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Photophysical properties and photoinduced polymerisation activity of novel 1-chloro-4-oxy/acyloxythioxanthone initiators

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Abstract

The excited state characteristics of 13 novel 1-chloro-4-oxy/acyloxy derivatives of thioxanthone were determined using micro-, nano- and picosecond flash photolysis techniques. Triplet energy levels have also been determined using phosphorescence analysis while photoinitiated polymerisation activities were measured using photocalorimetry. All the initiators exhibit high photopolymerisation activity except the 4-hydroxy model and 2-methyl-4-n-propoxy derivatives. The triplet energies are found to be fairly insensitive to solvent polarity with an observed spectral broadening from non-polar to polar solvents. This is consistent with close lying mixed triplet states of $^3\pi\pi^*$ and $^3n\pi^*$ character. Both the least active 4-hydroxy and 2-methyl-4-propoxy derivatives exhibit lower triplet energies suggesting the presence of a less active lower triplet $^3\pi\pi^*$ state. Triplet–triplet absorption spectra are obtained with all the thioxanthones in the range 600–680 nm with a marked blue shift from non-polar to polar solvents owing to stabilisation of the lowest triplet state by solvent reorganisation. In photoreductive solvents such as methyl alcohol and 2-propanol a longer lived species is observed absorbing in the region 400–500 nm associated with the formation of the ketyl radical. This observation is highly solvent dependent and further supported by microsecond flash spectroscopy in 2-propanol. The 4-hydroxy derivative gave only weak transient absorption and is consistent with its much lower initiation activity. In the presence of a tertiary amine no ketyl radical is observed. Triplet lifetimes increase with solvent polarity confirming the presence of mixed $^3\pi\pi^*$ and $^3n\pi^*$ states where vibronic coupling influences the rate of intersystem crossing to the ground S_0 state. Bimolecular triplet quenching rate constants indicate all the thioxanthones, except the 2-methyl-4-n-propoxy and 4-hydroxy, interact strongly with a range of tertiary amines, DABCO, triethylamine and methyldiethanolamine. The lower triplet quenching constants for the 2-methyl-4-n-propoxy and 2-hydroxy derivatives (an order of magnitude) indicates weaker interaction by the amine and is consistent with their lower photoinitiation activities. Low triplet quenching rates are also observed in the presence of monomer (methyl methacrylate). Bimolecular triplet quenching rates are also measured with naphthalene and are similar to those for benzophenone except the 2-methyl-4-n-propoxy and 4-hydroxy, derivatives which are an order of magnitude less. From this data triplet molar extinction coefficients are determined and found to be higher than that for benzophenone owing to the presence of mixed states. Again, the 2-methyl-4-n-propoxy and 4-hydroxy derivatives exhibited lower values as did the 4-benzoyloxy derivative. Relatively high quantum yields of intersystem crossing are observed (< 0.6) but are all lower than that of benzophenone with the side chain substituents having no significant effect on the rate. The growth rate of the triplet state could be measured and triplet maxima accurately determined via picosecond flash photolysis. Within the growth time of the triplet state (6–18 ps) there is a concurrent formation of the ketyl radical except for the 4-acetyloxy and 4-acryloxy derivatives. The importance of this technique in gaining valuable information on the relative rates of concurrent excited state reactions for thioxanthones is discussed. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The increasing market drive for better photoinitiators for coating technology can be answered only by improving our knowledge concerning the mode of action of the photoinitiators under various conditions [1–7]. In this context, structures based on the thioxanthone chromophore have attracted widespread academic and industrial interest. Over the years

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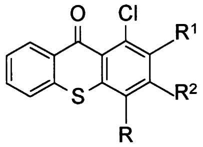
numerous derivatives were synthesised and characterised in terms of their photocuring activity and their photochemical properties. These initiators have extended absorption up to 420 nm, depending upon the type of substitution. They have particular application in dye and pigment-based, water and oil miscible, acrylated matrices. Thioxanthone itself has poor solubility and therefore, substituted derivatives are used. Many of the earlier oil soluble derivatives include hydroxy, alkoxy, acetoxy and halogen substituents in the 2-position of the chromophore [8–12] and 4-n-propoxy in the 4-position [13]. More recent developments include alkylamino [14,15], cinnamate ester [16] and 1-halogen substituents [17–20] as well as the incorporation of water solubilising groups [21–25]. Polymers and copolymers with thioxanthone side groups have also been synthesised and found to be highly active [26–32]. In general these molecules have characteristic long-lived excited triplet states coupled with the absence of any efficient hydrogen donor quenching, low monomer quenching, high rate constants of electron transfer and a quantum yield of electron transfer almost approaching unity [33,34].

Thioxanthones when alone are relatively inefficient and are therefore, utilised together with a tertiary amine cosynergist [44]. The coupling of the thioxanthone with the tertiary amine provides a centre for the generation of active initiating radical species [35,36]. The key to this process involves the formation of a low energy triplet exciplex between the thioxanthone triplet state and the amine [4,5]. This species will undergo a primary photochemical process of hydrogen atom abstraction or electron abstraction from the amine moiety to produce the corresponding semiquinone (ketyl) and radical anion intermediates. Both processes result in the formation of alkylamino radicals, which will then add to the monomer or prepolymer, initiating free radical polymerisation and/or crosslinking. The lower the ionisation potential of the amine the more efficient the process of electron transfer. The ketyl radical has low activity with the monomer while the alkylamino radical has high activity. Further, the latter is an effective scavenger of oxygen thus minimising triplet-state quenching of the thioxanthone by ground-state molecular oxygen. With regard to triplet-state quenching some early studies on laser photolysis of thioxanthone and its 2-chloro and 2-alkyl derivatives indicated a general decrease in the quenching rate constants with these substituents [39]. Laser flash photolysis data on thioxanthone intitiators with amines and monomers was related in many instances to the polymerisation rates of the monomers and the viscosity of the solvents [40–42]. Other works on thioxanthones have shown that the presence of oxygen accelerates the photopolymerisation of methyl methacrylate when triethylamine is used as a photoinitiator [43].

As with many other initiator chromophores structure–activity relationships have formed the basis of many studies in this area. Recent laser photolysis studies [45] have shown that substitution of electron donor groups in the 2-position decrease triplet-state activity towards amines and alkenes, whereas the incorporation of double bonds as side groups has no effect on the thioxanthone photoreactivity.

In order to enhance the photoactivity of the thioxanthone chromophore and its independence from tertiary amine co-synergies a number of 1-substituted halogen derivatives of thioxanthone were made [17–20]. The commercial product 1-chloro-4-n-propoxythioxanthone is known as CPTX and was compared with other 1-fluoro and bromo derivatives [17]. Interestingly whilst the fluorine derivative was found to be inactive in the absence of an amine cosynergist, the chloro and bromo derivatives exhibited significant activity in the photopolymerisation of methyl methacrylate. Whilst the photophysical characteristics of these initiators are not unlike that of other thioxanthone initiators the chloro and bromo derivatives undergo an additional reaction involving dehalogenation. The influence of 4-acyloxy and 4-oxy substituents on the overall photoactivity of the 1-chloro derivative was also studied. Compared with the commercial CPTX these compounds exhibit high photoconversion efficiencies during the photocuring of an ethoxylated bisphenol-A dimethacrylate. This work also showed that the efficiency of these initiators was independent of the presence of oxygen. This is an important step forward in verifying the role of a hybrid mechanism with such initiators where acid release is formed via the photolysis of the aromatic chlorine bond. The electron withdrawing effect of the acyloxy and oxy groups would enhance this effect. To gain a deeper understanding of the excited-state characteristics of the 1-chloro derivative the photophysical properties of 13 derivatives of thioxanthone with the 4-substituted oxy and acyloxy groups were examined and compared (see structures 1–13)



Here the triplet state and its rate of formation were characterised together with its reactivity using micro-, nano-and picosecond flash techniques. Triplet-state energies have also been recorded through phosphorescence analysis. The excited-state characteristics are discussed in relation to the photoinitiated polymerisation activities of the initiators using photocalorimetry.

