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Triplet state and photolysis of *S*-phenyl 1-thionaphthoate

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Abstract

Energy transfer between *S*-phenyl 1-thionaphthoate (1-SPTN) and several triplet-state energy donors and acceptors were studied by transient absorption spectra. The results indicate that the energy transfer can occur efficiently either from energy donors to 1-SPTN or from 1-SPTN to energy acceptors. The energy transfer rate constant of xanthene to 1-SPTN is 1.4×10^{10} s^{-1} mol^{-1} dm^3. This means that the energy transfer process is diffusion controlled. The triplet-state energy of 1-SPTN is about 252 kJ mol^{-1}, estimated from the energy transfer processes and the phosphorescence emission. Photolysis of 1-SPTN results in two main products: diphenyldisulphide and 1,1′-binaphthyl. The photolysis proceeds via the triplet state mainly, as proved by external magnetic effect.

Keywords: Photolysis; Photoinitiators; Triplet states

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1. Introduction

S-phenyl thiobenzoate (SPTB) and its derivatives are a new series of efficient photoinitiators in photoinduced polymerization [1–3]. The photolysis and the mechanism of the cleavage of these compounds have been studied. The cleavage of the compounds is from their excited triplet state to form a triplet-state radical pair. Further processes produce different products of the photolysis and the product distribution is affected by the media and magnetic field. The absorptions of these compounds, however, are mostly shorter than 300 nm. So, in applications they need a sensitizer as a coinitiator, forming a photoinitiator system to extend the absorption region. In the sensitized photolysis of SPTB, the products are quite different from that obtained in direct photolysis [4]. Another method for extension of absorption is the modification of the molecular structure. In this work, *S*-phenyl 1-thionaphthoate (1-SPTN) has been synthesized to extend the absorption region to longer wavelength. Triplet-state properties of 1-SPTN have been studied with transient absorption and energy transfer between 1-SPTN and energy donor or acceptor. Photolysis of this compound has also been measured and the results are discussed.

2. Experimental details

1-SPTN was prepared by the reaction between 1-naphthoyl chloride and thiophenol in the presence of a suitable amount of triethylamine which was used as promoter [5,6]. The product was characterized by ^{1}H nuclear magnetic resonance, IR and mass spectroscopy (MS) and the results indicated that the expected product was obtained. The compounds used as triplet donor or acceptor were purchased from Aldrich and Fluka companies with highest grade. All the solvents used were spectro-grade (Aldrich and Fluka) and were used without further purification.

Time-resolved spectra were recorded with a flash photolysis apparatus (Nd-doped yttrium aluminium garnet laser; excitation wavelength, 355 nm; 3 ns full width at half-maximum pulse; 40 mJ pulse^{-1}; rise time of the detection system, 3 ns) which has been described in an earlier report [7]. The solutions were bubbled with Ar for 20 min to remove oxygen before they were detected. The absorption of the samples at 355 nm had an optical density (OD) of 0.2–0.4 and the absorption of energy acceptor in the solution was lower, i.e. OD < 0.01 at 355 nm.

The photolytic products were analysed qualitatively and quantitatively by gas chromatography GC) (Shimadzu GC-7AG) and GC–MS (VG, Trio 2000).

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3. Results and discussion

The UV–visible absorption spectrum of 1-SPTN is shown in Fig. 1. The absorption maximum is about 305 nm and the end of the absorption extends to 370 nm. Compared with that of *S*-phenyl thiobenzoate [3] the absorption region of 1-SPTN is bathochromically shifted about 60 nm.

When the solution of 1-SPTN in acetonitrile was irradiated by a 355 nm laser pulse, a transient absorption spectrum was obtained, as shown in Fig. 2. The absorption maximum is at about 480 nm. This absorption decay lifetime is 8.7 μs in the absence of O_2 and it can be quenched quickly by O_2. In a non-degassed solution the decay lifetime is 0.40 μs. Thus this absorption could be considered as the triplet–triplet (T–T) absorption of 1-SPTN.

