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Photophysical and electron transfer studies of a few 2,6-dimethyl-4-(alkylphenyl)pyrylium and thiopyrylium derivatives [1]

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Abstract

The photoinduced electron transfer properties of pyrylium salts **1a–d** and the corresponding thiopyrylium derivatives **2a–d** were investigated. Electron transfer from biphenyl (BP) and 4,4′-dimethoxystilbene to the singlet and triplet excited states of the salts led to efficient formation of the separated radical pairs. Using BP as donor, we have estimated the extinction coefficients and also the yields of the pyranyl/thiopyranyl radicals. The yields obtained were higher than those observed in the cases of similar cationic sensitizers. We have tried to correlate the radical yields to the triplet quantum yields and also to the stability of the pyranyl radicals. The high radical ion yields observed in these cases suggest that these compounds can be used as efficient sensitizers for photoinduced electron transfer reactions. © 1997 Elsevier Science S.A.

Keywords: Photoinduced electron transfer; Pyrylium and thiopyrylium salts; Radical cations; Charge transfer complexes

1. Introduction

The study of the photophysical and spectroscopic properties of pyrylium salts and their derivatives is of considerable interest because of the potential applications of the compounds. These compounds have potential use as laser dyes [1–3], as Q switches in lasers [4,5] and as sensitizers in electrophotography [6]. Their use as liquid-crystal-forming materials [7,8] and as phototherapeutic agents [9,10] has been explored. We are interested in the photochemistry of pyrylium salts mainly because of their potential use as sensitizers for photoinduced electron transfer (PET) reactions. These cationic molecules are electron acceptors by virtue of their electron deficiency and hence should be good oxidizing agents in their excited states. A member of this group, namely 2,4,6-triphenylpyrylium (TPP) perchlorate or the tetrafluoroborate salt, has found some use as a sensitizer in PET reactions [11,12]. As TPP is positively charged, only charge exchange takes place when the radical cation of the donor is generated by an electron transfer process. Therefore, the formation of the radical ions will be enhanced and deactivation through back electron transfer (BET) will be reduced in comparison with neutral sensitizers [11]. In addition, TPP is also an efficient PET sensitizer in its triplet excited state. This allows the generation of triplet radical ion pairs and also allows examination of the effect of spin multiplicity on the fate of these intermediates [13,14]. With respect to PET oxygenation, a unique property of TPP is that it produces neither singlet oxygen nor superoxide anion [15,16]. Thus, TPP is a suitable sensitizer to study the reaction of organic radical cations with molecular oxygen. Despite the several advantages of TPP as a sensitizer, a systematic study of the electron transfer behaviour of its analogues is lacking.

As part of an extended study of the PET properties of the pyrylium class of compounds, we have now investigated the photophysical and electron transfer properties of a few 2,6-dimethyl-4-arylpyrylium and thiopyrylium derivatives, **1a–d** and **2a–d** (Scheme 1). We have examined the absorption and emission spectra of these molecules and also their triplet state properties. We have observed that both the singlet and triplet excited states of these molecules act as electron acceptors from electron rich aromatic hydrocarbons. Using the laser flash photolysis technique, we have characterized the pyrylium and thiopyrylium radicals formed as a result of electron transfer and also estimated their extinction coefficients. Using biphenyl as the electron donor, we have estimated the net efficiency of radical ion formation in these cases.

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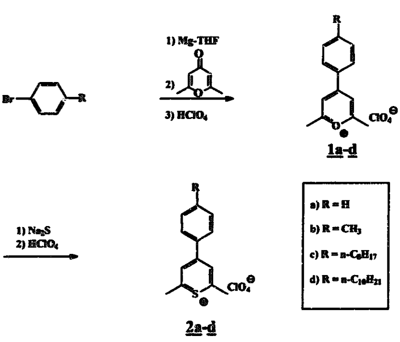

Scheme 1.

2. Experimental

2.1. Measurements

All melting points are uncorrected and were determined on a Büchi 530 melting point apparatus. IR spectra were recorded on a Perkin–Elmer 882 IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL EX-90 spectrometer. High resolution mass spectra (HRMS-FAB) were recorded on a JEOL JMS AX503 mass spectrometer. Microanalyses were performed with a Perkin–Elmer 2400 CHN Elemental Analyser. The absorption spectra were recorded on a GBC double beam UV–visible spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluorolog F 112X spectrofluorimeter with right angle geometry using 1×10^{-5} M solutions. Fluorescence quantum yields (Φ_f) were measured by using quinine sulphate in 1 N H_2SO_4 ($\Phi_f=0.54$) as the reference. Phosphorescence spectra of the compounds in a glycerol glass at 77 K were recorded on a SPEX 1934D phosphorimeter. Fluorescence lifetimes were determined using an IBH 5000 U single photon counting system. Electrochemical experiments were performed with a Wenking model POS 73 potentioscan and pulse generator. Solutions of the pyrylium or thiopyrylium salts (1×10^{-3} M) in acetonitrile, containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte, were thoroughly degassed before use. A glassy carbon electrode was used as the working electrode and a platinum gauze was used as the counter electrode. Laser flash photolysis experiments were carried out by employing an Applied Photophysics model LKS-20 laser kinetic spectrometer equipped with a GCR-12 Series Quanta Ray Nd:YAG laser. The analysing and laser beams were fixed at right angles to each other. The laser energy was 60 mJ at 355 nm. For quantum yield measurements, optically matched solutions of benzophenone in benzene were employed as reference (R). Values of $\Phi_T^R=1$ and $\epsilon_T^R=7600$ M^{-1} cm^{-1} at 530 nm for the benzophenone triplet were used in the calculations [17].

