ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 120 (1999) 29–36

Journal of
Photochemistry
and
Photobiology
A:Chemistry

Triplet energies, singlet state properties and singlet oxygen quenching rate constants and quantum yields for two cyan azamethine dyes

Richard J. Berry[a], Peter Douglas[a,*], Michael S. Garley[a], Tony Jolly[a], Dave Clarke[b], Helen Moglestue[b], Helen Walker[b], Christopher Winscom[b]

[a]*Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, UK*
[b]*Kodak European R&D Ltd., Headstone Drive, Harrow, HA1 4TY, UK*

Received 30 June 1998; accepted 15 September 1998

Abstract

The triplet energies of two photographic cyan azamethine dyes with absorption maxima around 640 nm have been studied using time-resolved energy transfer methods and found to be 94 (±4) and 87 (±4) kJ mol^{-1}. The rate constants for the quenching of singlet molecular oxygen by the two dyes in ethanol are 6.5 (±0.5) × 10^9 and 6.7 (±0.5) × 10^9 mol^{-1} dm^3 s^{-1}, close to the diffusion-controlled limit. Quantum yields of singlet oxygen production in air-equilibrated ethanol are 3.3 (±1.0) × 10^{-5} and $\leq 1 \times 10^{-5}$. Fluorescence spectra of the dyes in dibutyl phthalate at relatively high concentration have been obtained leading to estimates of 6.9 (±1.2) × 10^{-5} and 1.8 (±0.5) × 10^{-5} for the quantum yields of fluorescence. Excited singlet state radiative and non-radiative rate constants, calculated using the Strickler Berg method, for the two dyes are: 9.9 (±0.4) × 10^7 and 1.5 (±0.2) × 10^{12} s^{-1}; 8.7 (±0.7) × 10^7 and 5.0 (±2.0) × 10^{12} s^{-1}.

Keywords: Cyan azamethine dyes; Quantum yields; Rate constants

1. Introduction

Azamethine dyes are commonly used in photographic imaging where they form the yellow, magenta and cyan images [1]. Despite the good light stability of these dyes colour loss can still be noticed after prolonged exposure to normal room light. It is the purpose of this work to provide details of the characteristics of the excited states of the two cyan dyes shown in Fig. 1 in order to improve our understanding of the mechanism of photodegradation.

For the singlet state the radiative and non-radiative rate constants and the quantum yield of fluorescence are important. Several different methods exist for obtaining an estimate of the radiative rate constant [2] ($k_{\rm rad}$), such as that suggested by Strickler and Berg [3] Eq. (1).

$$k_{\rm rad} = 2.88 \times 10^{-9}\, n^2\, \upsilon_{fl}^3 \int \varepsilon \,\mathrm{d}\ln \upsilon \qquad (1)$$

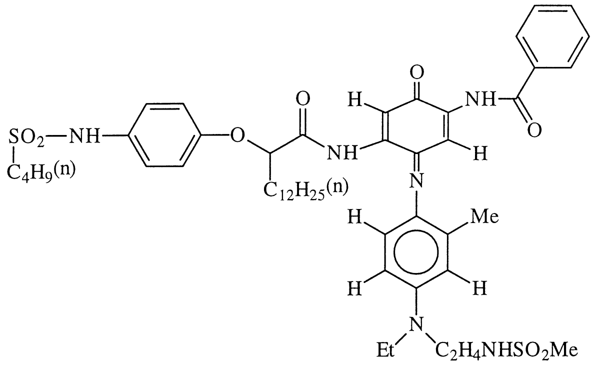
Here n is the refractive index of the solvent, $\upsilon_{\rm fl}$ is the mean reciprocal wavelength (cm^{-1}) of the fluorescence, ε is the extinction coefficient, and υ is the reciprocal wavelength (cm^{-1}) of the absorption.

For the triplet state the energy and lifetime are important. Previous work [4] suggests that the lifetimes of the triplet states of these dyes are very short, probably no more than a few nanoseconds, and it has been proved impossible to detect the triplet state with microsecond or nanosecond flash photolysis techniques. Investigation of the triplet state energy is also difficult. The π–π^* transition in azamethine dyes typically gives a triplet state with an energy of around half of the singlet state [4] and since the dyes under investigation have singlet energies of around 170 kJ mol^{-1} this implies that phosphorescence would lie at a wavelength of around 1300 nm, well outside the detection limits of most photomultipliers. An indirect method must, therefore, be used to determine the triplet state energies of these dyes. To this end the method described by Herkstroeter in 1975 [4] has been adopted. The process involves the use of triplet sensitisers with triplet energies covering a wide energy range centred upon that of the dye triplet energy. Energy transfer from the sensitiser to the dye means that the dye acts as a quencher, Eqs. (5)–(8), and this can be seen as an increase in the rate of decay of the triplet state of the sensitiser ($k_{\rm obs}$ in Eq. (10)). When the sensitiser triplet energy is significantly higher than that of the dye energy transfer from the sensitiser to the dye takes place at approximately the diffusion-con-

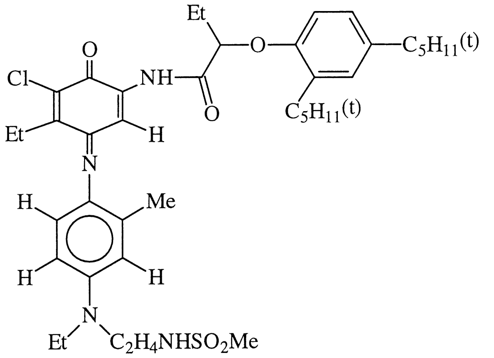
---

*Corresponding author.