2. Experimental

2.1. Materials

All the solvents, methyldiethanolamine, DABCO (diazabicyclooctane), triethylamine and benzophenone used in this work were obtained from Aldrich Chemical Co Ltd., UK and were of Analar, spectroscopic or HPLC grade quality. The 1-chloro-4-substituted thioxanthones, namely (1) 4-isopropoxy, (2) 4-(2-methylbutanoxy), (3)

Table 1

Quantum yields of photopolymerisation by photocalorimetry in anaerobic and aerobic butyl acrylate of 1-chloro-4-oxy/acyloxythioxanthones (3×10^{-3} M). Amine $= 6 \times 10^{-3}$ M diethylethanolamine

Thioxanthone	Aerobic (ϕ_p)[a]	Anaerobic (ϕ_p)[a]
4-Isopropoxy	63.8	97.1
4-(2-Methylbutanoxy)	80.1	84.1
4-Propoxy	64.0	96.5
3-Methyl-4-propoxy	50.8	86.9
2-Methyl-4-propoxy	32	47.6
4-Allyloxy	79.6	95.6
4-Benxyloxy	105.6	133.2
4-Oxyethylacrylate	102.9	131.7
4-Acetyloxy	94.3	109.3
4-Acryloxy	63.5	94
4-Phenacyloxy	96.1	99.5
4-Benzoyloxy	102.5	108.5
4-Hydroxy	3	71.3

[a] ± 2.

4-n-propoxy, (4) 2-methyl-4-n-propoxy, (5) 3-methyl-4-n-propoxy, (6) 4-allyloxy, (7) 4-benzyloxy, (8) 4-oxyethylacrylate, (9) 4-acetyloxy, (10) 4-acryloxy (11) 4-phenacyloxy, (12) 4-benzoyloxy and (13) 4-hydroxy were supplied by the Great Lakes Fines Chemicals Ltd., Widnes, UK (see Structures 1–13 for m.p. data). All the compounds are chromatographically pure and have verified elemental C, H and S analysis.

2.2. Spectroscopic measurements

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer and a Beckman DU7 spectrophotometer. Phosphorescence excitation and emission spectra were obtained using a Perkin-Elmer LS-50B luminescence spectrometer. Phosphorescence quantum yields were obtained in ethanol (absolute), ethanol : methanol (1 : 9 v/v) and diethyl ether : isooctane (1 : 2 v/v) at 77 K in liquid nitrogen using the relative method with benzophenone as a standard assuming a quantum yield of 0.74 in ethanol [12]. Clear glasses were obtained in all these solvents. All spectra were corrected using a Perkin-Elmer IBM compatible GEM package with an appropriate built-in correction factor for this purpose for the photoresponse of the photomultiplier and optics. Blank measurements were obtained on the solvents alone to correct for Raman scatter and subtracted from the original sample spectra. Phosphorescence lifetime measurements were obtained under the same condition (77 K) using benzophenone as a standard for lifetime comparison (6.0 ms). Under this condition the influence of oxygen diffusion will be insignificant. Measurements were obtained via the GEM software and electronically gating the emission signal decay taking into account the phosphorescence lifetime and delay/gate widths in the data acquisition.

2.3. Time resolved absorption spectroscopy set-ups

End-of-pulse transient absorption spectra on the millisecond time scale were obtained using a kinetic flash photolysis apparatus equipped with two xenon-filled flash lamps (operated at 10 kV) and a 150 W tungsten–halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope. Solutions were degassed using white spot nitrogen gas (< 5 ppm O_2).

Laser flash photolysis experiments in the UK were carried out using a frequency-tripled neodymium laser (J.K. Lasers Ltd.) which delivered 12 ns pulses of 355 nm radiation of energies up to 20 mJ. Transient absorption changes were measured by illuminating the quartz reaction cell (1 cm pathlength) with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating, high irradiance monochromator with a 5 nm bandwidth. Kinetic changes in the light signal at preselected wavelengths were detected and amplified using a Hamamatsu R1477 photo-multiplier prior to collection by a programmable digital oscilloscope (H P54510A). solutions were degassed under white spot nitrogen gas.

The experimental arrangement in France combines a nanosecond Nd : YAG laser (B.M. Industries) as the excitation source (pump) to a xenon pulsed lamp as the analysing light source (probe). The excitation source delivers a 10 ns light pulse at 355 nm, which is focused on the sample by a system of cylindrical lenses. The absorption of transient species is monitored by using an analysing device which is able to produce bright light pulses with homogeneous spectral bandwidth. According to this principle, a xenon pulsed lamp (XBO 450 W Osram) with a pulsing; unit (Muller SVX1450 and MSL05) is used to produce the probe analysing light. This light is then sent through the sample solution, orthogonally to the pump pulse, onto the slit of a monochromator. This monochromator allows selection of the observation wavelength. A photomultiplier acquires in real time the variation of the transmitted probe

Table 2

Triplet energies (E_{Triplet}) in eV of 1-chloro-4-oxy/acyloxythioxanthones in various solid glasses at 77 K from phosphorescence measurements. Precision ± 0.02

Thioxanthone	Ethanol	Ether/isooctane	Ethanol/methanol
4-Isopropoxy	2.61		
4-(2-Methylbutanoxy)	2.63	2.67	2.67
4-Propoxy	2.62		
3-Methyl-4-propoxy	2.72		
2-Methyl-4-propoxy	2.58		
4-Allyloxy	2.65	2.77	2.77
4-Benzyloxy	2.63	2.68	2.68
4-Oxyethylacrylate	2.63	2.69	2.69
4-Acetyloxy	2.73	2.69	2.69
4-Acryloxy	2.73		
4-Phenacyloxy	2.62	2.69	2.70
4-Penzoyloxy	2.74		
4-hydroxy	2.53		

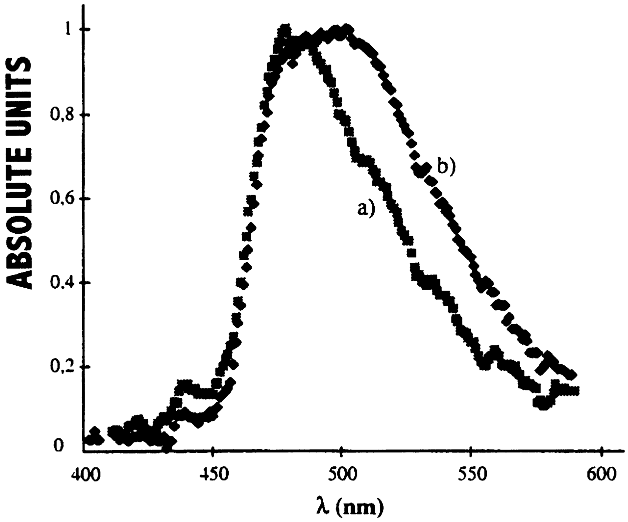


Fig. 1. Phosphorescence emission spectra of 1-chloro-4-(2-methylbutanoxy)thioxanthone in (a) diethyl ether : isooctane glass and (b) ethanol : methanol glass at 77 K.

light, then the electronic transient signal is fed into a transient digitiser (Tektronix DSA601) and mathematically treated by a computer. The synchronisation between the laser pulse excitation and the probe light is fixed using a home made electronic device.

