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Photochemistry of thioxanthen-9-one-10,10-dioxide: A remarkably reactive triplet excited state

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ABSTRACT

The steady state photolysis of thioxanthen-9-one-10,10-dioxide (**1**) in dichloromethane does not result in any product formation. In hydrogen donor solvents, such as 2-propanol, toluene or cyclohexane, the formation of the corresponding pinacol was readily observed. The phosphorescence spectrum of **1** in EPA, at 77 K, reveals a triplet energy of 66.3 kcal mol^{-1}. Laser flash photolysis irradiation of a degassed acetonitrile solution of **1** led to the formation of its triplet excited state (λ_{max} = 375 and 520 nm, τ = 11 μs) that was quenched by oxygen, β-carotene and 1,3-cycloexadiene at a diffusion controlled rate constant. The quenching rate constants for the triplet of **1** with 1,4-cyclohexadiene, methanol, ethanol, 2-propanol, cyclohexane, substituted phenols and amines were determined, ranging from 7.1×10^6 (for methanol) to 3.1×10^{10} L mol^{-1} s^{-1} (for triethylamine). From the quenching rate constants observed for the triplet excited state and from the steady state photolysis, it was concluded that the remarkable reactivity of **1** is due to the *n*,π* character of the carbonyl chromophore.

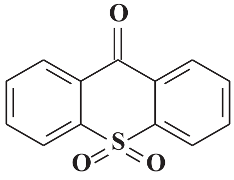
1. Introduction

Due to their role in photochemical and photobiological reactions, the triplet states of aromatic ketones continue to receive attention from both experimental and theoretical points of view. Hydrogen abstraction (HA) by the triplet state of aromatic ketones is the most thoroughly studied photochemical reaction [1–15]. The nature of the lowest triplet excited state (*n*,π* or ππ*) of a ketone is known to influence the rate of photoinduced HA from a donor species, where the *n*,π* triplet is the more reactive state.

The mechanisms for HA are influenced by the identity of the atoms involved in the transfer of the “hydrogen atom”, the bond energy, the oxidation potential of the hydrogen donor and by the solvent. Mechanisms spanning the extremes of alkoxyl-radical-like hydrogen atom transfer (HAT), as with alkanes or alcohols [16,17], and full electron transfer (as with amines) have been identified where intermediate mechanisms may have a proton coupled electron transfer (PCET) character [18–24]. In the case of excited state ketones abstracting hydrogen from phenols it has been suggested that a mechanism involving initial formation of a hydrogen-bonded triplet exciplex followed by coupled electron/proton transfer occurs where the nature and the reduction potential of the triplet state may influence the hydrogen abstraction mechanism [3,5,11,12,25–27].

Thioxanthen-9-one-10,10-dioxide derivatives have been shown to possess a number of potentially useful biological activities including anti-tumor, anti-allergic and monoamine oxidase (MAO) inhibitory activity [28–30]. However, some of the most promising drug candidates arising from this class of compounds have been shown to possess adverse toxic properties in Phase I clinical trials [31,32]. Despite the wide range of pharmacological properties, nothing is known about the photochemical reactivity of this compound.

In this study we wish to report our results of steady state and laser flash photolysis experiments on the photochemistry of thioxanthen-9-one-10,10-dioxide (**1**) towards hydrogen and electron donors in acetonitrile. The interest in this system is to investigate how the presence of the sulfone group influences the reactivity of the carbonyl group towards hydrogen abstraction and electron transfer reactions.



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2. Materials and methods

2.1. Materials

The solvents acetonitrile, toluene, cyclohexane, dichloromethane, methanol, ethanol and 2-propanol (all spectroscopic grade), as well as phenol, 4-cyanophenol, 4-methoxyphenol, indole, triethylamine, and 1,4-diaza[2.2.2]bicyclooctane (DABCO), from Aldrich, were used as received (purity >99%). 1,3-Cyclohexadiene and 1,4-cyclohexadiene, from Aldrich, were bulb-to-bulb distilled, at low pressure, just before their use.

Thioxanthen-9-one-10,10-dioxide (9-oxo-9H-thioxanthene-10,10-dioxide) was synthesized from thioxanthone, employing the method described by Brindle and Doyle [33]. The product was recrystallized from ethanol and pale yellow crystals were obtained, mp (uncorrected) 190–191 °C (literature mp = 181–185 °C) [34].

UV (acetonitrile) λ (nm): 264, 286, 348; IV (KBr) ν (cm^{-1}): 1677, 1299, 1169. RMN ^1H ($CDCl_3$) δ (ppm): 8.37–7.76 (m, aromatic, 8H), RMN ^{13}C ($CDCl_3$) δ (ppm): 178 (C=O). EM *m*/*z* (%): 244 ($M^{\bullet +}$,20); 227 (12); 196 (100); 168 (20); 136 (22).