PII: S1010-6030(98)00398-0



DYE A



DYE B

Fig. 1. Cyan dye structures.

trolled rate, but when the sensitiser triplet energy is less than that of the dye energy transfer is much slower than the diffusion-controlled rate. Hence a study of k_{obs} as a function of sensitiser triplet energy can be used to obtain the dye triplet energy.

A number of models have been proposed for the variation in energy transfer rates of triplet–triplet energy transfer reactions. Both Sandros [5] and Herkstroeter and Hammond [6] invoked the idea of non-vertical energy transfer and phantom triplets in order to explain their results. The more recent 'classical' theory proposed by Balzani [7] Eq. (2) shows a dependence of the rate of energy transfer from donor to acceptor on both the free energy change, ΔG, and the structural re-organisation energy, $\Delta G^{\#}$, (the energy required to re-organise a molecule such that it has the optimum structure for the energy transfer process). The rate of energy transfer is then given by Eq. (2),

$$k_{\mathrm{q}} = \frac{k_{\mathrm{d}}}{1 + \exp(\Delta G/\mathrm{RT}) + (k_{-\mathrm{d}}/k^{0}).\exp\frac{\{\Delta G + ((\Delta G^{\#}/\ln 2).\ln[1+\exp-(\Delta G.\ln 2/\Delta G^{\#})])\}}{\mathrm{RT}}} \tag{2}$$

where k_{q} is the quenching rate constant for energy transfer; k_{d} and $k_{-\mathrm{d}}$ are the rate constants for the formation and dissociation of the encounter complex and k^{0} is the pre-exponential factor. Using this method a series of triplet sensitisers with similar chemical and diffusional properties, whose triplet energies cover a wide range centred upon that of the dye, is required. The very low energy of the dye triplet states implies that very low energy sensitisers are required and because of this we have used porphyrins, phthalocyanines and naphthalocyanines as triplet sensitisers [8–11].

2. Materials

The azamethine dyes were provided by Kodak, Harrow, UK. Other chemicals were obtained from either Aldrich, [diphenylisobenzofuran (DPBF), cresyl violet (CV), gallium naphthalocyanine (GaN), palladium tetraphenylporphyrin (PdTPP), tetraphenylporphyrin (TPP), tin naphthalocyanine (SnN) and zinc tetraphenylporphyrin (ZnTPP)], or Eastman [chloro aluminium phthalocyanine (CAP) and anthracene] and were used as received. For studies using porphyrins and phthalocyanines, both synthetic grade (99%) ethanol and Avocado 98% 1-chloronaphthalene were used. The naphthalocyanines were studied exclusively in Avocado 98% chloronaphthalene. Dibutyl phthalate (Aldrich 'gold label') was used as solvent for fluorescence measurements since it is widely used in practical photographic systems.

3. Experimental

Microsecond flash photolysis studies were made with a standard Applied Photophysics 200 J instrument (pulse duration 10 µs), with either toluene (cut-off wavelength <280 nm) or sodium nitrite (cut-off wavelength <420 nm) filters to minimise photodegradation due to UV excitation. The photolysis solution (~30 ml) was contained in a 10 cm path length cell. Solutions were purged with nitrogen (ethanol ~15 min, chloronaphthalene ~30 min) to remove oxygen before starting the experiments. The necessary purge time was determined experimentally, i.e., solutions were purged until the rate of decay of the triplet states no longer decreased. Data were collected on a Gould OS470 oscilloscope and analysed on either a BBC Masterclass or Archimedes computer. Solutions were prepared to be approximately 1×10^{-5} mol dm^{-3} in sensitiser and 0.3--1.3×10^{-5} mol dm^{-3} in dye.

Nanosecond flash photolysis experiments were carried out using 355 nm radiation from a frequency tripled Nd/YAG laser (Spectron Lasers) and an Applied Photophysics

Laser kinetic Spectrometer. The unfocussed excitation beam was ≈1 cm in diameter, with a pulse duration of ≈ 16 ns. Samples were contained in 1 cm^2 cells and the transmission monitored at 90° to the excitation pulse at around 590 nm [for energy transfer measurements] or 413 nm [for singlet oxygen quenching rate constant measurements]. The transient data were recorded on a Gould OS4072 digital oscilloscope and transferred to an Acorn BBC Masterclass microcomputer for kinetic analysis. Solutions for energy transfer measurements using the laser system were prepared to be around 1×10^{-5} mol dm^{-3} in sensitiser and 2.0–5.5 $\times 10^{-5}$ mol dm^{-3} in dye. Singlet oxygen quenching data were obtained using ethanol as solvent, anthracene (6×10^{-5} mol dm^{-3}) as the sensitiser, and DPBF (2×10^{-5} mol dm^{-3}) as the $^1O_2$ acceptor.

It should be noted that the naphthalocyanines are insoluble in most solvents and show a propensity to aggregate even in solvents in which they appear to dissolve. In order to avoid aggregation it was found necessary to heat the solutions to around 180°C for between 30 and 120 min.

