*, *71* (1993) 205.

[19] G. Favaro et al., unpublished results.

[20] S.K. Lee, O. Valdes-Aguilera and C.D. Neckers, *J. Photochem. Photobiol. A: Chem.*, *67* (1992) 319.

[21] S. Monti, G. Orlandi, A. Kellmann and F. Tfibel, *J. Photochem.*, *33* (1986) 81.

[22] V.G. Luchina, V.S. Marevtsev, A.V. Liubimov, Y.D. Khamchukov, V.Y. Nedoshivin and M.I. Cherkashin, *Sov. J. Chem. Phys.*, *8* (1991) 1792.

[23] A. Kellmann, F. Tfibel and R. Guglielmetti, *J. Photochem. Photobiol. A: Chem.*, *91* (1995) 131.