The picosencond transient absorption set-up is based upon the spectroscopic arrangement built by other teams [46]. Briefly, the prcosecond pulses are delivered by a passively–actively mode locked NdMAG laser. The fundamental (1064 nm) generates a white light continuum by focalisation in a D_2O/H_2O mixture. This white pulse (of same duration as the excitation one) is used as the probe beam (probe pulse). The third harmonic (355 nm) is used to excite the sample (pump pulse). The probe pulse is sent through a reference and a sample cell (both 2 mm optical pathway). Pump and probe beams cross co-linearly the sample cell. Then, the probe light is collected by means of two optical fibres connected to a multichannel analyser. The signal is treated by a computer and the optical density (absorbance) is given by the following formula [47]:

$$OD = \log\left[\frac{I^0_{\mathrm{sample}} I^{\mathrm{e}}_{\mathrm{ref}}}{I^0_{\mathrm{ref}} I^{\mathrm{e}}_{\mathrm{sample}}}\right] \qquad (1)$$

where I^0_{ref} and I^0_{sample} refer to the intensities measured through reference and sample cells without any excitation, while $I^{\mathrm{e}}_{\mathrm{ref}}$ and $I^{\mathrm{e}}_{\mathrm{sample}}$ refer to the ones measured with excitation. A delay of up to 6 ns could be achieved between the pump and probe pulses by the use of a computer controlled micrometer translation state. The rise-time of the apparatus is about 35 ps. The solutions, for all the experiments, were deaerated by an argon stream.

3. Results and discussion

3.1. Photocalorimetry

Quantum yields of photopolymerisation of butyl acrylate are shown in Table 1 for all the thioxanthones studied in both aerobic and anaerobic conditions. In the presence of oxygen there is a high rate of conversion except for the 2-methyl-4-n-propoxy and 4-hydroxy derivatives. The rates are seen to increase in the absence of oxygen, the most significant being that for the 4-hydroxy derivative. The reactivities are all very high with the nature of the 4-substituent

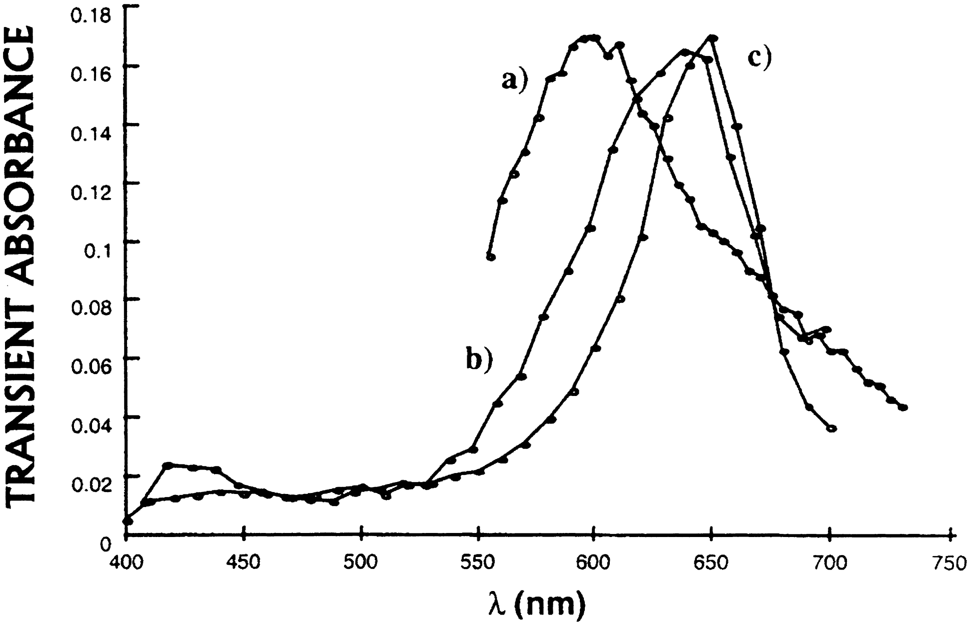


Fig. 2. Typical end-of-pulse transient absorption spectra of nitrogen saturated (a) 4-(2-methylbutanoxy) in methanol, (b) 4-allyloxy and (c) 4-acetyloxythioxanthones in acetonitrile produced on ns laser flash photolysis.

Table 3
Triplet absorption maxima (nm) of 1-chloro-4-oxy/acyloxythioxanthones in various anaerobic solvents from ns laser flash photolysis measurements. Precision ± 2

Thioxyanthone	Methyl alcohol	2-Propanol	Acetonitrile	Toluene
4-Isopropoxy		636	647	
4-(2-Methylbutanoxy)	600			680
4-Propoxy		634	650	
3-Methyl-4-propoxy		656	661	
2-Methyl-4-propoxy		633	649	
4-Allyloxy	610		640	
4-Benzyloxy				
4-Oxyethylacrylate				
4-Acetyloxy	620	654	650	
4-Acryloxy		660	660	
4-Phenacyloxy				
4-Benzoyloxy		656	663	
4-Hydroxy		626	639	

playing an important role except the 2-methyl-4-n-propoxy and 4-hydroxy derivatives (see Table 2).

3.2. Phosphorescence spectra

All the derivatives exhibited phosphorescence emission [19,20] with similar triplet energies in the range 2.5–2.8 eV. In this study some of compounds were recorded in a less polar glass (ether/isooctane). It is seen that the energies are independent of solvent polarity reinforcing the presence of a strongly mixed lower triplet $^3\pi\pi^*$ and $^3n\pi^*$ states [19,20]. The 2-methyl-4-n-propoxy and 4-hydroxy derivatives exhibit the lowest triplet energies suggesting the presence of a predominant lower triplet $^3\pi\pi^*$ state. In the more polar glass (ethanol : methanol) the emission spectra were found to be broader as shown in Fig. 1 for the 4-(2-methylbutanoxy) derivative suggesting strong solute–solvent interactions. The emission spectra were also lacking in vibrational character indicating the lower state to be highly sensitive to solvent polarity.