The yield of $^1O_2$ generated by irradiation of the dye was measured by following the rate of loss of the $^1O_2$ acceptor, DPBF. Light from a high pressure mercury lamp (100 W Rofin Arc lamp and power supply) was passed through a cooled water filter of 15 cm path length and brought to a focus at the slits of a high intensity monochromator (B and L 1/4 m). At the largest slit settings the bandwidth at λ_{max} of both dyes was 38 nm. From the exit slit the light passed through 5 layers of a WR16 filter to remove unwanted second order wavelengths in the UV and to suppress any intensity at the absorption wavelength of DPBF. The light at 650 nm was brought to a focus at the sample (1 cm^3 in a 1 cm cuvette) where it delivered ca. 2 mW of optical power. The sample cuvette was immersed in cooling water at room temperature. For each run an identical control sample which was not irradiated experienced the same thermal history. At intervals throughout the total irradiation time the DPBF concentration was monitored by a short sweep of ca. 20 nm across λ_{max}. The sample and reference arms of the UV/Vis spectrometer were attenuated by matched 10% transmission neutral density filters.

Fluorescence emission and excitation spectra, and relevant absorption spectra were recorded using either a Jobin-Y von JY3D spectrofluorimeter in conjunction with a PC-controlled Perkin-Elmer Lambda 9 UV/Vis spectrometer and a Pye Unicam 8720 UV/Vis spectrometer; or a Perkin-Elmer MPF-44E spectrofluorimeter in conjunction with a Perkin-Elmer Lambda 5 UV/Vis spectrometer.

The fluorescence spectrum of dye A was measured using a 3.3×10^{-5} mol dm^{-3} (absorbance at $\lambda_{max} = 0.9$) solution in dibutyl phthalate at room temperature. The excitation wavelength used was 580 nm, where the absorption of the solution was 0.3. Quantum yield measurements were made by comparison of the dye emission intensity with emission from a solution of cresyl violet ($\phi_{fl}^{cv} = 0.55$ [12]) with an absorbance of 0.114 at 620 nm in ethanol. Quantum yields of fluorescence were calculated according to Eq. (3)[13].

$$\left(\frac{A_{dye}}{A_{cv}}\right) = \left(\frac{\phi_{fl}^{dye}}{\phi_{fl}^{cv}}\right) \times \left(\frac{Abs_{dye}}{Abs_{cv}}\right) \times \left(\frac{n_{DP}}{n_{EtOH}}\right)^2 \tag{3}$$

where A is area beneath the emission spectrum; ϕ_{fl} is quantum yield of fluorescence; Abs is absorbance; n_{DP} is refractive index of dibutyl phthalate (1.4920); n_{EtOH} is refractive index of ethanol (1.3620). Cresyl violet and the dye of unknown quantum yield are denoted by 'cv' and 'dye', respectively.

The excitation spectrum of dye A was taken using a solution with an absorbance of 0.2 at λ_{max} and the signal was integrated over a period of 32 s. In all cases the slits used were 10 nm on the excitation and 20 nm on emission monochromators. All fluorescence spectra were corrected as follows for inner filter effects and reabsorption. The absorption of the solution (T) over the wavelength range in a 1 cm path length cell was determined and this then halved to allow for the fact that the fluorescence comes from the centre of the cell. Hence the relative % absorption $(1-T)$ was found and this used as a ratio $(1/(1-T))$. Spectra were also corrected for photomultiplier response by comparison of an emission spectrum of cresyl violet with the corrected spectrum given by Magde et al. [12].

For the studies with the MPF-44E spectrofluorimeter a slightly different technique was adopted using higher concentrations. All sample solutions were prepared in standard 1 cm cuvettes to have an absorbance of 1 at the chosen excitation wavelength. The photon sensitivity of the spectrometer detection channel was determined with the aid of a calibrated power meter (Photodyne 88XLC). Neutral density filters and interference filters in the range 500–750 nm, of which all transmission profiles were accurately known, were also used. The calibrant of known quantum yield of fluorescence was chosen to be rhodamine B in ethanol ($\phi_{fl}^{rhB} = 0.69$ [14]). An ethanol solution of rhodamine B (ca. 10^{-5} mol dm^{-3}) was prepared having an absorbance of 1.00 at 542 nm (λ_{max}). The sample was irradiated at 542 nm using a 15 nm excitation bandwidth, and the optical power in the excitation band at the sample, and hence the number of incident photons s^{-1} (I_{ex}), was measured. Since the rhodamine B/ethanol sample, and both dye samples, presented an absorbance of 1 to the exciting light, any absorption correction for the excitation intensity at the centre of the 1 cm path length would be common to all cases, and was, therefore, not taken into further consideration. However, reabsorption over the emission profile at these concentrations now becomes more significant. Emission was assumed to originate from the centre of the 1 cm cuvette, and correction was performed at 10 nm intervals throughout the range 500–700 nm. From the areas B_{dye} and B_{rhB}, under the corrected emission profiles, the quantum yields could be calculated from the relationship:

$$\frac{B_{dye}}{B_{rhB}} = \left(\frac{\phi_{fl}^{dye}}{\phi_{fl}^{rhB}}\right) \times \left(\frac{I_{ex}^{dye}}{I_{ex}^{rhB}}\right) \times \left(\frac{n_{DP}}{n_{EtOH}}\right)^2 \tag{4}$$

A modification of the Strickler–Berg Equation suggested by Berlman [15] in which $\upsilon_{\rm fl}^{3}$ is replaced by $< \upsilon_{\rm fl}^{-3} >_{\rm av}{}^{-1}$, where $< \upsilon_{\rm fl}^{-3} > = \int \upsilon^{-3} f(\upsilon)\, d(\upsilon) / \int f(\upsilon)\, d(\upsilon)$ was used for singlet state measurements using the MPF-44E fluorimeter. The necessary integrations were performed numerically.