Gas chromatograph–mass spectrometry analyses were performed using a HP 5987equipment employing a 25 m capillary column SE-54. Gas chromatograph analyses were performed in a chromatograph Varian 3340 containing a 25 m capillary column BP-1 and using a flame ionization detector.

^1H and ^{13}C NMR spectra were obtained with a Bruker AC 200 (^1H: 200 MHz; ^{13}C: 50.3 MHz), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard.

The infra-red (IR) spectra were obtained as KBr pellets using a Nicolet 505 Magma (FTIR).

Melting points were recorded in a Mel-Temp apparatus and were not corrected.

The ground state UV–vis spectrum was recorded on a Varian DMS-80. The low temperature (77 K) phosphorescence spectrum was recorded in EPA (ethyl ether:*iso*-pentane:ethanol mixture 5:5:2) [35], on a PTI model 100 spectrofluorimeter, employing a pulsed Xenon lamp and a low-temperature accessory.

2.1.1. Steady-state irradiation

Steady-state irradiation of **1** was performed with excitation at 300 nm, employing a Rayonet reactor containing four lamps, from New England Inc. Samples were degassed using oxygen-free nitrogen and irradiated for at least 12 h. When the irradiation was performed in 2-propanol, cyclohexane or toluene a white precipitate was clearly observed at the end of the irradiation. The product obtained in a quantitative yield showed mp 183–184 °C and its spectroscopic characteristics are listed below.

IR (KBr) cm^{-1}: 3417; 1274; 1149.

EM: *m*/*z* (%) 490 ($M^{\bullet +}$, not observed); 245 (100); 152 (10).

2.1.2. Laser flash photolysis

Laser flash photolysis experiments were carried out on a LuzChem Instrument model mLFP122. Samples were contained in a 10 mm × 10 mm cell made from Suprasil tubing and were purged by bubbling with oxygen-free nitrogen for about 30 min. The samples were irradiated with the third harmonic of a Nd/YAG Surelite laser (λ = 355 nm, ~4–6 ns, ≥40 mJ/pulse)

The concentration of **1** (~1 mM) was chosen in order to give an absorption in the wavelength of excitation (355 nm) of 0.3–0.5. Stock solutions of quenchers were prepared so that it was only necessary to add microliter volumes to the sample cell in order to obtain appropriate concentrations of the quencher.

Second-order rate constants for the reaction of the triplet excited state of **1** with the different quenchers employed in this work were obtained from Stern–Volmer plots [36], following Eq. (1)

$$k_{obs} = k_0 + k_q[Q] \quad (1)$$

where k_0 is the triplet decay rate constant in the absence of quencher; k_q is the triplet decay rate constant in the presence of the quencher and [Q] is the quencher concentration in mol L^{-1}. In all cases linear plots were obtained showing very good correlation coefficients.

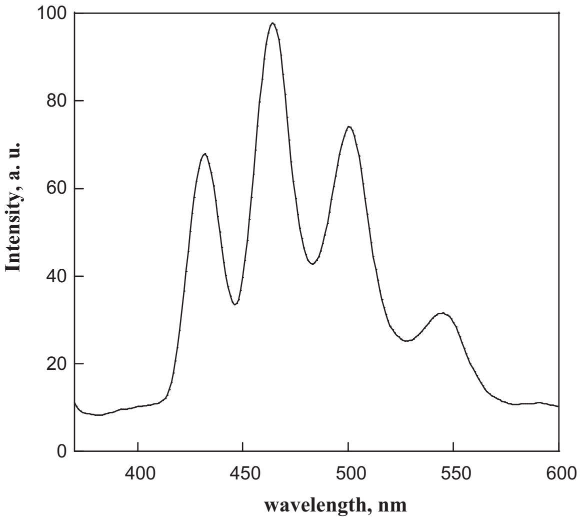


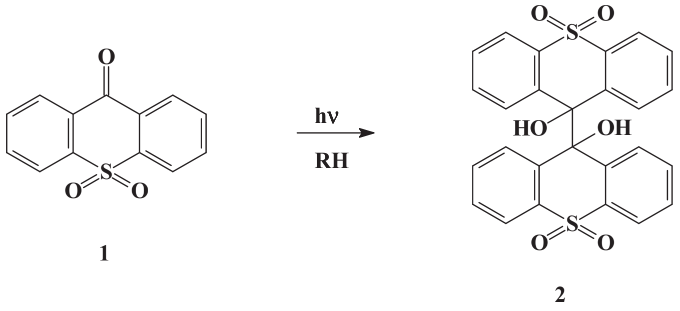
Fig. 1. Phosphorescence emission spectrum for thioxanthen-9-one-10,10-dioxide, in EPA glass, at 77 K (λ_{exc} = 340 nm).