2.2. Materials

The pyrylium derivatives **1a–d** and the thiopyrylium derivatives **2a–d** were synthesized by the general route outlined in Scheme 1. The appropriate Grignard reagent was prepared through the reaction of 1-(4-bromophenyl)alkane (0.02 mol) and magnesium (0.025 mol) in dry THF (20 ml). This reagent was added to a suspension of 2,6-dimethyl-4-pyrone (0.02 mol) in dry THF (50 ml) at 0 °C. The solution was allowed to warm to room temperature and stirred for 30 min. An ice cold solution of 10% perchloric acid (100 ml) was added and the precipitated pyrylium salt was collected by filtration. The salt thus obtained was dissolved in dichloromethane and reprecipitated by adding ether. This process was repeated until a constant melting point was obtained. **1a**: yield 34%; m.p. 224–225 °C (lit. [18] m.p. 217–220 °C). **1b**: yield 34%; m.p. 211–212 °C; IR (neat) 3094, 2931, 2860, 1643, 1092 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.35 (s, 3H), 2.9 (s, 6H), 7.3–8.2 (m, 6H); analysis, calculated for $C_{14}H_{15}O_5Cl$: C 56.36, H 5.07; found: C 56.21, H 5.34. **1c**: yield 34%; m.p. 129–130 °C; IR (neat) 3095, 2933, 2860, 1649, 1094 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.9–1.5 (m, 15H), 2.75 (t, 2H), 2.9 (s, 6H), 7.3–8.2 (m, 6H); HRMS calculated for cation $C_{21}H_{29}O^+$, 297.2218, found 297.2232; analysis, calculatedd for $C_{21}H_{29}O_5Cl$: C 63.61, H 7.38; found: C 63.26, H 7.77. **1d**: yield 33%; m.p. 131–132 °C; IR (neat) 3098, 2931, 2859, 1642, 1097 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.9–1.5 (m, 19H), 2.75 (t, 2H), 2.9 (s, 6H), 7.3–8.2 (m, 6H); HRMS calculated for cation $C_{23}H_{33}O^+$, 325.2531, found 325.2530; analysis, calculated for $C_{23}H_{33}O_5Cl$: C 65.06, H 7.84; found: C 65.05, H 8.11.

The thiopyrylium derivatives **2a–d** were prepared from **1a–d**. In a typical run, a solution of Na_2S (2 mmol) in water (5 ml) was added to a cold solution of **1a** (1 mmol) in acetone maintained at 5 °C. The solution was allowed to stand for 30 min and acidified with 5 ml of 10% perchloric acid. The mixture was cooled and filtered to yield the thiopyrylium perchlorate **2a**. Similar procedures were adopted for the preparation of **2b–d**. These were purified by repeated dissolution in dichloromethane, followed by reprecipitation by adding ether. **2a**: yield 66%; m.p. 224–225 °C; IR (neat) 3098, 2930, 1642, 1086 cm^{-1}; ^{1}H NMR (90 MHz, DMSO) δ 3.1 (s, 6H), 7.3–8.0 (m, 5H), 8.55 (s, 2H). **2b**: yield 66%; m.p. 204–205 °C; IR (neat) 3098, 2930, 2860, 1644, 1090 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.4 (s, 3H), 3.1 (s, 16H), 7.3–7.8 (m, 4H), 8.55 (s, 2H); analysis, calculated for $C_{14}H_{15}O_4SCl$: C 53.50, H 4.81; found: C 53.48, H 5.01. **2c**: yield 85%; m.p. 78–79 °C; IR (neat) 3098, 2933, 2861, 1644, 1090 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.9–1.5 (m, 15H), 2.7 (t, 2H), 3.1 (s, 6H), 7.3–8.0 (m, 4H), 8.55 (s, 2H); HRMS calculated for cation $C_{21}H_{29}S^+$, 313.1990, found 313.1969; analysis, calculated for $C_{21}H_{29}O_4SCl$: C 61.14, H 7.09; found: C 60.99, H 7.53. **2d**: yield 83%; m.p. 82–83 °C; IR (neat) 3099, 2927, 2859, 1645, 1091 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.9–1.5 (m, 19H), 2.7 (t, 2H), 3.1 (s, 6H), 7.3–8.0 (m, 4H), 8.55 (s, 2H); HRMS calculated for cation

$C_{23}H_{33}S^+$, 341.2303, found 341.2289; analysis, calculated for $C_{23}H_{33}O_4SCl$: C 62.70, H 7.56; found: C 62.53, H, 8.04.

All the quenchers used were commercial samples and were recrystallized before use from suitable solvents. Spectroscopic grade solvents were used throughout and solutions for flash photolysis experiments were deaerated with argon for 15 min prior to the experiments.