All errors have been quoted at one standard deviation.

4. Results

4.1. Singlet excited state measurements

Using the JY3D spectrofluorimeter, with ethanol as solvent, no fluorescence from either dye could be detected, suggesting $\phi_{\rm fl}$ for both dyes in ethanol is less than 4×10^{-5}. In contrast, in dibutyl phthalate, fluorescence of dye A was detected. Fig. 2 shows both the corrected emission and corrected excitation spectra of dye A obtained with the JY3D fluorimeter ($\lambda_{\max}$ (emission) = 712 nm). Table 1 contains the results of all singlet state calculations for both dyes. Fluorescence from dye B in dibutyl phthalate could not be detected with the JY3D fluorimeter and so estimates only have been made for $\phi_{\rm fl}$ and $\lambda_{\max}$ emission. However, with the MPF-44E the emission spectrum shown in Fig. 3 was obtained ($\lambda_{\max}$(emission) = 731 nm).

4.2. Triplet–triplet energy transfer measurements

Flash photolysis of the dyes in the absence of sensitiser produced no transient species on a microsecond or nanosecond time scale. In the absence of dye flash photolysis of the sensitiser generates the sensitiser triplet state (SENS T_1^*). Addition of dye leads to an increase in the rate of SENS T_1^* decay [16]. In all studies with dyes A and B no transients other than SENS T_1^* were observed, suggesting that electron transfer is unimportant and that the increase in decay of SENS $T_1{}^*$ is caused by triplet–triplet energy transfer to the dye.

Table 1
Values for $k_{\rm rad}$, k_n (non-radiative rate constant), $\phi_{\rm fl}$ and $\tau_{\rm s}$ (estimated lifetime of the first excited singlet state)

Characteristic	Dye A		Dye B	
$k_{\rm rad}$ (10^7 s^{-1})	10.0 ± 0.2	9.8 ± 0.5	8 ± 0.9	9.3 ± 0.5
k_n (10^{12} s^{-1})	1.2 ± 0.2	1.7 ± 0.3	> 8	5.0 ± 2.0
$\phi_{\rm fl}$ (10^{-5})	8.0 ± 1.0	5.7 ± 0.5	< 1.0	1.8 ± 0.5
$\tau_{\rm s}$/fs	800	600	< ~125	200

The first values were calculated using data from the JY3D spectrofluorimeter and the second values were calculated using data from the MPF-44E spectrofluorimeter.

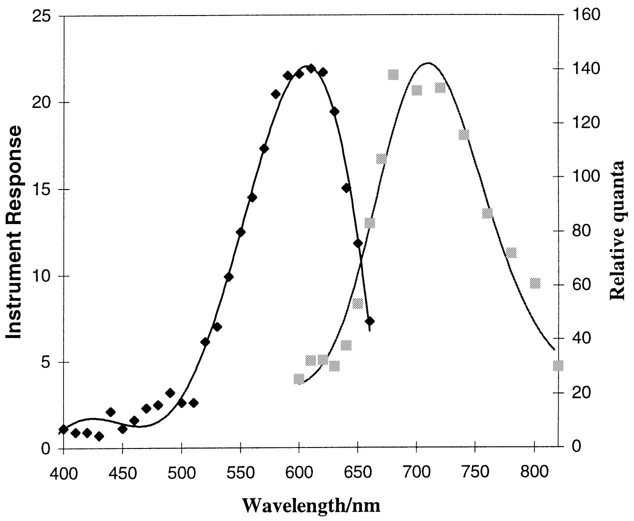


Fig. 2. Corrected excitation spectrum (wavelength against instrument response) – diamonds; and corrected emission spectrum (wavelength against relative quanta) – squares, of dye A.

$$\text{SENS}\, S_0 + h\upsilon \rightarrow \text{SENS}\, S_1^* \tag{5}$$

$$\text{SENS}\, S_1^* \xrightarrow{\text{ISC}} \text{SENS}\, T_1^* \tag{6}$$

$$\text{SENS}\, T_1^* \xrightarrow{k_{\rm r}} \text{SENS}\, S_0 \tag{7}$$

$$\text{SENS}\, T_1^* + \text{DYE}\, S_0 \xrightarrow{k_{\rm q}} \text{SENS}\, S_0 + \text{DYE}\, T_1^* \tag{8}$$

Here ISC is inter system crossing; $k_{\rm r}$ is the rate constant for radiative decay; $k_{\rm q}$ is the rate constant for quenching; * denotes an excited state.

$$\mathrm{d}[\text{SENS}]/\mathrm{d}\,t = k_{\rm r}[\text{SENS}\, T_1^*] + k_{\rm q}[\text{DYE}][\text{SENS}\, T_1^*] \tag{9}$$

and

$$k_{\rm obs} = k_{\rm r} + k_{\rm q}[\text{DYE}] \tag{10}$$

where $k_{\rm obs}$ = observed rate of decay of sensitiser triplet state.