3. Results and discussion

The ground state absorption spectrum of **1**, in acetonitrile, shows strong bands in the UV (λ = 264, 286 nm) and in the visible region of the electromagnetic spectrum (λ = 348 nm). Its phosphorescence emission spectrum was recorded at 77 K, in EPA glass solution, with excitation at 340 nm, showing clear vibrational resolution, characteristic of a triplet excited state with an $n\pi^*$ configuration (Fig. 1). From the 0,0 emission band of this spectrum (λ = 432 nm), it was possible to calculate the triplet energy for the triplet **1** as being 66.3 kcal mol^{-1}. Furthermore, the vibrational progression associated with the phosphorescence spectrum corresponds to vibrational states of the carbonyl group, $\nu_{C=O}$ = 1680 cm^{-1}. The phosphorescence spectrum at low temperature is in full agreement with that described in the literature for 3-carboxymethyl-thioxanthen-9-one-10,10-dioxide [37].

3.1. Steady state irradiation

Steady state irradiation (λ_{exc} = 300 nm) of **1** in dichloromethane did not result in the formation of any product. However, when the irradiation was performed in good hydrogen donor solvents, such as 2-propanol, cyclohexane or toluene, a new product was obtained. Based on its spectroscopic data, this species was assigned to the corresponding pinacol **2** formed through an initial hydrogen abstraction of triplet **1** from the solvent (Scheme 1). This is fully in accord with a literature report of pinacol formation upon steady-state photolysis of thiochroman-4-one 1,l-dioxide and isothiochroman-4-one 2,2-dioxide in the presence of hydrogen donor solvents [38].



Scheme 1. Steady state irradiation of thioxanthen-9-one-10,10-dioxide (**1**) in hydrogen donor solvents.

3.2. Laser flash photolysis

3.2.1. Triplet characterization

Laser flash photolysis of a degassed acetonitrile solution of **1** led to the formation of a readily detectable transient with absorptions at 375 and 520 nm (Fig. 2), with its decay showing mixed first and second-order kinetics (see inset Fig. 2). This decay is concentration dependent, reflecting self-quenching of the triplet. For acetonitrile we were able to measure a self-quenching rate constant of 5.0×10^7 L mol^{-1} s^{-1}. From the intercept of this plot one can obtained a lifetime of 11.5 μs for the transient obtained upon laser excitation of **1**. This transient was assigned as the triplet excited state due to the fact that it was quenched close to a diffusion controlled rate with 1,3-cyclohexadiene (8.4×10^9 L mol^{-1} s^{-1}, E_T = 53 kcal mol^{-1}) and β-carotene (in this case with the concomitant formation of the β-carotene triplet (E_T = 19 kcal mol^{-1}) [39,40], which is in accord with the triplet energy value of 66.3 kcal mol^{-1} obtained from the low temperature experiment. These kinetic and spectroscopic data are in full agreement with those from the literature for a thioxanthonedioxide derivative [37].

3.2.2. Triplet reactivity

Transient absorption spectra for **1** in the presence of methanol, ethanol or 2-propanol also show absorptions at ~380 and 520 nm. In these alcohols the absorption maxima remain unchanged even at long time scales (>50 μs) (Fig. 3). The main difference in the behavior of **1** in acetonitrile or in the alcohols resides in the kinetic profile. For the later, a long-lived transient could be observed, having a lifetime in excess of 50 μs, assigned to the ketyl radical **3**, formed through a direct hydrogen abstraction reaction of triplet **1** from the alcohols (Scheme 2). Moreover, in all cases it was possible to time-resolve the formation of the ketyl radical **3** (Fig. 3, inset). Thus, at short timescales and low alcohol concentration (10^{-3} to 10^{-2} mol L^{-1}, depending on the alcohol) one can note that the ketyl radical grows-in with first-order kinetics, which matches the triplet decay at this alcohol concentration (not shown). It is worth note that **3** does not decay to the baseline on the timescale employed in this experiment, which further confirms the above statement that the ketyl radical derived from thioxanthen-9-one-10,10-dioxide has a fairly long lifetime.