3.3. Nanosecond flash photolysis

The transient absorption spectra were obtained on the thioxanthones in different solvents to determine the influence of polarity. All solutions prepared were normalised to have an absorbance of 0.5 at 355 nm. The long wavelength absorption maxima (600–700 nm) are all summarised in Table 3 in different solvents. A weaker band was also observed at around 400–500 nm which is possibly associated with the

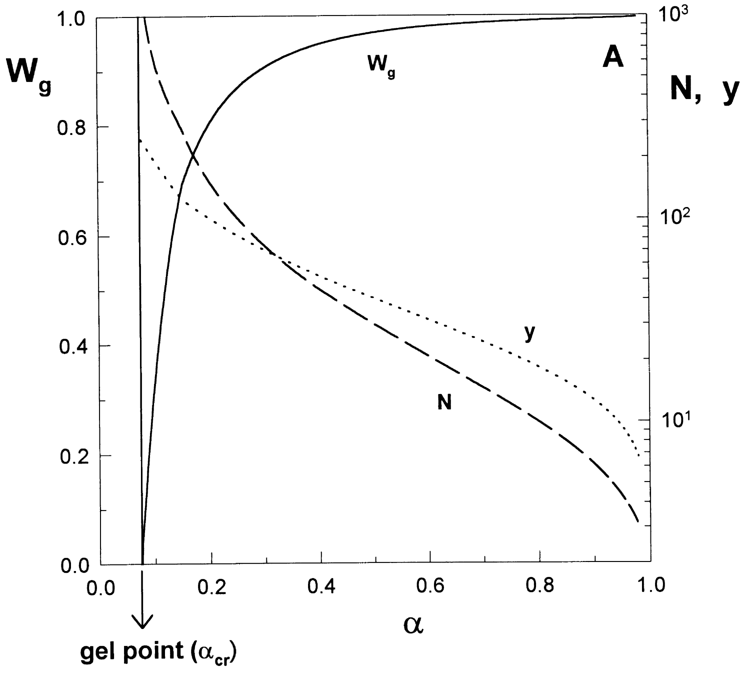


Fig. 2. (*continued*)

long wavelength side of the ketyl radical formed by the triplet state abstracting a hydrogen atom from the solvent or the molecule itself (intermolecular hydrogen atom abstraction). These bands are both quenched by the admissions of oxygen into the solutions and from our earlier work the long wavelength absorption can be assigned to the triplet–triplet absorption [27,37,38]. Typical transient absorption spectra for some of the compounds in different solvents are shown in Fig. 2. There is a noticeable blue shift in the triplet absorption maximum on going from non-polar to polar solvents owing to stabilisation of the lowest triplet state by solvent reorganisation. For the compounds studied in methanol a secondary longer lived species was found to develop and is associated with the formation of the ketyl radical shown three-dimensionally in Fig. 3. Both the 4-(2-methylbutanoxy) and 4-allyloxy derivatives gave this species in methanol. The 4-acetyloxy did not give the ketyl radical in methanol. In 2-propanol and acetonitrile relatively strong transients absorptions were observed except for the 4-hydroxy derivative. Typical triplet–triplet absorption spectra in acetonitrile at different time delays are shown in Fig. 4. At the longer time delay there is some evidence for weak ketyl radical formation. This would be associated with intermolecular hydrogen atom abstraction from itself (possibly the 4-hydroxy group). This would also explain its low photoinitiation activity.

Triplet lifetimes also showed a number of interesting features. Triplet lifetime data taken as the reciprocal of the first-order rate constants are summarised in Table 4 for all the solvent systems studied. It is seen that the triplet lifetime strongly increases with increasing solvent polarity. Since the triplet $^3\pi\pi^*$ and $^3n\pi^*$ states are close in energy in non-polar solvents, vibronic coupling between degenerate states enhances the rate of intersystem crossing to the ground S_o state thus reducing the triplet lifetime [48–50]. Likewise, in polar solvents the $^3\pi\pi^*$ state is stabilised while the $^3n\pi^*$ state is destabilised resulting in a decrease in vibronic coupling which reduces the rate of intersystem crossing enhancing the triplet lifetime. The 4-phenacyloxy exhibits very short triplet lifetimes. This may be associated with the loose bolt effect of the phenyl group deactivating the triplet state by rotational relaxation. The triplet state of the 4-hydroxy derivative is also very short lived indicating rapid deactivation to the ground triplet state and hence its low photoinitiation activity.

The reactivity of the thioxanthone triplet state toward tertiary amines is also important since these compounds are widely used as cosynergists in photocuring. The observed rate constant of deactivation of a transient triplet state in the presence of a quencher Q is described by the classical Stern–Volmer relationship:

$$K_{\mathrm{obsv}} = K_0 + K_{\mathrm{Q}}[\mathrm{Q}] \tag{2}$$

where K_{Q} is the bimolecular quenching rate constant of deactivation by the quencher Q (mol^{-1} dm^3 s^{-1}) and K_0 is the rate constant of deactivation in the absence of Q (s^{-1}). The data in Table 5 summarises the bimolecular triplet quenching constants for different tertiary amines in different solvents using nanosecond laser flash photolysis. All the thioxanthones exhibit relatively high quenching activity with the tertiary amines studied here. There was reduced interaction with methyldiethanolamine and an order of magnitude reduction in quenching in 2-propanol. In the latter case competition by the alcohol may be important.

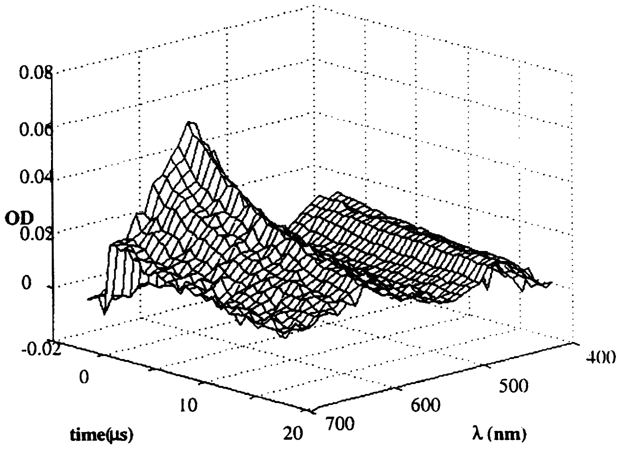


Fig. 3. 3D time dependent spectra of 4-allyloxythioxanthone in nitrogen saturated methanol produced on ns laser flash photolysis.

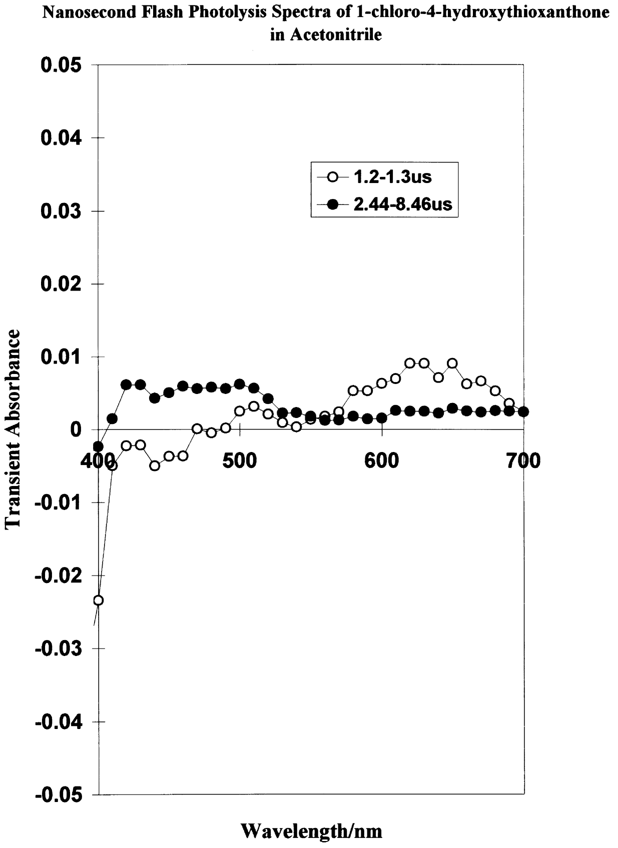


Fig. 4. End-of-pulse transient absorption spectra of nitrogen saturated 1-chloro-4-hydroxythioxanthone in acetonitrile at different time delays produced on ns laser flash photolysis.