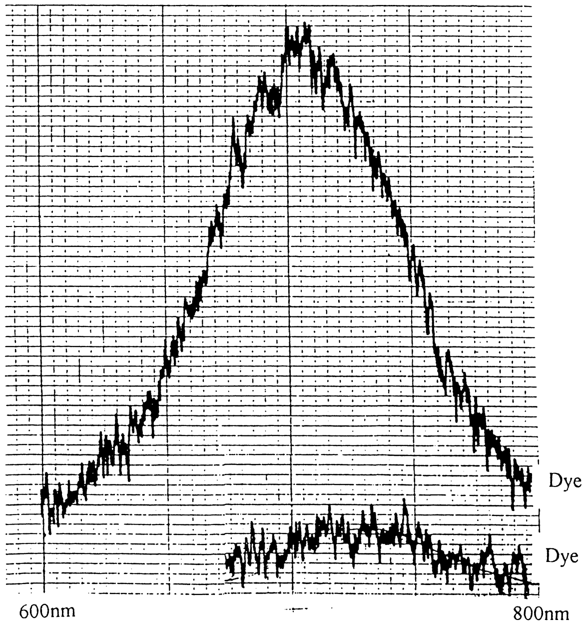


Fig. 3. Uncorrected emission spectra for dyes A and B.

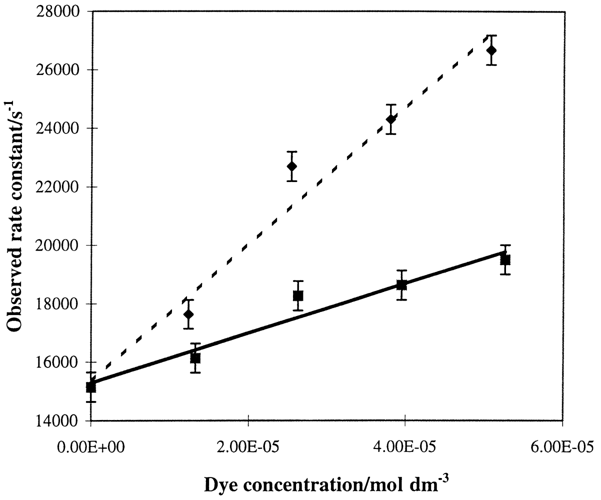


Fig. 4. An example of the results obtained for triplet energy transfer experiments. Sensitiser – 2,3-naphthalocyanine in 1-chloronaphthalene. Dye A – squares and solid line. Dye B – diamonds and dashed line.

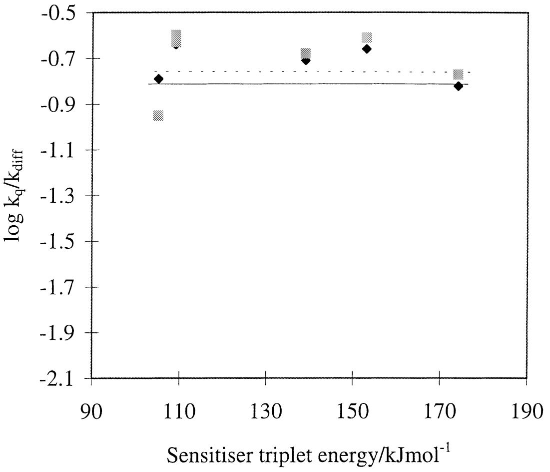


Fig. 5. Data for triplet–triplet energy transfer in ethanol. Dye A – squares and solid line. Dye B – diamonds and dashed line.

From Eq. (10) it can be seen that the quenching rate constant can be found by plotting k_{obs} against the concentration of dye present. This gives a straight line with gradient k_q, as shown in Fig. 4.

The triplet energies of the naphthalocyanines are not well-documented and so these have been calculated using a similar method to that of Ford et al. [17] who suggest that the S_1–T_1 energy gap remains constant at 65.3 ($\pm$1.7) kJ mol^{-1} [17,18] within the 2,3-naphthalocyanine family. However, we believe that rather than assuming a constant S_1–T_1 energy gap it is more reasonable to assume a constant S_1/T_1 energy ratio. We have used triplet energies assuming a constant S_1/T_1 energy ratio in the calculations of the dye triplet energies. The triplet energies of all of the sensitisers used are shown in Table 2.

It was found that the rate of energy transfer was to some extent dependent on the solvent used. In ethanol the maximum rate constant for energy transfer was found to be around 2×10^9 mol^{-1} dm^3 s^{-1} which is close to the diffusion-controlled rate of about 5.5×10^9 mol^{-1} dm^3 s^{-1} (Fig. 5). However, in 1-chloronaphthalene this value was found to be 1.5×10^8 mol^{-1} dm^3 s^{-1}, much lower than the diffusion-controlled rate of 2.2×10^9 mol^{-1} dm^3 s^{-1} (Figs. 6 and 7). Since other experiments using the same or similar sensitisers in various solvents have not shown this effect [19,20], we believe that this effect may be due to solvent–dye interactions.

Fig. 5 shows the results obtained using ethanol as a solvent. Unfortunately, it proved impossible to obtain good solutions of the lower energy sensitisers in this solvent and for all the sensitisers used k_{obs} lies very close to the diffusion-controlled limit, i.e., the rate of energy transfer is approximately constant over this sensitiser triplet energy range. Fig. 6 shows the results for dye A using chloronaphthalene as a solvent. The curve shown is a fit of the Balzani equation with $\Delta G^{\#} = 12$ kJ mol^{-1}. Similarly, Fig. 7 shows the results for dye B. It is interesting to note that here

Table 2
Triplet energies of the sensitisers used

Sensitiser	Triplet energy/ (kJ mol^{-1})	Reference
PdTPP	174	[8]
ZnTPP	153	[9]
TPP	139	[8]
ZnP	109	[10]
CAP	105	[11]
NC	89.5^a and 88^b	Calculated
GaN	85.5^a and 81^b	Calculated
SnN	84.3^a and 79^b	Calculated

a, Energies calculated using a constant S^1/T^1 energy ratio and used in the following calculations.
b, Energies calculated using a constant S^1/T^1 energy gap.