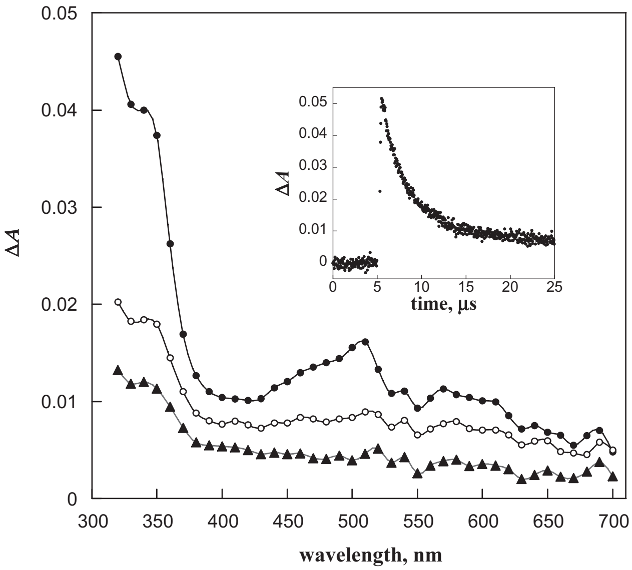


Fig. 2. Triplet–triplet absorption spectra for thioxanthen-9-one-10,10-dioxide, in acetonitrile (λ_{exc} = 355 nm), and recorded (●) 0.8; (□) 1.5; and (▲) 2.4 μs after the laser pulse. Inset: decay for this transient monitored at 510 nm.

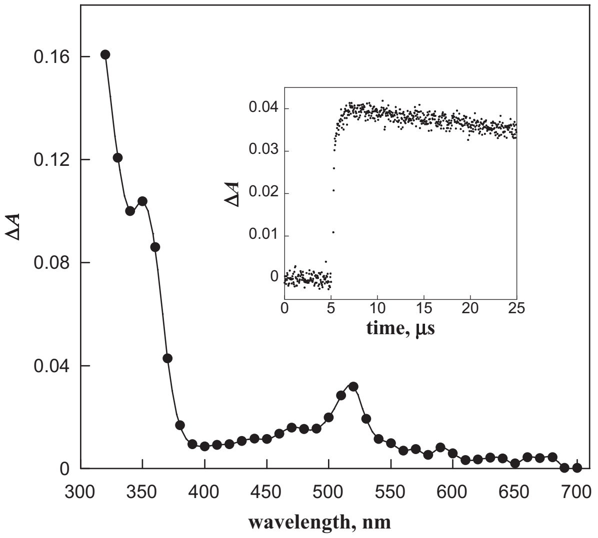


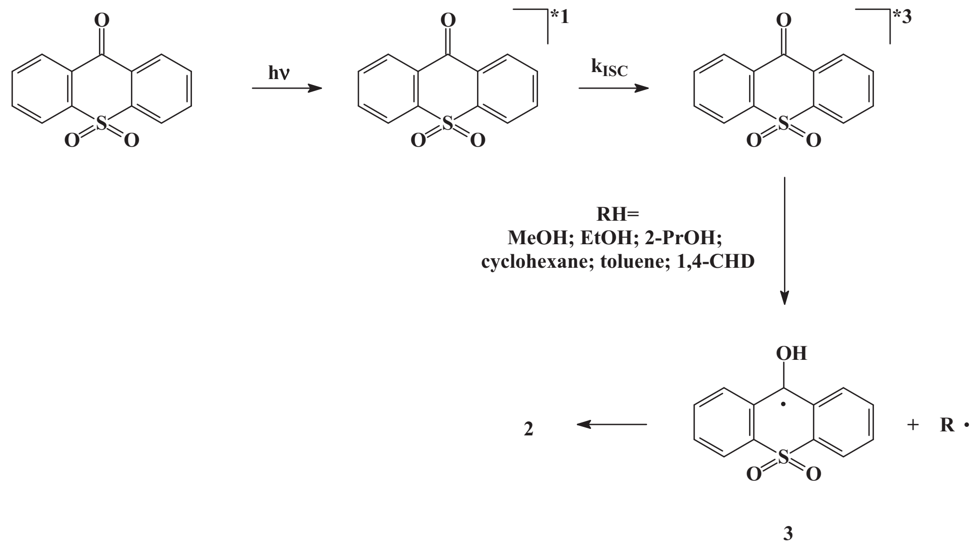
Fig. 3. Transient absorption spectrum for thioxanthen-9-one-10,10-dioxide dioxide in 2-propanol as solvent. Inset: growth and decay for this transient monitored at 530 nm.