Table 4
Triplet lifetimes (τ_{Triplet}) (μs) at the absorption maxima of 1-chloro-4-oxy/acyloxythioxanthones in various anaerobic solvents from ns laser flash photolysis measurements. Precision ± 0.2

Thioxanthone	Methyl alcohol	2-Propanol	Acetonitrile	Toluene
4-Isopropoxy		22.5	2.8	
4-(2-Methylbutanoxy)	16.8		9.4	3.2
4-n-Propoxy		24.8	5.4	
3-Methyl-4-propoxy		22.1	4.9	
2-Methyl-4-propoxy		22.2	1.3	
4-Allyloxy	13.2		7.3	2.5
4-Benzyloxy	15.0		7.9	4.9
4-Oxyethylacrylate	10.3		7.7	5.1
4-Acetyloxy	6.0	15.7	5.7	1.5
4-Acryloxy		8.7	3.0	
4-Phenacyloxy	11.8		1.0	0.4
4-Benzoyloxy		14.2	2.9	
4-Hydroxy		1.4	1.8	

Both the 2-methyl-4-n-propoxy and 4-hydroxy derivatives exhibit much lower quenching interactions with triethylamine by an order of magnitude and again corroborates their lower photoinitiation activity. In the presence of an amine, triethylamine, all the thioxanthones gave a residual longer-lived transient in the region 400–500 nm associated with either the ketyl radical or radical anion species. The latter would be formed by the triplet state of the thioxanthone abstracting an electron from the amine. It is difficult at this point to distinguish the two species since they absorb in similar regions. Typical spectra are shown in Fig. 5 for the 1-chloro-4-n-propoxy derivative.

For three of the thioxanthone derivatives bimolecular triplet rate constants were also determined in the presence of a monomer methyl methacrylate (MMA). The values are shown in Table 6 and verify earlier triplet quenching data indicating the low activity of the triplet thioxanthone toward monomer quenching [33,34].

The molar absorption coefficients of the triplet states of the thioxanthones (TX's) in acetonitrile solution were then estimated by monitoring the energy transfer reaction between the triplet-state TX's and ground-state naphthalene:

$$^3\text{TXs}^* + {}^1\text{N} \rightarrow {}^3\text{N}^* + {}^1\text{TXs} \tag{3}$$

where ^{1}N and ^{3}N* represent the naphthalene ground-state and excited-triplet states respectively (see Table 7). In these experiments, 5×10^{-5} mol dm^{-1} TX solutions containing 10^{-3}–10^{-1} mol dm^{-3} of N in acetonitrile were given a laser pulse at 355 nm. Under these conditions, all the light energy absorbed was taken up by the TX's. The triplet state of the TX's (^{3}TXs*) was thus produced within the laser pulse lifetime, with an absorption maximum at around 640 nm followed by the formation of a new absorption band at 410 nm after 1 μs (when the concentration of naphthalene was 10^{-2} mol dm^{-3}). This may be attributed to the triplet

Table 5
Bimolecular triplet quenching rate constants of 1-chloro-4-oxy/acyloxythioxanthones by various amines in anaerobic acetonitrile and 2-propanol from ns laser flash photolysis measurements. Precision ± 0.5%

Thioxanthone	$K_{3,\text{Q}}$ (dm^3 mol^{-1} S^{-1})			
	Acetonitrile			2-Propanol Triethylamine
	DABCO	Triethylamine	MDEA	
4-Isopropoxy				1.41×10^8
4-(2-Methylbutanoxy)	4.1×10^{10}	1.1×10^9	3.3×10^8	
4-n-Propoxy				1.58×10^8
3-Methyl-4-propoxy				4.55×10^8
2-Methyl-4-propoxy				5.17×10^7
4-Allyloxy	4.4×10^{10}	1.2×10^9		
4-Benxyloxy	9.9×10^{10}	1.5×10^9	5.0×10^8	
4-Oxyethylacrylate	1.5×10^{10}	1.5×10^9	4.8×10^8	
4-Acetyloxy		5.0×10^9		9.67×10^8
4-Acryloxy				1.04×10^9
4-Phenacyloxy		1.5×10^9		
4-Benzoyloxy				9.71×10^8
4-Hydroxy				8.05×10^7

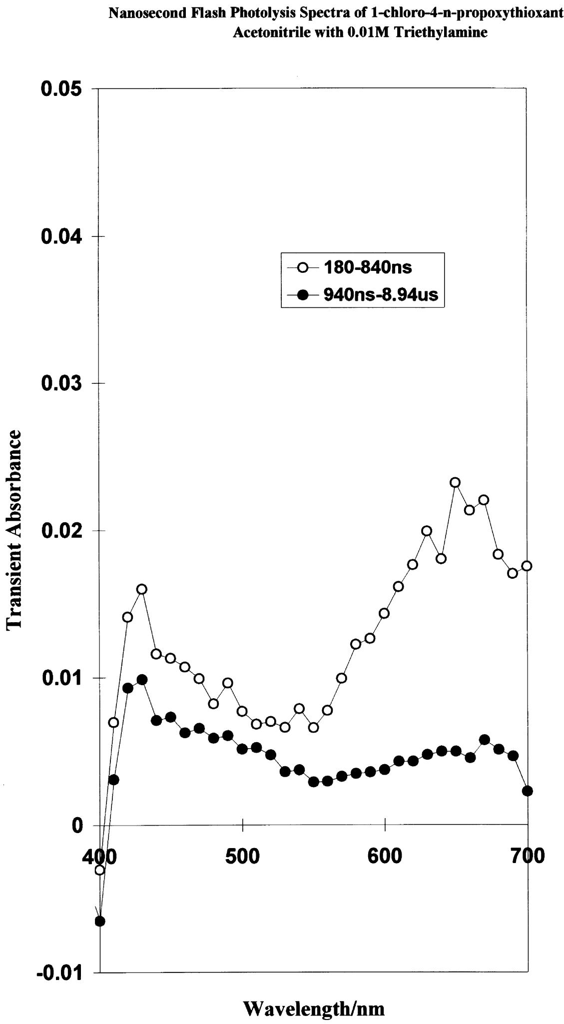


Fig. 5. End-of-pulse transient absorption spectra of nitrogen saturated 1-chloro-4-n-propoxythioxanthone in acetonitrile in the presence of 0.01 M triethylamine at different time delays produced on ns laser flash photolysis.