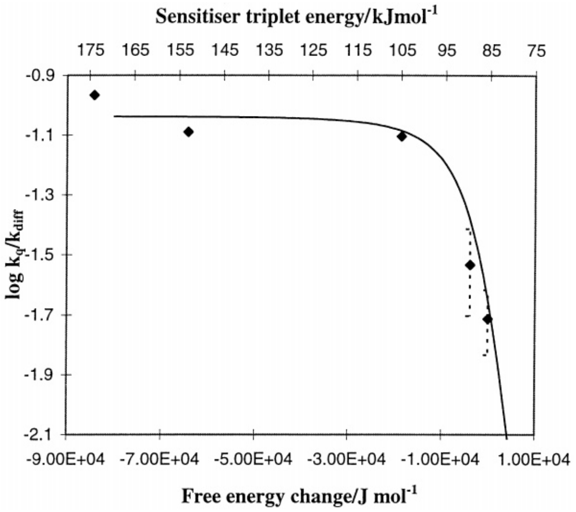


Fig. 6. Fit of the Balzani equation to the data obtained for dye A in chloronaphthalene.

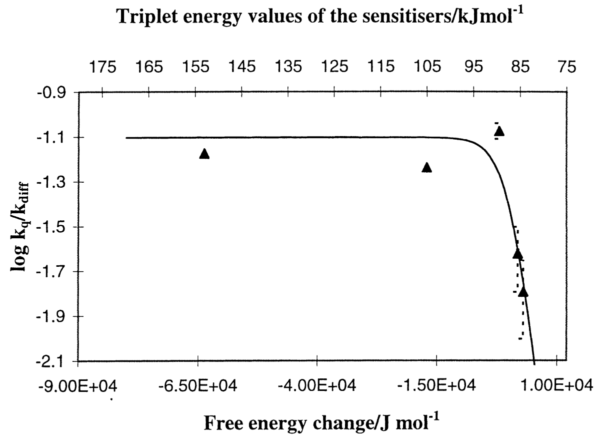


Fig. 7. Fit of the Balzani equation to the data obtained for dye B in chloronaphthalene.

the best fit of the Balzani equation is obtained using a $\Delta G^{\#}$ value of only 4 kJ mol^{-1}.

4.3. Singlet oxygen quenching rate constants

The rates of reaction of the dyes with singlet oxygen has been measured using a flash photolysis technique. The method relies on generating $^1O_2$ using a sensitiser and then determining the rate of loss of a $^1O_2$ acceptor in the presence and absence of the dye. The laser pulse is used to generate a small concentration of $^1O_2$ rapidly, subsequent reaction of which causes loss of the $^1O_2$ acceptor over a period of a few microsecond. The reaction scheme and analysis are as follows [21].

$$\mathrm{SENS} + h\upsilon \rightarrow {}^3\mathrm{SENS}^* \tag{11}$$

$${}^3\mathrm{SENS}^* \rightarrow \mathrm{SENS} \tag{12}$$

$${}^3\mathrm{SENS}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{SENS} + {}^1\mathrm{O}_2^* \tag{13}$$

$${}^3\mathrm{SENS}^* + {}^3\mathrm{O}_2 \rightarrow \mathrm{SENS} + {}^3\mathrm{O}_2 \tag{14}$$

$${}^3\mathrm{SENS}^* + \mathrm{DYE} \rightarrow \mathrm{SENS} + {}^3\mathrm{DYE}^* \tag{15}$$

$${}^1\mathrm{O}_2^* \rightarrow {}^3\mathrm{O}_2 \tag{16}$$

$${}^1\mathrm{O}_2^* + \mathrm{DPBF} \rightarrow \mathrm{PRODUCTS} \tag{17}$$

$${}^1\mathrm{O}_2^* + \mathrm{DYE} \rightarrow (\mathrm{LOSS\ OF\ DYE}) \tag{18}$$

$${}^1\mathrm{O}_2^* + \mathrm{DYE} \rightarrow {}^3\mathrm{O}_2 + {}^{\#}\,\mathrm{DYE} \tag{19}$$

Where * indicates an excited state and numerical superscripts indicate spin multiplicity with # used to denote unspecified spin multiplicities.

Provided the concentration of DPBF stays effectively constant throughout any one kinetic run, after the decay of the sensitiser triplet (complete within 2 µs or so), the observed first-order rate constant for the decay of [DPBF], k_{obs}, is given by:

$$k_{\mathrm{obs}} = (k_{18} + k_{19})[\mathrm{DYE}] + k_{17}[\mathrm{DPBF}] + k_{16} \tag{20}$$

so that a plot of k_{obs} against [DYE] has a slope $= k_{18} + k_{19}$.