Second-order quenching rate constants for triplet thioxanthen-9-one-10,10-dioxide when in the presence of methanol, ethanol and 2-propanol (Table 1) were obtained from the Stern–Volmer plots shown in Fig. 4 and clearly indicate that the reactivity of triplet **1** towards these alcohols is dependent on the stability of the ketyl radical derived from them. These ketyl radicals cannot be spectroscopically detected with our experimental set-up. For this type of quencher it is commonly assumed that a "pure" alkoxyl-radical-like mechanism involving a simple hydrogen transfer from the donor to the carbonyl triplet excited state is operating [5]. A very good correlation can be observed when one compares the quenching rate constants shown in Table 1 with the

Table 1
Second-order quenching rate constant for the reaction of triplet thioxanthen-9-one-10,10-dioxide towards hydrogen and electron donors.

Quencher	$k_{quenching}$ (L mol^{-1} s^{-1})[a]
Methanol	7.1×10^6
Ethanol	3.3×10^7
2-Propanol	1.8×10^8
Cyclohexane	8.8×10^6
Toluene	1.2×10^8
1,4-Cyclohexadiene	9.1×10^9
Phenol	1.5×10^{10}
4-Cyanophenol	1.8×10^{10}
4-Methoxyphenol	9.8×10^9
Indole	3.1×10^9
Triethylamine	3.1×10^{10}
DABCO	1.3×10^{10}

[a] Error: ±10%.



Scheme 2. Proposed mechanism for the formation of ketyl radical **3** upon photolysis of **1** in the presence of hydrogen donors.

bonding energy for the abstractable hydrogen from the alcohol, i.e. the H–C bond for the hydroxyl containing carbon. Thus, for methanol, having a C–H bond energy of 95.98 kcal mol^{-1} [41], a quenching rate constant of *ca.* 7.1×10^6 L mol^{-1} s^{-1} was obtained, whereas for ethanol (C–H bond energy = 94.77 kcal mol^{-1}) [42] $k_q = 3.3 \times 10^7$ L mol^{-1} s^{-1} and for 2-propanol (C–H bond energy of 90.98 kcal mol^{-1}) [43] $k_q = 1.8 \times 10^8$ L mol^{-1} s^{-1}. These quenching rate constants exceed in two orders of magnitude those obtained for typical aromatic carbonyl compounds, such as benzophenone ($k_q = 3.2 \times 10^6$ L mol^{-1} s^{-1}, in the presence of 2-propanol) [44,45]. This behavior is characteristic of triplet excited states having $n\pi^*$ character, which is fully in accord with the phosphorescence emission spectra shown in Fig. 1, and with the fast quenching rate constants measured for triplet **1** indicating a remarkably reactive species. It is also worth noting that the remarkably high reactivity of thioxanthen-9-one-10,10-dioxide triplet is observed even in acetonitrile, a highly polar solvent. This is in sharp contrast with what was observed for triplet xanthone, another example of a carbonyl triplet having an extremely high reactivity towards hydrogen abstraction reaction. For xanthone, a large change of the reactivity towards 2-propanol as a function of the solvent polarity was reported, due to a change in the triplet excited state character ($n\pi^*$ in non-polar solvent; $\pi\pi^*$ in polar solvent) as a consequence of a low energy-gap between the two states [46].