state of naphthalene formed in accordance with reaction (3) [51]. A similar absorption was observed when benzophenone was used as the sensitiser. The extent of reaction (3) was estimated by comparing the first-oder decay rate constants of the TXs' triplet states in these experiments with the rate constant measured in similar experiments carried out in the absence of naphthalene as described previously [17]. It is seen that the bimolecular triplet quenching constants for the thioxanthones are an order of magnitude lower than that of benzophenone except for the 4-acryloxy derivative where the rate constant is similar. The rate constants for the 2-methyl-4-n-propoxy and 4-hydroxy derivatives are the lowest measured. The fraction of TX triplet state converted to the naphthalene triplet is given by $F = (k_1 - k_0)/k_1$. The molar absorption coefficients of the triplet states of TXs were then calculated using:

$$\frac{FA_{\mathrm{TX*(640\ nm)}}}{A_{\mathrm{N*(410\ nm)}}} = \frac{\epsilon_{\mathrm{TX(640\ nm)}}}{\epsilon_{\mathrm{N*(410\ nm)}}} \qquad (4)$$

where the A values refer to the absorbances of the triplet states of the TXs at the beginning of reaction (I) and of the naphthalene triplet state at the end of reaction (3). Since the molar absorption coefficient of the naphthalene triplet-state absorption at 410 nm, in acetonitrile, is not known, the value was determined using benzophenone as the triplet sensitiser. Experiments similar to those described earlier were carried out using solutions of benzophenone instead of the TX's. A value of 8300 $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$ was obtained for the molar absorption coefficient of the naphthalene triplet state at 410 nm. This value was then used to calculate the molar absorption coefficient of the TX triplet states at 640 nm in accordance with Eq. (4). Care was taken in these and other laser flash photolysis experiments to work with solutions

Table 6
Bimolecular triplet quenching rate constants of some 1-chloro-4-oxy/acyloxythioxanthones by MMA in anaerobic acetonitrile from ns laser flash photolysis measurements. Precision ± 0.5%

Thioxanthone	$K_{3,Q}$ ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$)
4-(2-Methylbutanoxy)	6.3×10^5
4-Benzyloxy	6.4×10^5
4-Oxyethylacrylate	7.1×10^5

Table 7
Bimolecular triplet quenching rate constants of 1-chloro-4-oxy/acyloxythioxanthones by naphthalene in anaerobic acetonitrile from ns laser flash photolysis measurements[a]

Thioxanthone	$K_{3,Q}$ ($\mathrm{dm^3\ mol^{-1}\ s^{-1}}$)
Benzophenone	1.18×10^{10}
4-Isopropoxy	2.76×10^9
4-n-Propoxy	4.37×10^9
3-Methyl-4-propoxy	9.13×10^9
2-Methyl-4-propoxy	1.02×10^9
4-Acetyloxy	9.89×10^9
4-Acryloxy	1.04×10^{10}
4-Benzoyloxy	9.97×10^9
4-Hydroxy	2.59×10^9

[a] Precision ± 0.5%.

Table 8
Triplet molar extinction coefficients and quantum yields of intersystem crossing of 1-chloro-4-oxy/acyloxythioxanthones in anaerobic acetonitrile from ns laser flash photolysis measurements. Precision ± 0.5%

Thioxanthone	ϵ[a] ($\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$)	Φ_{isc}
Benzophenone	6.64×10^3	1.0
4-Isopropoxy	1.14×10^4	0.64
4-Propoxy	1.09×10^4	0.68
3-Methyl-4-propoxy	1.08×10^4	0.64
2-Methyl-4-propoxy	8.59×10^3	0.86
4-Acetyloxy	1.34×10^4	0.77
4-Acryloxy	1.16×10^4	0.64
4-Benzoyloxy	8.56×10^3	0.79
4-Hydroxy	9.72×10^3	0.62

[a] Absorbance = 0.3 at 355 nm (λ_{max}).

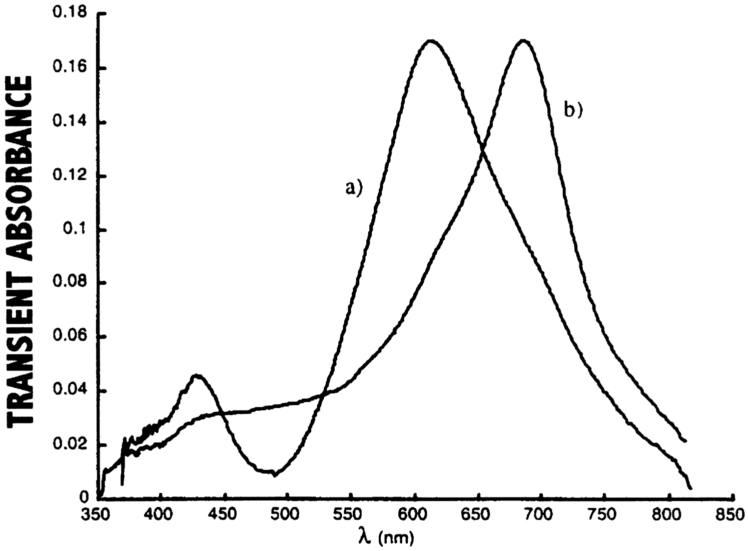


Fig. 6. Pico-second triplet spectra of 1-chloro-4-oxyethylacrylatethioxanthone in (a) methanol and (b) toluene.

with relatively low absorbance at the excitation wavelength (typically less than 0.5) to provide as homogeneous a distribution of excited states in the optical detection path as possible.

Similarly, the lowest laser pulse energies were employed (typically 3 mJ or less) to avoid unwanted biphotonic processes or unnecessarily high triplet–triplet annihilation reaction rates. In this way, by using a range of naphthalene concentrations and making several repeats of each measurement, the molar absorption coefficients of the TX's in acetonitrile solution were obtained and are given in Table 8 at their respective absorption maxima.

The molar absorption coefficients can be used to calculate the quantum yields for intersystem crossing for the TX's (Φ_{isc}) in acetonitrile solutions. This was achieved by giving laser pulses to deaerated solutions of benzophenone (ca. 5×10^{-3} mol dm^{-3}) and comparing the maximum absorbance observed at 520 nm, attributable to the triplet state of benzophenone, with that of the absorbance observed at 640 nm, after giving an identical laser pulse to deaerated solutions of the TXs. The comparisons were made using benzophenone and the TX's solutions of identical absorbances at the excitation wavelength. The quantum yield of the TX's triplet states are then calculated by application of the following:

$$\frac{A_{\mathrm{BZ^*(520\ nm)}}}{A_{\mathrm{TZ^*(640\ nm)}}} = \frac{\epsilon_{\mathrm{BZ^*(520\ nm)}}\,\Phi_{\mathrm{isc(BZ)}}}{\epsilon_{\mathrm{TX^*(640\ nm)}}\,\Phi_{\mathrm{isc(TX)}}} \qquad (5)$$

where the absorbances A, and molar absorption coefficients, ϵ are of the corresponding triplet states of benzophenone and TX's. The quantum yields for intersystem crossing for the TX's were calculated from these comparative experiments taking Φ_{isc} for benzophenone to be 1.0. The molar absorption coefficient of the triplet state of benzophenone [51,52] was found to be 6640 dm^3 mol^{-1} cm^{-1}.