A triplet-state energy donor, benzophenone (BP), was introduced into the 1-SPTN solution in acetonitrile and most of the irradiation light was absorbed by BP. In BP–1-SPTN solution a spectrum shift of the transient absorption could be observed on increase in the delay time. At the beginning after the irradiation of the laser pulse, a T–T absorption spectrum of BP was obtained; the absorption maximum is at 520 nm. On increase in the delay time, the absorption maximum shifted to 480 nm. This means that the triplet-state energy of BP is transferred to 1-SPTN after BP is excited and the triplet state is formed via intersystem crossing. This energy transfer process is evidently observed in the decay processes of BP and formation and decay processes of 1-SPTN, shown in Fig. 3. In the BP–1-SPTN system the decay of the T–T absorption of BP is faster than in the absence of 1-SPTN, and a formation process of the T–T absorption of 1-SPTN is recorded (in about 0.8 μs). After formation the decay process of the T–T absorption of 1-SPTN in the BP–1-SPTN system is similar to that in the 1-SPTN solution without BP; the triplet-state decay lifetime is about 8.7 μs.

Xanthone (XT), a triplet-state energy donor with higher triplet-state energy [8], gives a more obvious change in the transient T–T absorption spectra. The T–T absorption maximum of XT is at 630 nm. In the presence of 1-SPTN in the solution of XT in acetonitrile, when the molecules of XT were excited by the laser pulse, only the T–T absorption of XT was observed in shorter delay time. On increase in the delay time, the T–T absorption of 1-SPTN formed at 480 nm and the peak at 630 nm disappeared gradually, as shown in Fig. 4. In this case, as can be seen in Fig. 5, the decay of the T–T absorption of XT is very fast. The triplet-state decay lifetime is 0.34 μs when the concentration of 1-SPTN is 1.5×10^{-4} mol dm^{-3} (it is 1.1 μs in the absence of 1-SPTN). The T–T absorption of 1-SPTN became a maximum in about 0.8 μs and decayed, similar to that in the BP–1-SPTN system. These results indicate evidently that the molecules of XT transfer their triplet-state energy to the molecules of 1-SPTN to form the triplet state of 1-SPTN.

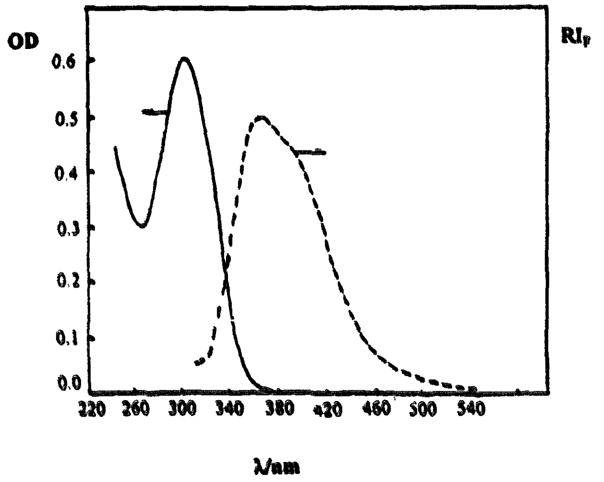


Fig. 1. UV–visible absorption and fluorescence spectra of 1-SPTN in acetonitrile: ——, absorption, [1-SPTN] = 1.7×10^{-5} mol dm^{-3}; – – –, fluorescence, [1-SPTN] = 3.4×10^{-5} mol dm^{-3}.

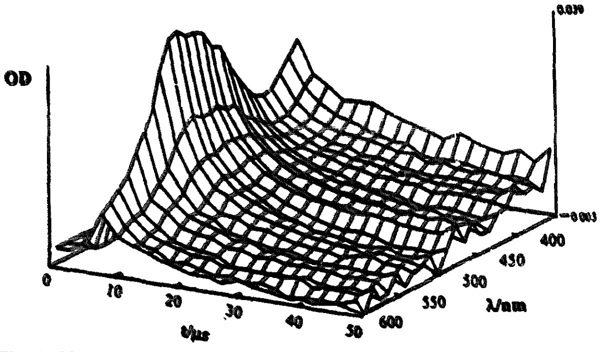


Fig. 2. Three-dimensional transient absorption of 1-SPTN in acetonitrile.