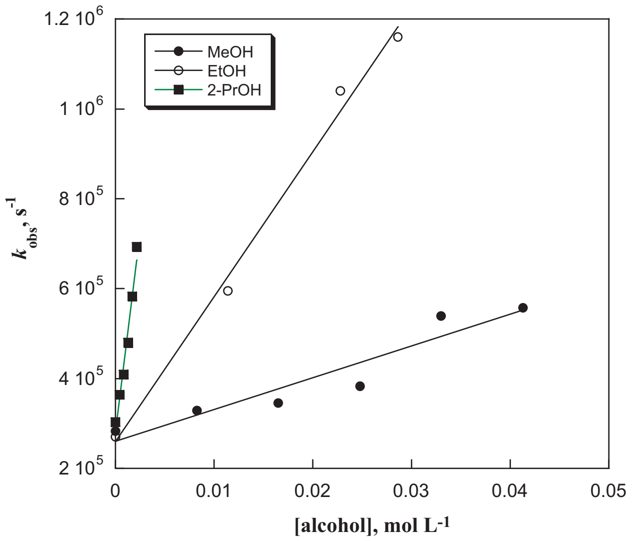


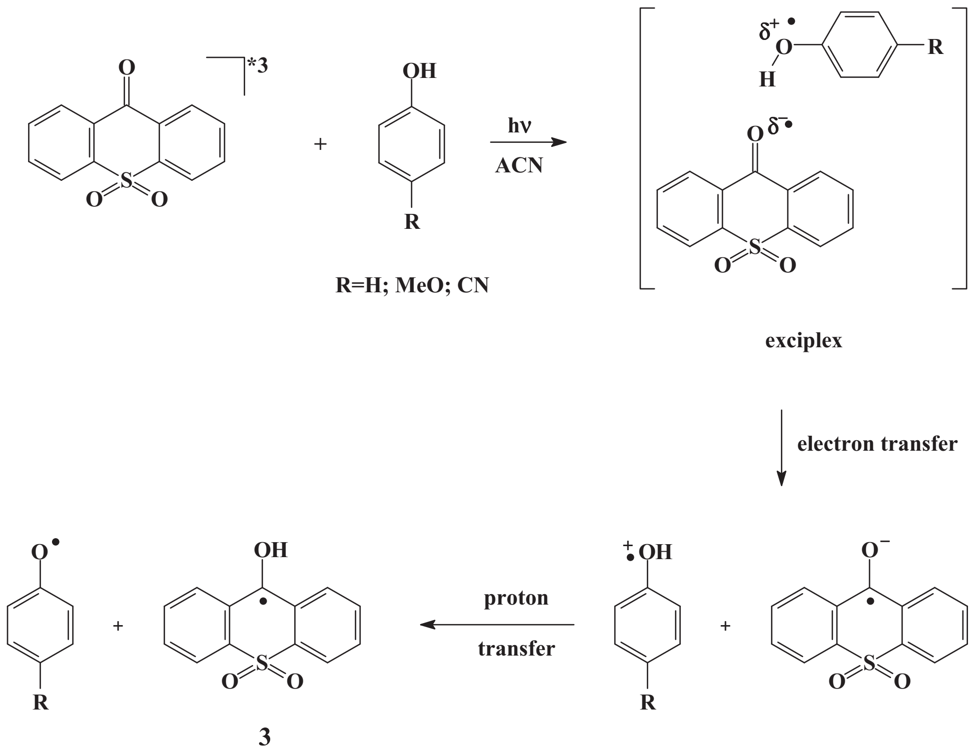
Fig. 4. Stern–Volmer plots for the quenching of thioxanthen-9-one-10,10-dioxide by several alcohols.

Efficient quenching rate constants for the alkoxyl-type hydrogen abstraction by triplet **1** were also measured for cyclohexane ($k_q = 8.8 \times 10^6$ L mol^{-1} s^{-1}), toluene ($k_q = 1.8 \times 10^8$ L mol^{-1} s^{-1}), and 1,4-cyclohexadiene ($k_q = 9.1 \times 10^9$ L mol^{-1} s^{-1}), (Table 1). The almost diffusion-controlled quenching rate constant for the later quencher reinforces the fact that thioxanthen-9-one-10,10-dioxide displays an extremely reactive triplet excited state. For comparison, the triplet state of 10,10-dimethylanthrone and benzophenone react with l,4-cyclohexadiene with a rate constant of 6.6×10^8 L mol^{-1} s^{-1} and 2.9×10^8 L mol^{-1} s^{-1}, respectively [47,48]. In all cases, the transient absorption spectrum obtained after laser excitation of **1** in the presence of any of these quenchers is identical to that obtained for the quenching by 2-propanol (Fig. 3), with the ketyl radical **3** being the only species observed.

Quenching of triplet thioxanthen-9-one-10,10-dioxide by phenols, indole, triethylamine and DABCO in acetonitrile were also performed, with the quenching rate constants measured for these reactions being diffusion-controlled in all cases ($k_q \sim 10^{10}$ L mol^{-1} s^{-1}) (Table 1).

The reaction of triplet **1** with phenols leads to the formation of the corresponding phenoxyl radicals (Scheme 3). These radicals have strong absorption bands in the 370–505 nm region, that can be easily detected by LFP experiments [25]. For example, the transient absorption spectrum obtained in the presence 0.02 mol L^{-1} 4-methoxyphenol shows an absorption band at 405 nm that can be attributed to the 4-methoxyphenoxyl radical (Fig. 5) [49]. Similar behavior was observed when 4-cyanophenol was employed as the hydrogen donor. In this case, the transient absorption spectrum (not shown) shows absorptions at 440 nm (due to the 4-cyanophenoxyl radical) and at 320 and 525 nm, assigned to the ketyl radical derived from **1**.

It is very well known from experimental and theoretical calculations that phenolic hydrogen abstraction by aromatic ketones is faster than the corresponding reaction with alcohols, alkanes or substituted toluene [11,12,25–27,50,51]. This is mainly due to the low bond dissociation energy and low oxidation potential of phenols. Besides, theoretical calculations showed that triplet carbonyls have a low excited state reduction potential, which accounts



Scheme 3. Proposed mechanism for the quenching of triplet **1** by phenols.

for their high reactivity [3,5]. It has been suggested that hydrogen abstraction from phenols occurs by a mechanism involving initial formation of a hydrogen-bonded triplet exciplex followed by coupled electron/proton transfer, leading to the experimental observation of ketyl and phenoxyl radicals (Scheme 3).