Table 9
Triplet absorption maxima (nm) of 1-chloro-4-oxy/acyloxythioxanthones in various anaerobic solvents from ps laser flash photolysis measurements. Precision ± 2

Thioxanthone	Methyl alcohol	2-Propanol	Acetonitrile	Toluene
4-Isopropoxy		636	647	
4-(2-Methylbutanoxy)	611	615	650	685
4-Propoxy		634	650	
3-Methyl-4-propoxy		656	661	
2-Methyl-4-propoxy		633	649	
4-Allyloxy	613	631	650	686
4-Benzyloxy	686	651	631	615
4-Oxyethylacrylate	615	631	649	686
4-Acetyloxy	620	654	660	
4-Acryloxy		660	660	
4-Phenacyloxy			650	685
4-Benzoyloxy		656	663	
4-Hydroxy		626	639	

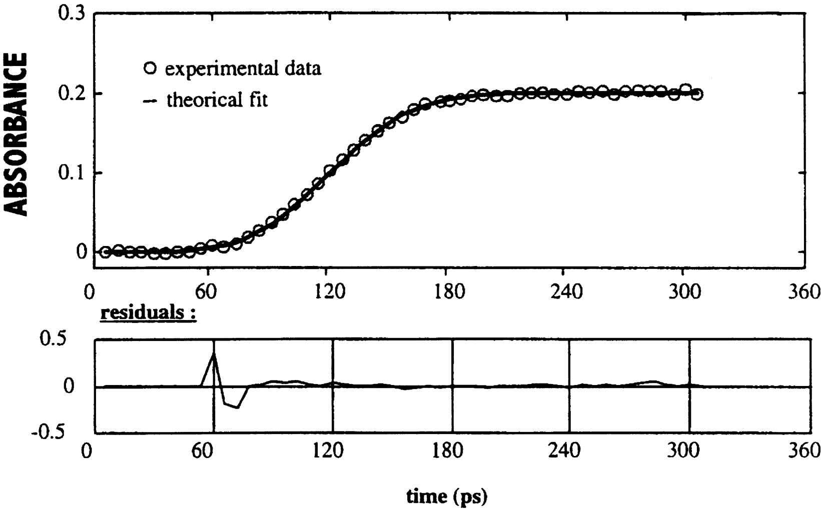


Fig. 7. Formation of the triplet-state of 1-chloro-4-oxyethylacrylatethioxanthone in acetonitrile on ps laser flash photolysis. The signal was fitted with a non-exponential rise. Residual plots indicate some deviations of the calculated points from the experiment.

The triplet–triplet molar absorption coefficients given in Table 8 show that the values for the TX's are less than that for benzophenone. The interesting feature of the data however, is the small variation in quantum yields for the TX's implying that the side chain does not significantly affect the intersystem crossing efficiency.

3.4. Picosecond flash photolysis

Following the initial pulse excitation, the TX's decay from a high vibrational excited singlet state to a relaxed lower excited singlet state. Then, intersystem, crossing leads to the formation of their lowest excited triplet state. With the picosecond technique it was possible to record the growth of the triplet state and to obtain the triplet absorption spectra of the TX's with enhanced resolution and quality. Typical spectra are illustrated in Fig. 6 for the 4-oxyethylacrylate derivative in methanol and toluene. The data in Table 9 gives all the absorption maxima for the thioxanthones. Again it is seen that there is an evident blue shift in the maxima from toluene to methanol/2-propanol. This is consistent with the nanosecond laser study and is a result of stabilisation of the lowest triplet state by interaction with the solvent molecules. In polar solvents the $^3\pi\pi^*$ state is stabilised while the $^3n\pi^*$ state is destabilised.

A second species is also formed by this technique in the more polar solvents in the region 400–500 nm which is assigned to the formation of the ketyl radical. Like the nanosecond experiments this spectrum occurs at around 430 nm and is the ketyl radical and will be formed by the triplet state of the TX abstracting a hydrogen atom from either the solvent or itself. Interestingly, both the 4-acetyloxy and acryloxy derivatives did not show significant ketyl radical formation on this timescale.

This picosecond study also allows us to see the risetime of formation of this ketyl radical: it is a very fast reaction, about 10 ps. This radical appears at the same time as the triplet state of the thoxantone derivatives. Thus, the mechanism of the ketyle radical formation should include reactions from the singlet state of the compounds: reactions from the triplet state induce a very long risetime. However, the real mechanism is not clearly understood and further studies are underway.

Some experiments on 2-chloro-thioxanthone (CTX) in toluene were also done for comparison. These experiments permit a comparison of the results on the CTX with those of the thioxanthone derivatives here. Excited by nanosecond laser pulses (355 nm), CTX in toluene leads to the formation of the ketyl radical by hydrogen atom abstraction from the solvent. The ketyl was only detected by the nanosecond experiment. The picosecond experiments did not show any ketyl radical formation for CTX in toluene. Thus, the formation of the radical arises from the triplet state of the CTX.

This picosecond study also allowed measurement of the rate of intersystem crossing in acetonitrile by simulating the risetime of the triplet formation. The transient absorbance obtained from the picosecond spectra is fitted according to [47,53] (Fig. 7):

$$\mathrm{Abs}(t) = \int_o^t I(\chi)F(t-\chi)\,\mathrm{d}\chi = I(t) \otimes F(t) \tag{6}$$

where $I(t)$ is the instrument response (the convolution of pump and probe beams) [53,54] and is assumed to be Gaussian [53,54]:

$$I(t) = \frac{1}{\sqrt{2}\Pi\sigma}\exp\left(-(t-t_0)^2/2\sigma^2\right) \tag{7}$$

and $F(t)$ is a single exponential rise for the species:

$$F(t) = A\left(1-\exp(-t/\tau)\right) \tag{8}$$

where τ is the risetime of the signal. The rise-times τ_r of the

Table 10
Transient absorption maxima of 1-chloro-4-oxy/acyloxythioxanthones in the absence and presence of triethylamine in anaerobic 2-propanol from μs flash photolysis measurements. Precision ± 0.5%.

Thioxanthone	No amine		Triethylamine	
	λ_{max} (nm)	ABS	λ_{max} (nm)	ABS
4-Isopropoxy	345 (425)	0.055 (0.015)	345 (425)	0.046 (0.018)
4-(2-Methylbutanoxy)	345 (420)	0.050 (0.011)	325 (445)	0.054 (0.014)
4-n-Propoxy	345 (425)	0.140 (0.015)	320 (425)	0.015 (0.02)
3-Methyl-4-propoxy	350 (325)	0.062 (0.019)	320 (425)	0.12 (0.027)
2-Methyl-4-propoxy	325 (425)	0.046 (0.01)	330 (425)	0.085 (0.014)
4-Allyloxy	335 (425)	0.058 (0.016)	335 (425)	0.074 (0.023)
4-Benzyloxy	335 (425)	0.065 (0.018)	335 (425)	0.068 (0.024)
4-Oxyethylacrylate	330 (425)	0.053 (0.016)	345 (425)	0.096 (0.022)
4-Acetyloxy	320 (420)	0.07 (0.022)	320 (420)	0.086 (0.034)
4-Acryloxy	320 (420)	0.080 (0.02)	325 (420)	0.10 (0.28)
4-Phenacyloxy	320 (420)	0.11 (0.034)	320 (420)	0.13 (0.04)
4-Benzoyloxy	335 (425)	0.044 (0.01)	335 (420)	0.045 (0.018)
4-Hydroxy	335	0.2	–	–

lowest triplet state population of all the compounds in acetonitrile are estimated to be in the range of 6–18 ps at the wavelength maximum of the absorption spectra of the species. This suggests that the structure of the thioxanthone has no significant effect on the rate constants of intersystem crossing as found by nanosecond laser techniques.