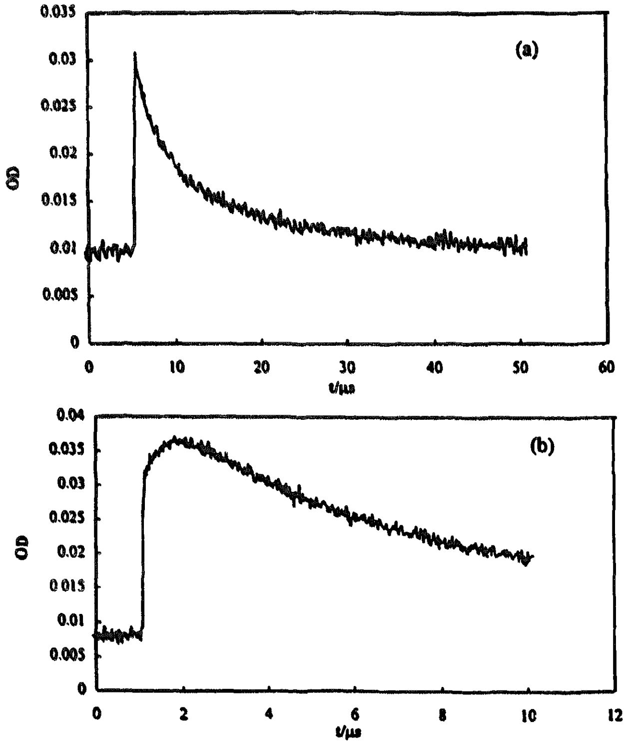


Fig. 3. Dynamic processes of the transient absorption of BP–1-SPTN solution in acetonitrile after irradiation of BP by 355 nm laser pulse: (a) detected at 530 nm; (b) detected at 480 nm.

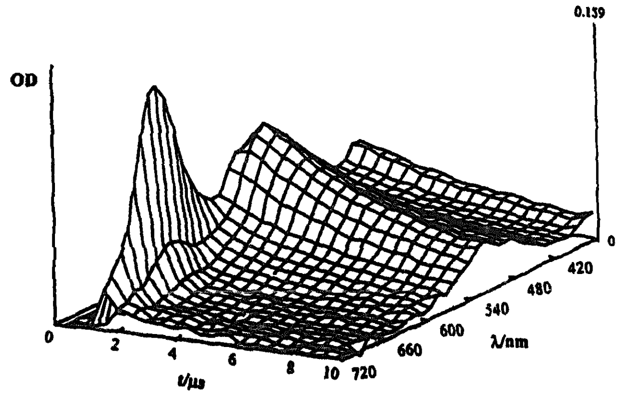


Fig. 4. Three-dimensional transient absorption of XT–1-SPTN solution in acetonitrile after irradiation of XT by a 355 nm laser pulse.

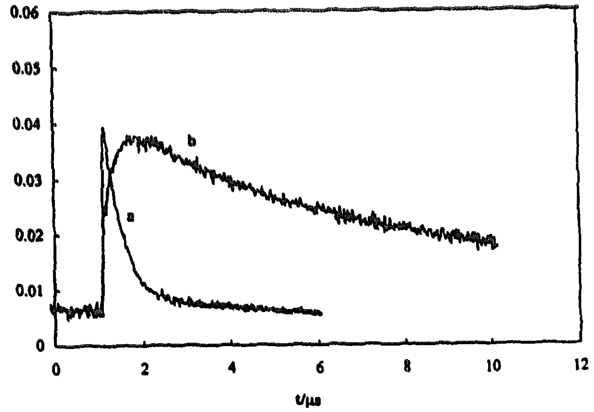


Fig. 5. Dynamic processes of the transient absorption of XT–1-SPTN solution in acetonitrile after irradiation of XT by 355 nm laser pulse: curve a, detected at 630 nm; curve b, detected at 480 nm.

In the XT–1-SPTN system, the decay process of the sensitizer is quite reliable because there is no overlap of the T–T absorption spectra between the energy donor and acceptor. In this case the energy transfer rate constant can be estimated exactly. In XT solution, the decay processes of the triplet state are shown as in Scheme 1.

In the absence of 1-SPTN, the triplet-state molecules of XT decay to the ground state via intersystem crossing and some chemical reactions. The rate constants of these processes are k_{isc} and k_r respectively. The lifetime of the triplet is

$$\tau_1 = \frac{1}{k_r + k_{isc}} \tag{1}$$

In the presence of 1-SPTN in the solution a new energy transfer path of the triplet-state decay is added (the rate constant is k_{et}). The lifetime of the triplet state is