A similar mechanism to the one shown in Scheme 3 for phenols can be proposed for the quenching of triplet **1** by indole. In this case, the radicals obtained after the coupled electron/proton process are the ketyl radical **3**, derived from the thioxanthonedioxide, and the indolyl radical. Fig. 6 shows the transient absorption spectra obtained upon laser excitation (355 nm) of **1** in the presence of indole, in acetonitrile, at different time windows after the laser pulse. The end absorption band at 330 and as well as the broad absorption at 450–550 nm can be assigned to a mixture of the ketyl radical **3** plus the indolyl radical, since both transients have absorptions in these regions of the electromagnetic spectrum [8,52,53].

For good electron donors such as triethylamine and DABCO, a different mechanism can be proposed in which a full electron transfer process occurs. In this case, the main transients expected to be formed are the anion radical **4** derived from thioxanthen-9-one-10,10-dioxide and the cation radical derived from the amine (Scheme 4). The representative transient absorption spectra for the

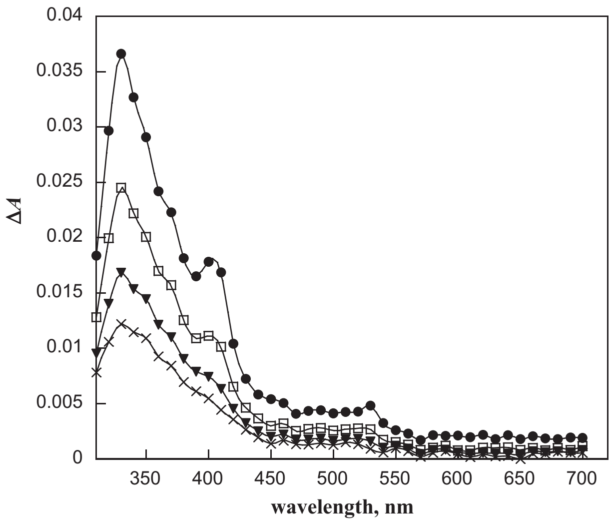


Fig. 5. Transient absorption spectra (λ_{exc} = 355 nm) for thioxanthen-9-one-10,10-dioxide in the presence of 0.02 mol L^{-1} 4-methoxyphenol, in acetonitrile, recorded at (●) 13 μs, (□) 47 μs, (▼) 132 μs and (x) 293 μs after the laser pulse.

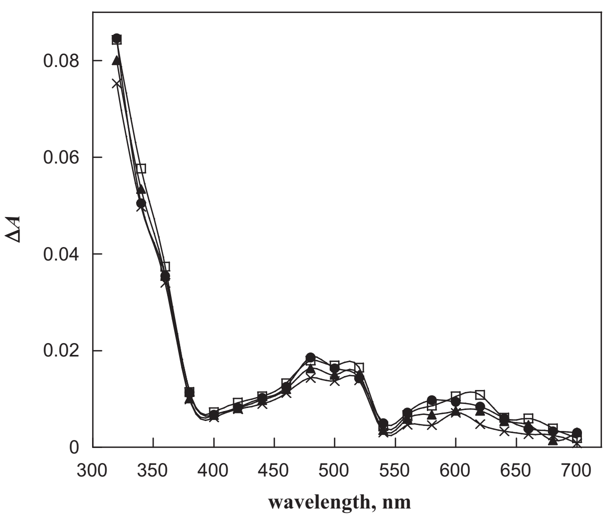
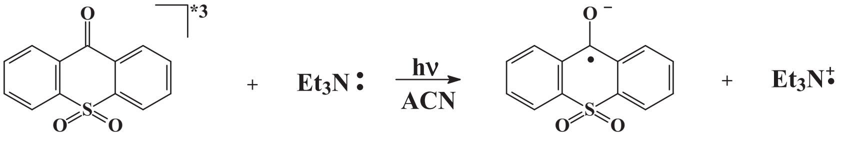


Fig. 6. Transient absorption spectra (λ_{exc} = 355 nm) for thioxanthen-9-one-10,10-dioxide in the presence of 0.02 mol L^{-1} indole, in acetonitrile, recorded at (●) 48 ns, (□) 424 ns, (▼) 1,4 μs and (×) 2,86 μs after the laser pulse.