3. Results and discussion

3.1. Photophysical properties

3.1.1. Absorption and Emission Properties

The absorption and emission properties of substrates **1a–d** and **2a–d** in acetonitrile are summarized in Table 1. Examination of Table 1 shows that substitution of an alkyl group at the *para* position of the phenyl ring leads to slight changes in the photophysical properties of these compounds. Similar observations were made by earlier workers in this area [19,20]. In acetonitrile solution at low concentration, the 2,6-dimethyl-4-arylpyrylium and thiopyrylium cations, as their ClO_4^- salts, are expected to exist as independently solvated ions [20]. Under these conditions their singlet energies (E_{00}), fluorescence quantum yields (Φ_f) and fluorescence lifetimes (τ_f) depend on the specific substitution of the 4-aryl group [20]. In order to explain this behaviour, it was suggested that these cations have two excited singlet states with similar energies and the substituent determines which of these has the lower energy. In this regard, Ecoffet et al. recently reported that theoretical calculations and spectroscopic measurements show that there are two close lying excited states for triarylpyrylium cations [21]. The absorption spectra of all these compounds are red shifted by ≈20 nm in dichloromethane solution (Table 1). Such a red shift in the lowest energy absorption in nonpolar solvents was observed earlier for several pyrylium salts [22,23].

3.1.2. *Laser flash photolysis studies*

Laser flash photolysis of **1a–d** and **2a–d** in acetonitrile or dichloromethane saturated with argon led to the formation of transients characterized by strong bleaching below 400 nm and broad absorption above 400 nm. Representative examples of the transient absorption spectra are given in Fig. 1 and the values of the absorption maxima are given in Table 2. The transients in all cases decay with first order kinetics and the decays are independent of the concentration of these materials (i.e., no self quenching is evident). The lifetimes of these transients are listed in Table 2. The transients from all these compounds were quenched by oxygen. Hence we assign these transients as triplets of these substrates. We have determined the oxygen quenching rate constants ($k_q(O_2)$) in all the cases and the values are reported in Table 2. The $k_q(O_2)$ values we obtained are similar to the values obtained for TPP by Akaba and co-workers [15].

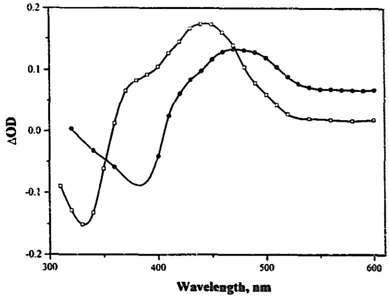

Fig. 1. Transient absorption spectra of **1a** (□) and of **2c** in dichloromethane (●) recorded at 60 ns and 200 ns after the laser pulse respectively.

As mentioned above, all the transient absorption spectra obtained showed strong bleaching in the region of the ground state absorptions. This enabled us to determine the extinction coefficients of the triplet absorptions by the singlet depletion method [24]. This method assumes that the triplet does not absorb in the region of the depletion. The maxima of the bleaching coincided with the absorption maxima for all compounds in dichloromethane solution (except for **1a**, for which the bleaching maximum was blue shifted by ≈10 nm). The values of the extinction coefficients are reported in Table 2. Using these extinction coefficients, we have determined the triplet quantum yields Φ_T for all the substrates by the relative actinometry method [25]. The values thus obtained are given

Table 1

Absorption maxima (λ_{max}(Abs)), extinction coefficients (ϵ_{max}), emission maxima (λ_{max} (Em)), fluorescence quantum yields (Φ_f), and fluorescence lifetimes (τ_f) for pyrylium derivatives **1a–d** and thiopyrylium derivatives **2a–d** in acetonitrile. Values given in parentheses are those in dichloromethane

Compound	λ_{max}(Abs)/nm	$\epsilon_{max}/(M^{-1} cm^{-1})$	λ_{max}(Em)/nm	Φ_f	τ_f/ns
1a	326 (343)	2.3×10^3	462	0.10	12.1
1b	347 (365)	2.9×10^4	435	0.28	8.7
1c	350 (370)	2.9×10^4	435	0.32	8.0
1d	350 (370)	2.9×10^4	435	0.37	8.0
2a	335 (350)	1.88×10^4	471	0.07	12.3
2b	365 (387)	2.5×10^4	471	0.35	5.1
2c	365 (387)	2.5×10^4	471	0.45	5.8
2d	365 (387)	2.5×10^4	471	0.44	5.7

Table 2
Triplet–triplet absorption maxima (λ^{T}_{max}), extinction coefficients (ϵ^{T}_{max}), triplet quantum yields(Φ_T), triplet lifetimes (τ_T), triplet energies (E_T) and oxygen quenching rate constants ($k_q(O_2)$) for pyrylium derivatives **1a–d** and thiopyrylium derivatives **2a–d** in dichloromethane solution

Compound	λ^{T}_{max}(Abs)/nm	ϵ^{T}_{max}(Abs)/(M^{-1} cm^{-1})	Φ_T	τ_T/µs	E_T/(kcal M^{-1})	$k_q(O_2)$/(M^{-1} s^{-1})
1a	440	2.7×10^4	0.5	0.3	63.1	1.5×10^8
1b	430	5.2×10^4	0.2	2.4	61.1	5.9×10^7
1c	430	5.4×10^4	0.2	2.7	–	4.8×10^7
1d	430	6.0×10^4	0.2	2.7	–	5.1×10^7
2a	460	2.2×10^4	0.4	0.3	64.3	9.9×10^7
2b	470	1.4×10^4	0.3	3.0	64.5	3.8×10^7
2c	470	1.4×10^4	0.3	3.0	–	3.7×10^7
2d	470	1.6×10^4	0.3	3.0	–	3.9×10^7

in Table 2. Note that Φ_T values for **1a** and **2a** are higher than those of the other compounds.