Anthracene was used as sensitiser and DPBF as $^1O_2^*$ acceptor. The DPBF concentration was kept low to maximise the lifetime of $^1O_2^*$ and only a small fraction of the DPBF present was consumed in the reaction to maintain simple kinetics. These conditions result in relatively small signals. The data obtained for dyes A and B shown in Fig. 8 give reaction rate constants of 6.5 (±0.5) × 10^9 and 6.7

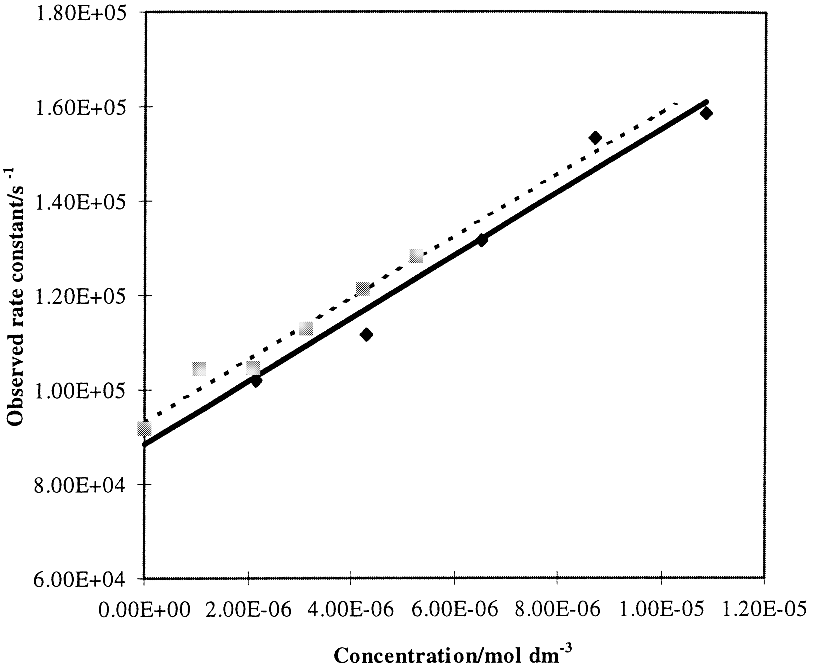


Fig. 8. Singlet oxygen quenching results for dye A (squares and dashed line) and dye B (diamonds and solid line).

(±0.5) × 10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively. No loss of dye was detected in these experiments and thus $k_{19} \gg k_{18}$. We can, therefore, equate the experimental quenching rate constant with physical quenching by the dye, i.e., k_{18}. Literature values of k_{16} and k_{17} are 1.0 (±0.1) × 10^5 $\mathrm{s^{-1}}$ and 6.34 × 10^8 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively [21]. Together these give, in the absence of dye, a predicted rate constant of 11 (±1.2) × 10^4 $\mathrm{s^{-1}}$ for loss of DPBF which is in good agreement with our experimental value of 9.2 (±0.8) × 10^4 $\mathrm{s^{-1}}$.

4.4. Singlet oxygen quantum yields

Plots of the quantum yield for loss of DPBF following irradiation of the dye ($[\phi_{\mathrm{ox}}]^{-1}$) against $[\mathrm{DPBF}]^{-1}$ gave good straight lines (Fig. 9) and from the intercepts, ($[\phi_{\mathrm{sing\ ox.}}]^{-1}$), singlet oxygen quantum yields of 3.7 (±1.0) × 10^{-5} and ≤ 1 × 10^{-5} were obtained for dyes A and B, respectively.

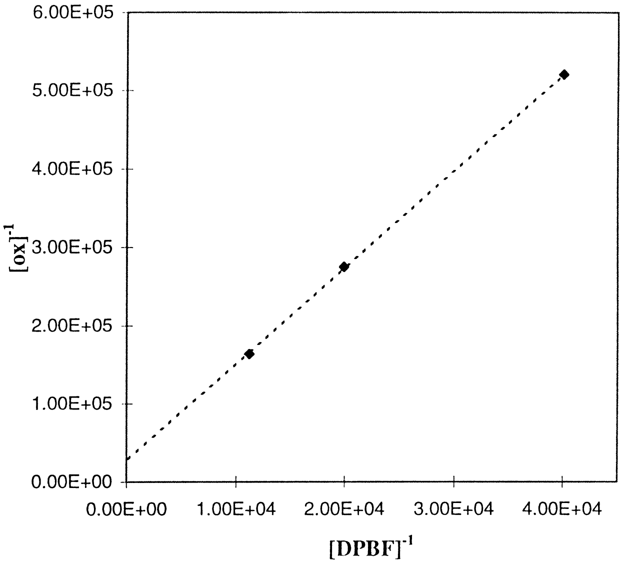


Fig. 9. Quantum yield of singlet oxygen production by dye A.

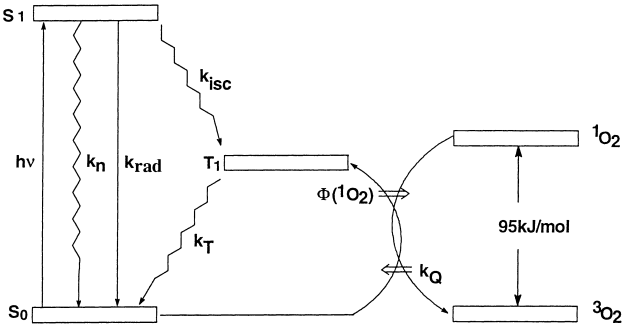


Fig. 10. Summarised photochemical characteristics of the two dyes. Symbols refer to those in Table 3.

5. Conclusions

All the results obtained are summarised in Fig. 10 and Table 3, along with estimates for the rate constants for inter system crossing and decay of the triplet state. Very weak fluorescence emission ($\phi_{\mathrm{f}} = 6.9$ (±1.2) × 10^{-5} and 1.8 (±0.5) × 10^{-5} for dyes A and B, respectively) has been detected in dibutyl phthalate. The combination of weak fluorescence and high absorption extinction coefficients for these dyes leads to calculated singlet lifetime of at most a few hundred femtoseconds: 800 fs for dye A, and 200 fs for dye B.

