

# Spectroscopic properties and photopolymerization activities of water soluble 1-substituted derivatives of 2-hydroxy-3-(9-oxo-9H-thioxanthene-4-yloxy)-N,N,N-trimethyl-1-propanaminium chloride salt

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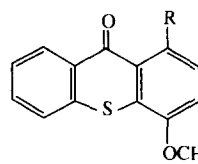
The spectroscopic, photochemical and photopolymerization properties of four novel 1-substituted water soluble 2-hydroxy-3-(9-oxo-9H-thioxanthene-4-yloxy)-N,N,N-trimethyl-1-propanaminium chloride salts are examined. From absorption and fluorescence and phosphorescence analysis substitution in the 1-position by halogen groups induces more charge-transfer character than aliphatic alkyl groups. The photoreduction quantum yields of all the 1-substituted derivatives in the presence of a tertiary amine are lower than that for the unsubstituted derivative which is again indicative of the higher degree of charge-transfer content of the lowest excited states. The reduced activity of the 1-substituted derivatives is also reflected in the microsecond flash photolysis data on radical and radical anion formation. The addition of a tertiary amine, however, enhances the formation of both species probably due to triplet exciplex formation. Photopolymerization and photoinitiation rates for acrylamide are also reduced by 1-substitution. The data are discussed in terms of the nature of 1-substitution increasing the degree of charge-transfer character of the lowest excited singlet and triplet states.

(Keywords: spectroscopy; photochemistry; photopolymerization)

## INTRODUCTION

Thioxanthone compounds have widespread application as photoinitiators for oil- and water-based pigmented coating systems<sup>1-3</sup>. Of particular interest is the development of new structural types for improved property requirements such as grafting and copolymerization as well as increased activity<sup>4-7</sup>. Thus, for oil soluble compounds substitution of acrylic, alkyl, alkylamino and halogen groups in the 2- and 4-positions of the thioxanthone chromophore gives rise to enhanced photochemical activity<sup>1,3,4,7</sup>. The same effects have also been observed for water soluble 2- and 4-substituted chloro and methylsulphonate salts of (2-hydroxy-3-N,N,N-trimethylammonium prop-1-oxy) thioxanthone<sup>5,6</sup>. In this case photochemical activity was associated with the lowest excited singlet and triplet states with 4-substitution

giving the highest activity and 3-substitution the lowest. In this paper we have extended this earlier work to cover a range of 1-substituted derivatives of the 2-hydroxy-3-(9-oxo-9H-thioxanthene-4-yloxy)-N,N,N-trimethyl-1-propanaminium chloride salt shown by structures I-V (Scheme 1). Here we have examined the effect of alkyl versus halogen substitution on photochemical and photopolymerization activity. In this case 1-substitution reduced the overall activity of the thioxanthone chromophore in terms of its photochemical properties and this was reflected in the ability of the derivatives to induce the photopolymerization of water-based monomers.



- I R=H
- II R=CH<sub>3</sub>
- III R=CH<sub>2</sub>CH<sub>3</sub>
- IV R=F
- V R=Cl

Scheme 1 Structures I-V

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## EXPERIMENTAL

## Materials

Samples of the thioxanthenes of structures I–V were supplied by International Biosynthetics Ltd, Widnes, Cheshire, UK. The water used in this study was doubly distilled and the 2-propanol was of spectroscopic quality and, together with the amines, tri-*n*-butylamine, diethylaminoethanol and *N,N*-dimethylamine and acrylamide, were obtained from the Aldrich Chemical Company, UK. The water miscible acrylic prepolymer RCP 2492 was supplied by Harcros Chemicals Ltd, Manchester, UK.

## Spectroscopic measurements

U.v. absorption spectra were recorded by means of a Shimadzu UV-265-FS spectrophotometer. Fluorescence and emission spectra were obtained using a Perkin-Elmer LS-5 luminescence spectrometer. Fluorescence quantum yields were obtained at 300 K using the relative method with quinine sulphate as a standard assuming a quantum yield of 0.55 in 0.1 M sulphuric acid<sup>8</sup>. Phosphorescence quantum yields were obtained by the same method using benzophenone as a standard assuming a quantum yield of 0.74 in ethanol glass at 77 K<sup>9</sup>. Data on the fluorescence and phosphorescence of compounds I and II have been referred to previously<sup>6</sup> but are in error due to printing. This includes reference to lifetimes in nanoseconds which should be in milliseconds.