3.2. *Electron transfer studies*

3.2.1. *Fluorescence quenching studies*

We have observed that electron rich aromatic hydrocarbons such as biphenyl (BP) and naphthalene (NP) quench the fluorescence of **1a–d** and **2a–d** very efficiently. It is known from the literature that pyrylium salts form charge transfer (CT) complexes with polycyclic condensed arenes and substituted benzenoid compounds [26,27]. If CT complexes are formed, then fluorescence quenching may involve both static and dynamic mechanisms. In order to see whether any CT complex is formed, the absorption spectra of the pyrylium salts **1a–d** and thiopyrylium salts **2a–d** were recorded in the presence of various concentrations of NP and BP.

Fig. 2 shows the absorption spectra of **1a** in acetonitrile in the absence and presence of 0.1 M naphthalene. The red end of the absorption shifts to longer wavelengths in the presence of naphthalene, indicating the formation of a CT complex. The difference absorption spectrum (λ_{max} 372 nm) shown in Fig. 2 corresponds to the CT complex. It can be noted from Fig. 2 that CT formation is very weak at 0.1 M naphthalene concentration. Similar behaviour was noted for **1b–d** and **2a–d**. However, we did not observe any complex formation when biphenyl was added to the pyrylium salt solutions. We also did not observe any emission from the CT complexes in acetonitrile solutions.

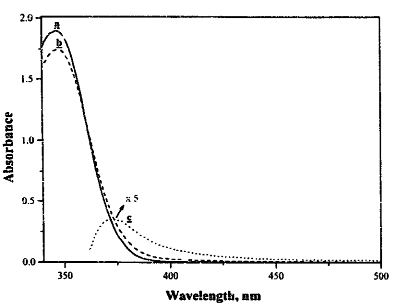

Fig. 2. (a) Absorption spectrum of **1a**, (b) absorption spectrum of **1a** in the presence of 0.1 M naphthalene and (c) difference absorption spectrum obtained by subtracting (a) from (b). All the spectra were recorded in acetonitrile solution.

Using BP and NP as the quenchers, plots of the fluorescence intensity vs. quencher concentration [Q] fitted the Stern–Volmer equation

$$\frac{I_0}{I} = 1 + K_{SV}[Q] \qquad (1)$$

where K_{SV} ($=k^{S}_{q}\tau$) is the Stern–Volmer constant. Quencher concentrations varied from $(1\text{–}5)\times10^{-3}$ M in these studies. The K_{SV} values and the quenching rate constants k^{S}_{q} calculated from the K_{SV} values are given in Table 3. The diffusion rate calculated for **1a** using the Smoluchowski equation, assuming a radius of 4 Å, is 1.75×10^{10} M^{-1} s^{-1}. We can see that the quenching rates obtained are close to the diffusion controlled limit. We have observed CT formation between the substrates and naphthalene. CT formation some times leads to an upward curvature in the Stern–Volmer plots, indicating a combined dynamic and static quenching process [28]. In the present case, no curvature was observed and the fits to Eq. (1) were very good (correlation coefficient >99%). This indicates that only dynamic quenching is taking place in the concentration range studied.

3.2.2. *Electrochemical studies*

As will be discussed below, the fluorescence quenching of **1a–d** and **2a–d** with electron rich aromatics occurs by electron transfer quenching of the singlet excited state of these salts, as indicated in Eq. (2).

$$^{*}P^{+} + Q \rightarrow P^{\bullet} + Q^{\bullet +} \qquad (2)$$

In order to estimate the free energy change (ΔG_{et}) associated with this electron transfer reaction, we have measured the reduction potentials of the salts **1a–d** and **2a–d** in acetonitrile by using cyclic voltammetry. In acetonitrile solution, the first reduction peak for these substrates appeared in the range −0.48 to −0.65 V vs. the SCE (Table 3). The cyclic voltammograms of these substrates did not show a reverse anodic peak and the values reported in Table 3 as reduction potentials

Table 3
Excitation energies ($E_{0,0}$), reduction potentials (E_{red}), free energies of electron transfer to the singlet state (ΔG_{et}), Stern–Volmer quenching constants (K_{SV}) and singlet quenching rate constants (k_q^S) for the pyrylium salts **1a–d** and thiopyrylium salts **2a–d** in acetonitrile solution

Compound	$E_{0,0}$/(kcal M^{-1})	E_{red}/V vs. SCE	Biphenyl			Naphthalene		
			ΔG_{et}/(kcal M^{-1})	K_{SV}/M^{-1}	k_q^S/(M^{-1} s^{-1})	ΔG_{et}/(kcal M^{-1})	K_{SV}/M^{-1}	k_q^S/(M^{-1} s^{-1})
1a	77.5	−0.48	−21.2	188	1.6×10^{10}	−24.9	213	1.8×10^{10}
1b	75.5	−0.62	−16.0	104	1.2×10^{10}	−19.7	130	1.5×10^{10}
1c	74.9	−0.63	−15.1	103	1.3×10^{10}	−18.8	118	1.5×10^{10}
1d	74.9	−0.63	−15.1	98	1.2×10^{10}	−18.8	123	1.5×10^{10}
2a	74.8	−0.57	−16.1	48	3.9×10^{9}	−20.0	57	4.6×10^{9}
2b	70.3	−0.55	−12.4	67	1.3×10^{10}	−16.1	97	1.9×10^{10}
2c	71.0	−0.58	−12.4	80	1.4×10^{10}	−16.1	91	1.6×10^{10}
2d	70.9	−0.57	−12.4	73	1.3×10^{10}	−16.1	83	1.5×10^{10}

(E_{red}) are the peak potentials. The absence of the reverse anodic peak in the cyclic voltammogram is reported in the literature for several pyrylium salts [29–31]. It is suggested that pyrylium salts substituted with H and CH_3 in position 2 or 4 of the pyrylium ring show no reverse anodic peak owing to the rapid and irreversible dimerization of the pyranyl radicals formed in the reduction [30].