$$\tau_2 = \frac{1}{k_r + k_{isc} + k_{et}[\text{1-SPTN}]} \tag{2}$$

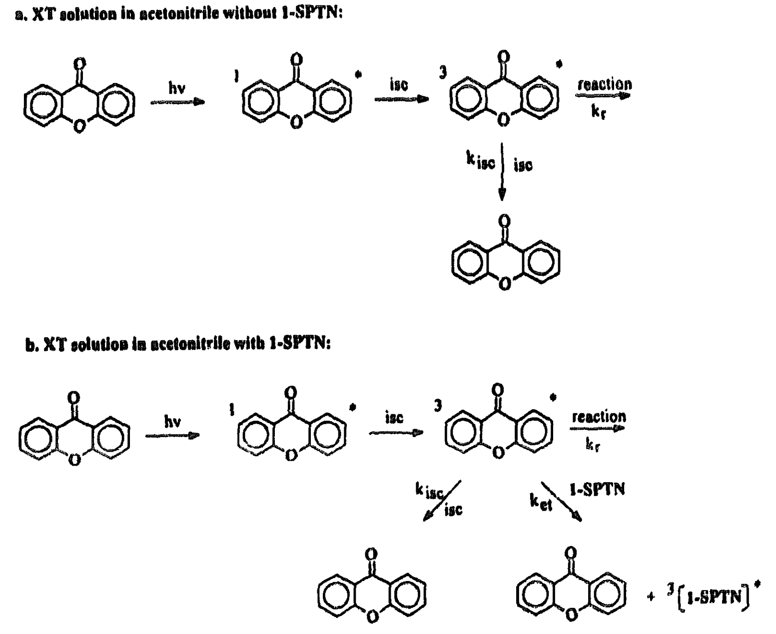
So,

$$k_{et} = \frac{1/\tau_2 - 1/\tau_1}{[\text{1-SPTN}]} \tag{3}$$

The rate constant k_{et} of the triplet-state energy transfer from XT to 1-SPTN is 1.4×10^{10} s^{-1} mol^{-1} dm^3. It is in the region of typical T–T energy transfer rate constant, i.e. from acetophenone to naphthalene, and is diffusion controlled [9].

The triplet state of 4-phenyl benzophenone (PBP) can also be quenched by 1-SPTN efficiently. This means that the energy of the triplet state of 1-SPTN is lower than that of PBP.

1-SPTN is also used as an energy donor to transfer its triplet energy to energy acceptor. 1-methylnaphthalene



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Scheme 1.

(Mna) was selected first as the acceptor because its triplet state energy is the same as that of PBP [8]. In the experiment, however, when Mna was added to the solution of 1-SPTN (total Mna was 5.5×10^{-2} mol dm^{-3}), the decay process of the T–T absorption of 1-SPTN was the same as in the absence of Mna. This indicates that energy transfer cannot occur from 1-SPTN to Mna and confirms again that the triplet energy of 1-SPTN is lower than that of PBP.

Butadiene (BD) and 1,3-cyclohexadiene (CHD), with lower triplet-state energy, were introduced in the solution of 1-SPTN as energy acceptors. Both of them quenched the triplet state of 1-SPTN evidently. In the presence of BD or CHD the T–T absorption of 1-SPTN decayed more rapidly, as shown in Fig. 6. With the decay of the 1-SPTN triplet-state absorption a new component seems to be formed, whose absorption maximum is about 450 nm, and these maxima are similar in both 1-SPTN–BD and 1-SPTN–CHD. Because of the similar conjugated structure (diene group) in both acceptor molecules, maybe the absorption centred at 450 nm is produced by the triplet state of BD and CHD respectively.

The triplet-state energies of the energy donor and acceptor used in this work are listed in Table 1. From the results obtained above and the triplet-state energy listed in Table 1, the triplet-state energy of 1-SPTN can be estimated. It is lower than that of PBP or Mna and higher than BD. So the triplet energy of 1-SPTN is about 252 kJ mol^{-1}.

The phosphorescence of 1-SPTN was measured in diethyl ether at 77 K and it is shown in Fig. 7. The compound emits phosphorescence from about 480 nm and the maxima are 503 nm and 540 nm respectively. The triplet-state energy of 1-SPTN is about 250 kJ mol^{-1}, estimated from its phosphorescence. This result is compatible with that obtained by triplet-state energy transfer.