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Scheme 4. Proposed mechanism for the quenching of triplet **1** by the electron donor triethylamine.

quenching of **1** employing triethylamine (0.02 mol L^{-1}) as the electron donor (Fig. 7) clearly shows a new transient with absorption bands at 365 and 620 nm, which are not decaying even at 36 μs after the laser pulse, denoting the fairly long lifetime for this species, to which we assigned the anion radical **4**.

The absorption spectrum for anion radicals derived from carbonyl compounds is strongly dependent on the solvent polarity. For example, the absorption for benzophenone radical anion has maximum at 735 nm in benzene, 715 nm in acetonitrile and 615 nm in methanol [54,55], with the blue shift observed in the absorption spectrum in methanol being a result of hydrogen bonding. Since wet acetonitrile was employed in our experiments, hydrogen bonding between **4** and water can be responsible for the absorption of the anion radical **4** at 620 nm. Under our experimental conditions the cation radical derived from triethylamine could not be observed.

From the above results it is clear that the triplet excited state of thioxanthen-9-one-10,10-dioxide displays a remarkable reactivity towards hydrogen and electron donors and in many cases the quenching rate constant is diffusion-controlled. Since one can consider this ketone a benzophenone-like molecule (in fact its triplet–triplet absorption spectrum is quite similar to that of benzophenone) the reason behind this high reactivity must reside in the presence of the sulfone group. It is known from the literature that the photochemistry of aromatic sulfones such as dibenzothiophene-S-S-dioxide, in hydroxylic solvents, results in the formation of biphenyl in quantitative yield via two sequential photochemical reactions [56]. However, our results clearly show that the photochemistry of thioxanthen-9-one-10,10-dioxide (**1**) does not involve the cleavage of the C–S bond of the sulfone group. The low temperature phosphorescence spectrum for **1**, shown above, clearly reveals that the chromophore associated with the triplet excited state of lowest energy is a carbonyl with *n*,π* character, which is responsible for the reactivity of the thioxanthonedioxide**1**. The difference in reactivity is readily explained by comparing the triplet energy associated with each chromophore. Thus, for the nπ* carbonyl group we measured a triplet energy of 66.3 kcal mol^{-1}, whereas for the diarylsulfone a value of 79 kcal mol^{-1} has been reported [57]. These values clearly indicate that for conjugated bichromophoric compounds containing carbonyl and sulfone groups, such as **1**, their photochemistry will be fully controlled by the nπ* carbonyl group.

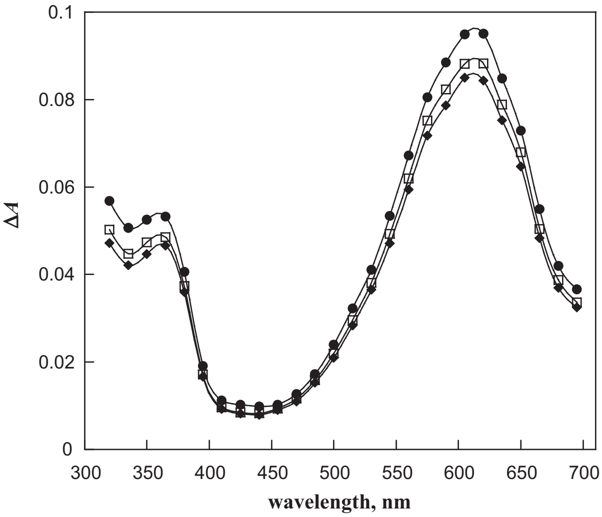

Fig. 7. Transient absorption spectra (λ_{exc} = 355 nm) for thioxanthen-9-one-10,10-dioxide in the presence of 0.02 mol L^{-1} triethylamine, in acetonitrile, recorded at (●) 10 μs, (□) 23 μs and (▾) 36 μs after the laser pulse.

4. Conclusion

To conclude, the reactivity of the triplet excited state of thioxanthen-9-one-10,10-dioxide (**1**) towards hydrogen and electron donors has been investigated. Laser excitation (355 nm) of a nitrogen-purged solution of **1** in acetonitrile results in the formation of the corresponding triplet excited state of nπ* character. This triplet state is readily quenched by alcohols, toluene, cyclohexane, 1,4-cyclohexadiene, phenols, indole, triethylamine, and DABCO, with the quenching rate constants obtained indicating an extremely reactive triplet state. Finally it is worth noting that unlike simple aromatic sulfones, thioxanthen-9-one-10,10-dioxide does not yield any product arising from a C–S bond cleavage. This can be explained by the difference in energy between the triplet excited state of both chromophores, where the *n*π* carbonyl group has the lowest triplet energy.

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