The oxidation potentials of the donor molecules are known in the literature [32]. Using the redox potentials, the free energy change for electron transfer from the donors to the singlet excited states of the salts **1a–d** and **2a–d** can be calculated by the Weller equation [33], Eq. (3)

$$\Delta G_{et}=\left[(E_{D^+/D}-E_{A/A^-})-\frac{e^2}{\epsilon d}\right]-E_{0,0} \qquad (3)$$

where $E_{D+/D}$ and $E_{A/A}-$ are the electrochemical oxidation potential of the donor and the reduction potential of the acceptor, respectively, and $E_{0,0}$ is the excitation energy of the acceptor salts. The term $e^2/\epsilon d$ in Eq. (3) represents the energy gained in bringing the radical ion species into an encounter distance d in a solvent of relative permitivity ϵ. Since the pyranyl radicals are not charged, this term has no meaning in the present context and is ignored in the calculations. The ΔG_{et} values calculated are given in Table 3. ΔG_{et} values are in the range −16 to −20 kcal M^{-1} and should lie in the normal region according to the Marcus equation [34].

3.2.3. Laser flash photolysis studies: triplet quenching experiments

The quenching of the triplets of **1a–d** and **2a–d** by electron donors such as BP, NP and 4,4′-dimethoxystilbene (DMS) was attempted by laser flash photolysis. The bimolecular triplet quenching rate constants (k_q^T) were obtained by measuring the pseudo-first-order rate constants (k_{obs}) at different quencher concentrations [Q] and plotting the data according to Eq. (4)

$$k_{obs}=k_0+k_q^T[Q] \qquad (4)$$

where k_0 ($=1/\tau_0$) is the decay rate in the absence of any quencher. In these experiments, the quencher concentration [Q] was varied over a narrow range of $(1–4)\times10^{-4}$ M. When BP was used as the quencher, good single exponential fits were obtained for the decay, and we obtained quenching rate constants k_q^T in the range $(3.5–20)\times10^8$ M^{-1} s^{-1}. When NP was the quencher, the decays could not be fitted well to a single exponential, especially at higher NP concentrations, and hence the data could not be analysed properly. For the DMS quencher, k_q^T values were measured for only **1a** and **1b** and the values obtained were in the range $(1–2)\times10^9$ M^{-1} s^{-1}.

Triplet energies of **1a–d** and **2a–d** are not known in the literature. In order to calculate the triplet energies of these compounds, phosphorescence spectra of representative examples (**1a,b** and **2a,b**) were recorded. Fig. 3 shows the phosphorescence spectra of **1a** and **2a** in glycerol glass at 77 K. The triplet energies calculated from the 0–0 band of the phosphorescence spectra are listed in Table 2. Using these values of the triplet energy, the free energies for electron transfer (ΔG_{et}^T) from the hydrocarbons to the triplet excited states of **1a–d** and **2a–d** were calculated. The values obtained are in the range −1.6 to −10.5 kcal M^{-1}. The ΔG_{et}^T values are only weakly exothermic and lie in the normal region according to Marcus theory. Consequently, the quenching rate constants are all low, $(3.5–20)\times10^8$ M^{-1} s^{-1}, and there is a good correlation between ΔG_{et}^T and k_q^T values in these cases.

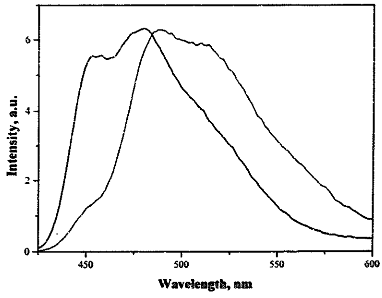

Fig. 3. Phosphorescence emission spectra of **1a** (———) and **2a** (—) in glycerol glass at 77 K.

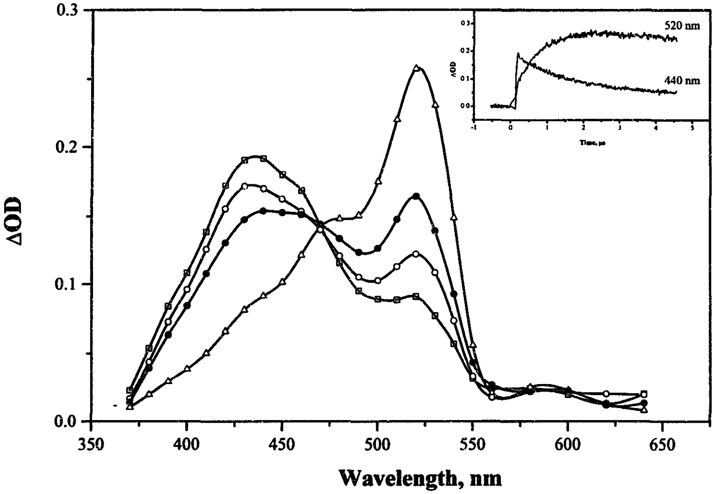

Fig. 4. Transient absorption spectra at (▲) 0.2, (○) 0.35, (●) 0.55 and (△) 2 μs following the 355 nm laser pulse excitation of **1a** (2×10^{-4} M) in the presence of 4,4′-dimethoxystilbene (2×10^{-4} M) in acetonitrile. The inset shows the decay of the transient at 440 nm and growth at 520 nm.