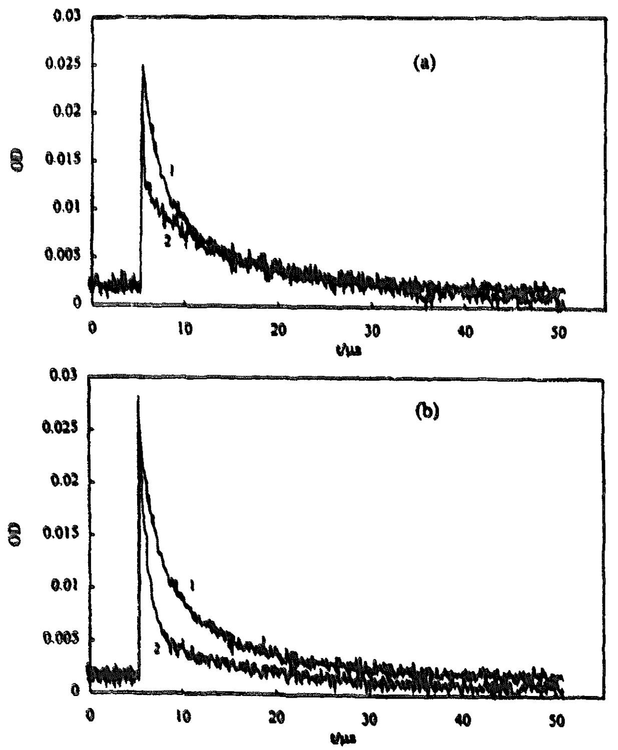


Fig. 6. Transient absorption decay processes of 1-SPTN and 1-SPTN–acceptor solutions in acetonitrile: (a) 1-SPTN and 1-SPTN/BD: curve 1, 1-SPTN; curve 2, 1-SPTN–BD; (b) 1-SPTN and 1-SPTN/CHD: curve 1, 1-SPTN; curve 2, 1-SPTN–CHD.

Table 1
Triplet-state energy E_T of the energy donor and acceptor in polar solvents [8]

Compound	XT	BP	PBP	Mna	BD	CHD
E_T (kJ mol^{-1})	310	289	254	254	250 [a]	219 [a]

[a] Obtained in non-polar solvent.

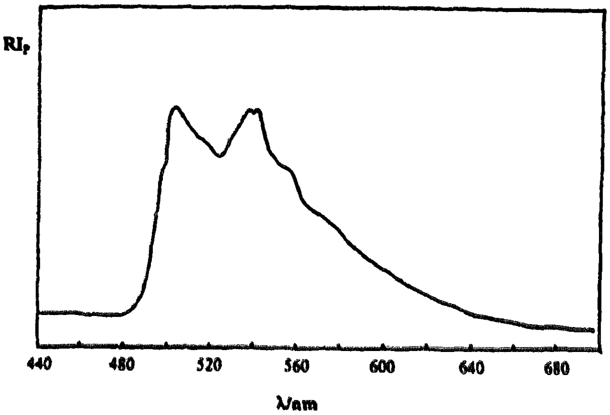


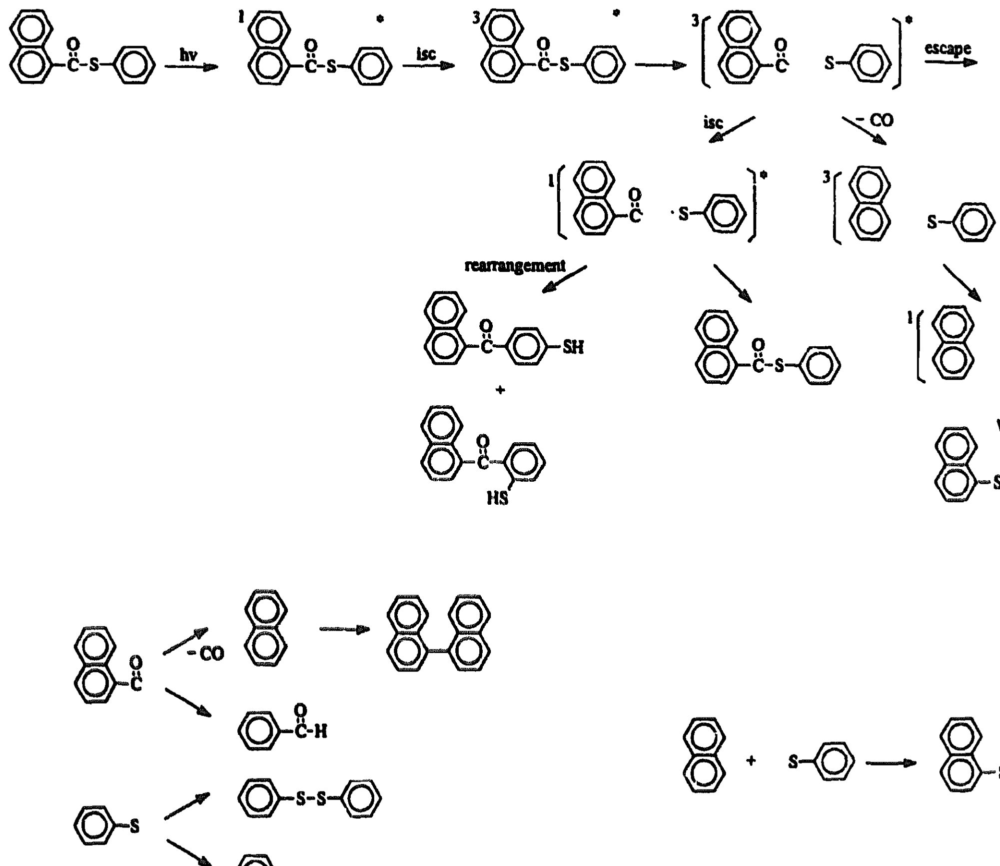
Fig. 7. Phosphorescence spectrum of 1-SPTN in diethyl ether at 77 K ([1-SPTN] = 3.4×10^{-5} mol dm^{-3}).