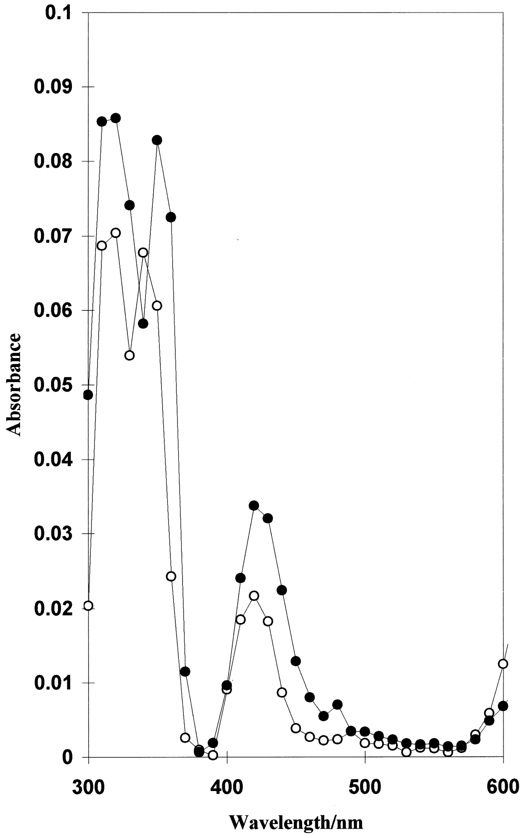


Fig. 8. Microsecond flash photolysis spectra of 1-chloro-4-acetyloxythioxanthone (5×10^{-5} M) in the absence (○) and presence (●) of triethylamine (10^{-3} M) in 2-propanol.

3.5. Microsecond flash photolysis

Using microsecond flash photolysis transient absorption spectra were obtained for all the TX's in 2-propanol in the absence of an amine. The data are shown in Table 10. Two maxima were obtained, the first and strongest was observed in the region 300–400 nm while second weaker band was observed in the region 400–500 nm. The ketyl radical formed by hydrogen atom abstraction from solvent by the triplet state of the TX's absorbs strongly in both regions. The radical anion tends to predominate in the latter region. Typical spectra are shown for the 1-chloro-4-acetyloxy derivative in Fig. 8. The strongest transient is seen for the 4-hydroxy derivative and may be owing to the involvement of some intermolecular hydrogen atom abstraction from itself. The addition of triethylamine strongly enhances both absorption bands as seen in the data (Table 10). However, the transient absorption in both regions for the 4-hydroxy derivative is completely quenched by the amine. This is illustrated by the spectra in Fig. 9 and clearly shows the involvement of some other photochemical mechanism.

4. Conclusions

From the photocalorimetry study all the initiators exhibit high photopolymerisation activity except the 4-hydroxy model and 2-methyl-4-n-propoxy derivatives. Both these compounds exhibit distinctly lower activities. The low temperature phosphorescence analysis shows that the triplet energies are found to be fairly insensitive to solvent polarity with an observed spectral broadening from non-polar to polar solvents. This is consistent with close lying mixed triplet states of $^3\pi\pi^*$ and $^3n\pi^*$ character. Both the least active 4-hydroxy and 2-methyl-4-propoxy derivatives exhibit lower triplet energies suggesting the presence of a less active lower triplet $^3\pi\pi^*$ state.

Laser flash photolysis experiments show triplet–triplet

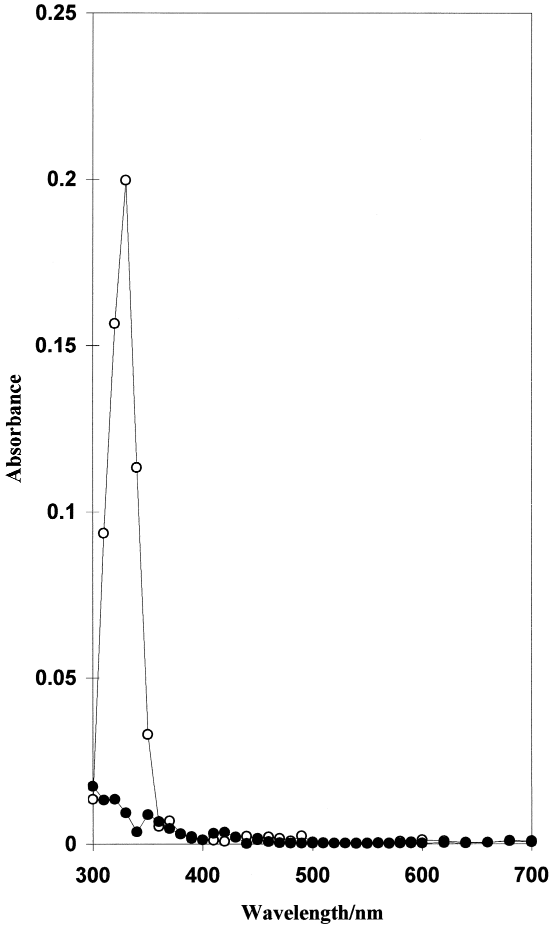


Fig. 9. Microsecond flash photolysis spectra of 1-chloro-4-hydroxythioxanthone (5×10^{-5} M) in the absence (○) and presence (●) of triethylamine (10^{-3} M) in 2-propanol.

absorption spectra with all the thioxanthones in the range 600–680 nm with a marked blue shift from non-polar to polar solvents owing to stabilisation of the lowest triplet state by solvent reorganisation. In photoreductive solvents such as methyl alcohol and 2-propanol a longer lived species are observed absorbing in the region 400–500 nm which is associated with the formation of the ketyl radical. This observation is highly solvent dependent. Microsecond flash spectroscopy in 2-propanol shows ketyl radical formation in all cases. The 4-hydroxy derivative gave only weak transient absorption on laser flash photolysis and none on microsecond flash photolysis in the presence of triethylamine. Triplet lifetimes increase with solvent polarity confirming the presence of mixed $^3\pi\pi^*$ and $^3n\pi^*$ states where vibronic coupling influences the rate of intersystem crossing to the ground S_0 state. Bimolecular triplet quenching rate constants indicates that all the thioxanthones, except the 2-methyl-4-n-propoxy and 4-hydroxy, interact strongly with a range of tertiary amines, DABCO, triethylamine and methyldiethanolamine. The lower triplet quenching constants for the 2-methyl-4-n-propoxy and 2-hydroxy derivatives (an order of magnitude) indicates weaker interaction by the amine and is consistent with their lower photoinitiation activities. Low triplet quenching rates are also observed in the presence of monomer (methyl methacrylate). Bimolecular triplet quenching rates measured with naphthalene are similar to those for benzophenone except the 2-methyl-4-n-propoxy and 4-hydroxy derivatives which are an order of magnitude less. From this data triplet molar extinction coefficients are found to be higher than that for benzophenone owing to the presence of mixed states. Again, the 2-methyl-4-n-propoxy and 4-hydroxy derivatives exhibited lower values as did the 4-benzoyloxy derivative. Relatively high quantum yields of intersystem crossing are observed (< 0.6) but are all lower than that of benzophenone with the side chain substituents having no significant effect on the rate. Through picosecond flash photolysis the growth rate of the triplet state is found to be 6–18 ps and there is a concurrent formation of the ketyl racidal except for the 4-acetyloxy and 4-acryloxy derivatives.

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