At the very low concentration used for these studies (4×10^{-4} M), quenching of the singlets of **1a–d** and **2a–d** by the quenchers is negligible (2–7% for **1a** and somewhat lower for other substrates, based on K_{SV} values). Hence the transient absorption spectra recorded under these conditions will give us information about the triplet quenching pathways. The transient absorption spectra of **1a** in the presence of DMS (2×10^{-4} M) obtained at different time intervals following the laser pulse are shown in Fig. 4. The spectrum immediately following the pulse showed mainly the absorption due to the triplet at 440 nm. The absorption at 520 nm, which is assigned to the radical cation of DMS [32], grows with time. The triplet decay time matched very well with the growth of the radical cation. This indicated that the decay of the triplet leads directly to the formation of radical ions by an electron transfer mechanism in this case.

Transient absorption spectra of **1a** recorded in the presence of BP (10^{-4} M) also showed peaks at 440 nm due to the triplets and very weak absorptions above 680 nm corresponding to the radical cation of BP. However, growth of the radical cation is not observed in these cases. This may be due to the lower extinction coefficients of the radicals (see below) compared with those of the triplets. In the case of DMS, the growth becomes very noticeable because of the very high extinction coefficient of $DMS^{\cdot +}$ ($\epsilon = 65\,000$ M^{-1} cm^{-1}) [32].

3.2.4. Singlet quenching experiments

Transient absorption spectra of **1a–d** and **2a–d** were recorded in the presence of 0.1 M biphenyl and naphthalene. The transient absorption spectrum in the presence of DMS at high concentrations was not recorded because this compound has substantial absorption at 355 nm under these conditions. At 0.1 M concentration of BP, more than 90% of the singlets of **1a–d** and **2a–d** were quenched by BP. The transient absorption spectra obtained in the case of **1a** and **2c** are shown in Figs. 5 and 6, respectively. In the case of the pyrylium salts **1a–d**, the transient spectra were characterized by absorptions at 385 nm and at 680 nm. The 680 nm peak is due to the well known BP radical cation [32] and hence we assign the 385 nm peak to the pyranyl radicals formed as a result of electron transfer according to Eq. (2). The absorption maxima of all the pyranyl and thiopyranyl radicals derived from **1a–d** and **2a–d** are listed in Table 4.

In the above experiments, $BP^{\cdot +}$ is formed by electron transfer from biphenyl to the excited states of the pyrylium salts according to Eq. (2), and hence the concentration of $BP^{\cdot +}$ should be equal to the concentration of the pyranyl/thiopyranyl radicals. This enabled us to determine the extinction coefficients of the radical absorptions using the following equation

$$\epsilon_{PY^{\cdot}} = \frac{\Delta OD_{PY^{\cdot}} \cdot \epsilon_{BP^{\cdot +}}}{\Delta OD_{BP^{\cdot +}}} \qquad (5)$$

where the ϵ are the extinction coefficients and the ΔOD are the end-of-pulse optical densities at the corresponding absorption maxima. A value of 14.5×10^{3} M^{-1} cm^{-1} for the extinction coefficient of $BP^{\cdot +}$ was used for the calculation [32]. $\epsilon_{PY^{\cdot}}$ values of the radicals thus obtained are given in Table 4.

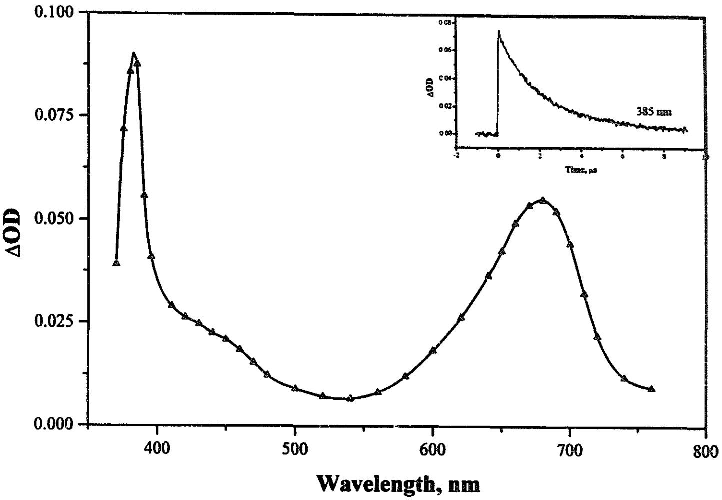

Fig. 5. Transient absorption spectrum of **1a** (2×10^{-4} M) in the presence of biphenyl (0.1 M) in acetonitrile at 200 ns following the laser pulse. The inset shows the decay of the transient at 385 nm.