The fluorescence of 1-SPTN is very weak ($\Phi_f = 0.008$) and the emission peak wavelength is about 360 nm (Fig. 1). It is very interesting to observe that in the experiment the emission intensity at 360 nm was enhanced on increase in the irradiation time of the solution.

Photolytic products of 1-SPTN in acetonitrile were characterized by GC–MS. Two main products were diphenyldisulphide and 1,1′-binaphthyl. Thiophenol, 1-naphthaldehyde, 1-naphthyl phenyl sulphide, 2(or 4)-thiobenzoyl 1-naphthalene were also detected. The mechanism of the photolysis is suggested to be as in Scheme 2, according to the products and previous work [10,11].

2(or 4)-Thiobenzoyl 1-naphthalene is the product of Fries rearrangement reaction in solvent cage. 1-Naphthyl phenyl sulphide can be formed both in the solvent cage and out of the solvent cage. Diphenyldisulphide, 1,1′-binaphthyl, thiophenol and 1-naphthaldehyde come from the radicals which escape from the solvent cage. One of the products, 1,1′-binaphthyl, emits fluorescence with higher quantum yield ($\Phi_f = 0.77$) and the emission peak wavelength is also 360 nm [12,13]; so the solution gives stronger fluorescent emission at 360 nm after irradiation in the photolysis experiment.

Fig. 8 shows the change in the fluorescence intensity of the solution with increasing irradiation time with a magnetic field (0.2 T) and without a magnetic field, detected at 360 nm. If a photochemical reaction proceeds via a radical pair intermediate and the radical pair is generated from a triplet precursor, the application of an external magnetic field would



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Scheme 2. Photolysis mechanism of 1-SPTN.

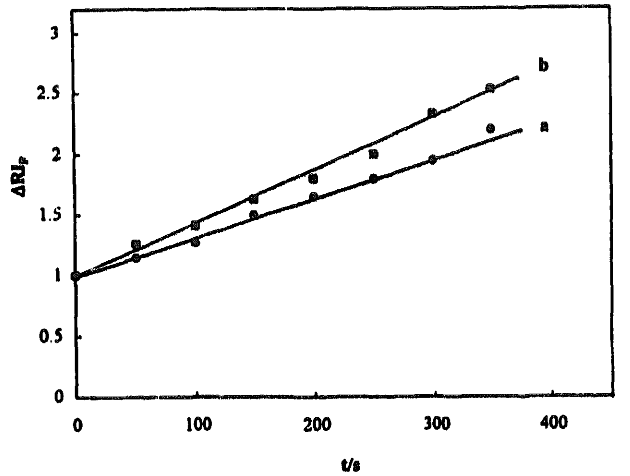

Fig. 8. Relative fluorescence intensities of 1-SPTN solution in acetonitrile at 360 nm with increasing irradiation time ($[\text{1-SPTN}] = 3.4 \times 10^{-5}$ mol dm^{-3}): line a, without a magnetic field; line b, with a magnetic field (0.2 T).

decrease the cage effect [14–16]. On the contrary, if the radical pair is generated from a singlet precursor, a decreased cage effect would not be expected. Thus magnetic field effects on cage reactions can provide information concerning the nature of the intermediates and the multiplicity of the excited state of the precursor [17,18]. In the photolysis of the solution the fluorescence intensity at 360 nm increased more rapidly with a magnetic field with increasing irradiation time than without a magnetic field. This indicates that more 1,1′-binaphthyl is formed in the photolytic process under an external magnetic effect and proves that the photolysis of 1-SPTN occurs via the triplet state mainly.

Acknowledgements

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