Rate constants for triplet–triplet energy transfer from a series of porphyrin, phthalocyanine and naphthalocyanine triplet sensitisers have been analysed using the Balzani equation [7]. This analysis indicates dye triplet energies of 94 (±4) and 87 (±4) kJ $\mathrm{mol^{-1}}$, and structural reorganisation energies ($\Delta G^{\#}$) of 12 and 4 kJ $\mathrm{mol^{-1}}$ for dyes A and B, respectively.

The triplet energy of dye A is very close to that of singlet oxygen while the triplet state energy of dye B is somewhat lower than that of singlet oxygen. As expected for dyes with triplet energies in this range the rate constants for quenching of singlet oxygen by the dyes (6.6 (±0.5) × 10^{-9} $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$) are close to those calculated for diffusion-controlled reactions. The relative singlet oxygen generation yields of 3.7 (±1.0) × 10^{-5} and ≤ 1 × 10^{-5} are consistent with the low triplet energies of the dyes and/or their short triplet lifetime.

Although these dyes are structurally very similar there is enough of a difference in singlet state lifetime, triplet state energies and $^1O_2$ generation yields to generate a small but significant difference in photostability. These differences in

Table 3
Summarised values for the photochemical properties of two dyes

Property	Dye A	Dye B	Method used for calculation of property
$E(\mathrm{S1})$	190 kJ $\mathrm{mol^{-1}}$	182 kJ $\mathrm{mol^{-1}}$	UV/Vis absorption
$E(\mathrm{T_1})$	94 kJ $\mathrm{mol^{-1}}$	87 kJ $\mathrm{mol^{-1}}$	Quenching of triplet sensitisers
k_{rad}	9.9 × 10^7 $\mathrm{s^{-1}}$	8.7 × 10^7 $\mathrm{s^{-1}}$	Absorption spectra
k_n	1.5 × 10^{12} $\mathrm{s^{-1}}$	5.0 × 10^{12} $\mathrm{s^{-1}}$	Fluorescence quantum yield and k_{rad}
k_{ISC}	≥5×10^8 $\mathrm{s^{-1}}$	≥3 × 10^8 $\mathrm{s^{-1}}$	Limit from $\phi(^1O_2)$ and k_n
k_{T}	≥10^8 $\mathrm{s^{-1}}$	≥10^8 $\mathrm{s^{-1}}$	Estimated
$\phi(^1O_2)$	3.3 × 10^{-5}	≤1 × 10^{-5}	Decay of $^1O_2$ quencher
k_{Q}	6.5 × 10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	6.7 × 10^9 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$	$^1O_2$ quenching studies

photochemical properties may be important in determining the relative photostability of these dyes when used in photographic imaging.

Acknowledgements

We would like to thank the organic synthesis laboratory of Kodak European R&D Ltd., which supplied the dyes. Financial support from the EPSRC and Kodak Ltd. (CASE award to RJB) is gratefully acknowledged.

References

[1] R.J. Tuite, J. Appl. Photogr. Eng. 5 (1979) 200.
[2] N.J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings, London, 1978, p. 86.
[3] S.J. Strickler, R.A. Berg, J. Chem. Phys. 37 (1962) 814.
[4] W.G. Herkstroeter, J. Am. Chem. Soc. 97 (1975) 3090.
[5] K. Sandros, Acta. Chem. Scand. 27 (1973) 3021.
[6] W.G. Herkstroeter, G.S. Hammond, J. Am. Chem. Soc. 88 (1966) 4769.
[7] V. Balzani, F. Bolletta, F. Scandola, J. Am. Chem. Soc. 102 (1980) 2152.
[8] J.R. Darwent, P. Douglas, A. Harriman, C. Porter, M.c. Richoux, Coord. Chem. Rev. 4 (1982) 83.
[9] D.J. Quimby, F.R. Longo, J. Am. Chem. Soc. 97 (1975) 5111.
[10] P.S. Vincette, E.M. Voigt, K.E. Rieckhoff, J. Chem. Phys. 55 (1971) 4131.
[11] P. Douglas, S.M. Townsend, R. Ratcliffe, J. Imag. Sci. 35 (1991) 211.
[12] D. Magde, J.H. Brannon, T.L. Cremers, J. Olmsted III, J. Phys. Chem. 83 (1978) 696.
[13] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.
[14] C.A. Parker, W.T. Rees, Analyst 85 (1960) 587.
[15] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1971, p. 28.
[16] W.G. Herkstroeter, J. Am. Chem. Soc. 98 (1976) 6210.
[17] W.E. Ford, B.D. Rikter, M.A.J. Rodgers, J. Am. Chem. Soc. 111 (1989) 2362.
[18] P.A. Firey, W.E. Ford, J.R. Sounik, M.E. Kenney, M.A.J. Rodgers, J. Am. Chem. Soc. 110 (1988) 7626.
[19] J. Mc Vie, R.S. Sinclair, T. George Truscott, J. Chem. Soc., Faraday Trans. II. 74 (1978) 1870.
[20] E.I. Kapinus, V.P. Starvi, I.I. Dilung, Doklady Akedemii Nauk SSSR. 251 (1979) 1429.
[21] F. Wilkinson, J.G. Brummer, J. Phys. Chem., 1981, Ref. Data 10, 809.