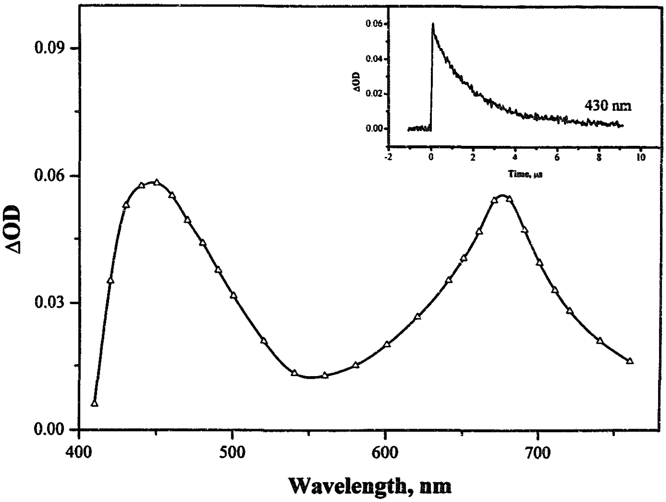

Fig. 6. Transient absorption spectrum of **2c** (2×10^{-4} M) in the presence of biphenyl (0.03 M) in acetonitrile at 200 ns after the laser pulse. The inset shows the decay of the transient at 430 nm.

The radical ions decay by second order kinetics. As no long-lived absorptions due to product formation were observed, it was assumed that decay occurs by BET. Monitoring the decay of $BP^{\cdot+}$ at 680 nm, the decay rate was calculated by second order equal concentration kinetics. The value of the rate constant obtained ($=k_2/\epsilon$) was in the range

Table 4
Absorption maxima ($\lambda_{max}^{Py^\bullet}$), extinction coefficients ($\epsilon_{Py^\bullet}$) and quantum yields of formation (Φ_{ion}) for the pyranyl and thiopyranyl radicals obtained from **1a–d** and **2a–d** in acetonitrile solution

Compound	$\lambda_{max}^{Py^\bullet}$/nm	$\epsilon_{Py^\bullet}$/(M^{-1} cm^{-1})	Φ_{ion}
1a	385	1.9×10^4	0.42
1b	385	2.6×10^4	0.20
1c	385	2.6×10^4	0.17
1d	385	2.5×10^4	0.19
2a	385	2.2×10^4	0.51
2b	430	1.4×10^4	0.38
2c	430	1.4×10^4	0.35
2d	430	1.6×10^4	0.35

$(1–1.2) \times 10^7$ cm s^{-1}. Substituting for ϵ, we get k_2 in the region of 1.5×10^{11} M^{-1} s^{-1}. This value is an order of magnitude slower compared with the BET rates in the dicyanonaphthalene/BP system studied under identical conditions.

With BP as the donor, the yields of the radicals (Φ_{ion}) in the case of **1a–d** and **2a–d** were determined as follows. Optically matched solutions of benzophenone in benzene (actinometer) and of pyrylium salts containing BP (0.1 M) in acetonitrile were deaerated and flash photolysed at 355 nm. Φ_{ion} values were then calculated according to Eq. (6)

$$\Phi_{ion} = \Phi_T^R \frac{\Delta OD_{BP^{\bullet+}} \epsilon_T^R}{\Delta OD_T^R \epsilon_{BP^{\bullet+}}} \tag{6}$$

where the ΔOD are the end-of-pulse absorbance changes, the ϵ are the extinction coefficients, and "R" refers to the reference compound benzophenone. From the known values of Φ_T^R, ϵ_T^R and $\epsilon_{BP}^{\bullet+}$ (see above), Φ_{ion} values were calculated, and these values are given in Table 4.

The Φ_{ion} values obtained are much larger than those observed for similar cationic sensitizers [35,36]. An inspection of the values shows that Φ_{ion} values are higher for the thiopyrylium derivatives **2a–d** compared with their pyrylium analogues **1a–d**. Among the pyrylium salts, **1a** exhibits a much higher Φ_{ion} value than **1b–d**. The same trend is seen among the thiopyrylium salts, where **2a** shows a higher value of Φ_{ion}. We believe that the primary factor responsible for the high values of Φ_{ion} for **1a** and **2a** is their higher triplet yields. It is well established that electron transfer involving triplet excited states leads to efficient separation of ion pairs [37,38]. This is a consequence of the fact that recombination in the geminate triplet radical pair to regenerate the starting materials is spin forbidden. An inspection of Tables 2 and 4 shows that there is good correlation between the triplet yields and Φ_{ion} values.

Another factor responsible for the variation in the Φ_{ion} values is the stability of the pyranyl and thiopyranyl radicals. Niizuma and co-workers have studied the formation of pyranyl and thiopyranyl radicals by photoillumination of several pyrylium and thiopyrylium salts in THF solution [39,40]. They observed high Φ_{ion} values for the thio derivatives compared with the oxygen analogues. They also observed that electron donating substituents decrease the Φ_{ion} values. These authors have suggested that electron donating substituents destabilize the lowest unoccupied molecular orbital (LUMO) of the cation and, as a consequence, destabilize the highest occupied molecular orbital (HOMO) of the radical. This argument is supported by the observation that pyrylium salts substituted with electron donating groups have a higher absolute value of reduction potential [26,31]. Comparing the pyranyl and thiopyranyl radicals, the oxygen atom destabilizes the radical more than sulphur does and hence the radical yield will be lower in the case of pyrylium salts. The Φ_{ion} values that we have observed are also in line with these observations.

In contrast to the behaviour of BP, the transient absorption spectra of **1a–d** in the presence of NP (0.1 M) in acetonitrile did not show absorptions due to $NP^{\bullet+}$ at 660 nm or the pyranyl radicals at 385 nm. Instead, the transient absorption spectra in these cases showed maxima at 460 and 560 nm. The transient absorption spectrum obtained for the **1a**/NP system is given in Fig. 7. In the case of the thiopyrylium derivatives **2a–d**, the transient absorption spectra under these conditions showed bands at 480 and 560 nm. In all cases, these absorptions were observed within the laser pulse. The absorptions have slightly different decay rates, with the 460 (or 480) nm species decaying faster than the 560 nm species. Addition of $LiClO_4$ (0.1 M) or saturating the solution with oxygen did not lead to any noticeable change in the spectra. Decay rates were only marginally affected by the presence of oxygen. The transient spectrum in a nonpolar solvent such as dichloromethane, however, was slightly different (Fig. 7). In this case, the 560 nm peak was much more intense compared with the 460 nm peak.

In the case of the **1a**/NP system, irradiation leads to the excitation of the CT complex. The photochemistry of CT complexes has been reviewed by several authors [41–43]. According to Mulliken's theory [44], excitation of a CT complex leads to the ion pair state. In general, three mechanistic pathways are available for the excited states of these complexes. Path 1 leads to the formation of the triplet state of the donor arising from a fast ISC process occurring in the non-equilibrated FC state, as observed by Orbach and Ottolenghi [41]. The second pathway leads to the formation of separated ion pairs, which undergo BET in microsecond time scales [45]. The third route involves fast formation of the ion pairs, which undergo extremely rapid BET (30–300 ps) [46,47]. In the last case, the transient absorption will not be observed in the nanosecond time scale. In the present case of the **1a**/NP system, the first two pathways can be ruled out owing to the lack of spectroscopic evidence (absorptions due to radicals or triplets are not detected in these experiments).

In a similar study, Lin and Schuster have shown that 2,6-di-*t*-butyl-6-arylpyrylium cation forms a CT complex when 2-naphthalenesulphonate anion is used as the counter ion [20]. Excitation of this complex in dimethyl carbonate solution led to the formation of ion radicals, as evidenced by the absorptions at 485 nm (pyranyl radical) and 650 nm (naphthalene radical cation). These radicals were short-lived and

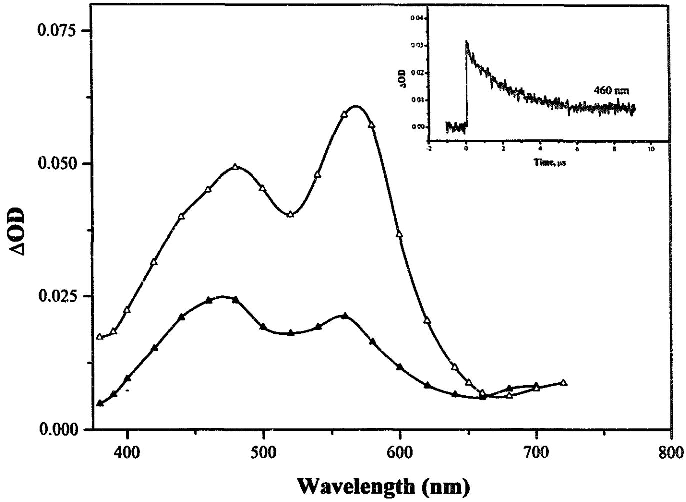

Fig. 7. Transient absorption spectra of **1a** (2×10^{-4} M) at 300 ns after the laser pulse in the presence of naphthalene (0.1 M) in (▲) acetonitrile and (△) dichloromethane. The inset shows the decay of the transient at 460 nm in acetonitrile.

decayed to the ground state by BET within 330 ps. In the present case we did not see the absorptions due to the radicals, most probably because of their short lifetimes. A fraction of these ions decays to the observed transient species (Fig. 7), and we assign this species as the triplet excited state of the CT complex.

It is widely recognized (based on the enhancement of phosphorescence in CT complexes) that intermolecular CT interactions may provide a general mechanism for the induction of spin–orbit coupling, leading to triplet formation [48,49]. Lim et al. [50] suggested a "selection rule" for ISC in CT complexes which states that effective ISC to the ^{3}(CT)* state requires a locally excited triplet state, ^{3}LE*, in proximity to the CT singlet state. In the light of these studies, we assign the 460 nm species to a LE triplet state and the 560 nm species to the ^{3}(CT)*. The ^{3}LE* has the excitation localized more on the pyrylium moiety. This assignment is supported by the fact that, in the case of **2a–d**, this peak is shifted to 480 nm (note that the triplet absorption maxima for **1a–d** are at 430–440 nm whereas those for **2a–d** occur at 460–470 nm). Also, in dichloromethane solution, where the CT complex is more rigid, the absorption due to ^{3}(CT)* at 560 nm is much more intense than that at 460 nm due to ^{3}LE*. In these experiments we have noted that decay of these species leads to small residual absorptions, indicating the formation of products on longer time scales. However, the transient absorption spectra recorded at long delay times were very weak and no definite assignment could be made in this case. We believe that a major fraction of the triplet excited states of the CT complex decays to the ground state to regenerate the starting materials.

4. Conclusions

We have investigated the photophysical and electron acceptor properties of pyrylium salts **1a–d** and the corresponding thiopyrylium derivatives **2a–d**. Electron transfer from hydrocarbons such as biphenyl and 4,4′-dimethoxystilbene to the singlet and triplet excited states of the salts leads to efficient formation of the separated radical pairs. We have tried to correlate the radical yields to the appropriate triplet quantum yields and also to the stability of the pyranyl radicals. The important point to note here is that yields of radical ions were very high and hence these compounds can be effectively used as sensitizers for photoinduced electron transfer reactions.

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