## Photoreduction quantum yields

Absolute quantum yields of photoreduction were determined in water at a chromophore concentration of  $10^{-5} \text{ mol l}^{-1}$  and in the presence of 1% w/w dimethylaniline. Irradiation was carried out at 365 nm and has been described previously<sup>10</sup>.

## Flash photolysis

Transient absorption spectra were recorded using a microsecond kinetic flash photolysis apparatus utilizing two 16 kV xenon-filled flash lamps with 300 J energy output (operated at 10 kV) and a 150 W tungsten/halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope and solutions were deoxygenated using white spot nitrogen gas (< 5 ppm oxygen).

## Photopolymerizations

The initial rates of polymerization  $R_p$  of acrylamide were determined by photocalorimetry in 20% w/w aqueous solution in air at 35°C using 365 nm u.v. light. In all cases the aluminium pan used was sealed in quartz glass in order to avoid evaporation of the monomer. The kinetics of photoinitiated polymerization were monitored using a modified Perkin-Elmer DSC-4 calorimeter. The thioxanthone derivatives were dissolved in the monomer-solvent mixture at a concentration of  $10^{-3} \text{ M}$  using a cell path length of 1 mm, where  $10 \mu\text{l}$  were placed in order to reduce the possible size effect on the polymerization rate. The irradiation was carried out in the presence of air in order to simulate the real conditions of application and 2-*N,N*-diethylaminoethanol was used as the cosynergist at  $10^{-2} \text{ M}$  concentration. The experimental details of the system have been reported earlier<sup>10</sup>.

The photocuring ability of the initiators was also measured in a water-based acrylic prepolymer RCP 2492 (undisclosed composition) at 1% w/w concentration

together with 5% w/w water addition. Films ( $50 \mu\text{m}$  thick) were cast on salt flats and irradiated for 30 s using a 100 W high pressure mercury lamp. The rate of cure was determined by measuring the decrease in the vinyl absorption at  $812 \text{ cm}^{-1}$  relative to that of the ester absorption at  $1740 \text{ cm}^{-1}$ . The latter band compensates for changes in film thickness upon curing. FTi.r. spectra were recorded using a BIORAD FTS-7 spectrometer coupled to an SPC-320 data station and the following calculation was used to measure the degree of cure:

$$\% \text{ Cure} = 1 - (A_{812}/A_{1740 \text{ cm}^{-1}})_t / (A_{812}/A_{1740 \text{ cm}^{-1}})_0 \times 10^2$$

where  $A$  is absorbance and subscripts 0 and  $t$  are irradiation times initially and after some time  $t$ .

## RESULTS AND DISCUSSION

## Spectroscopic properties

The absorption and luminescence (fluorescence and phosphorescence) properties of the five thioxanthone initiators are compared in Table 1. The phosphorescence spectra are recorded in 2-propanol due to problems with water cracking the quartz tubes used in the measurement at 77 K. Both the absorption wavelength maxima and extinction coefficients are little influenced by the nature of the 1-substitution. The former are slightly enhanced as might be expected due to the electron donating ability of the groups. The fluorescence emission wavelength maximum however, is markedly red shifted by the 1-substitution with the two alkyl groups exhibiting the greatest effect. This trend is consistent with the lowest excited singlet state decreasing in energy and becoming more  $\pi-\pi^*$  in character. In general the fluorescence quantum yields are lower for the 1-substituted derivatives with the effect being greater for the alkyl than that for the halogen groups. In the former case the quantum yield is lower for the methyl substitution than that for ethyl. Here, intramolecular hydrogen atom transfer will be efficient. In the case of halogen substitution the chlorine atom deactivates the lowest excited singlet state more than that for the fluorine atom. In the latter case this may be due to internal heavy-atom spin orbit coupling increasing the rate of intersystem crossing. This is reflected by the increased phosphorescence quantum yield for the chloro derivative compared with that of fluorine. Substitution of the alkyl groups significantly reduces the phosphorescence quantum yield compared with that of the unsubstituted derivative with no emission being observed in the case of the ethyl derivative. Intramolecular hydrogen atom transfer would account for this effect and this is confirmed by the marked reduction in the triplet lifetime for the methyl derivative.

**Table 1** Spectroscopic properties of 1-substituted thioxanthenes in water and 2-propanol

R =	Absorbance (water)		Fluorescence (water)		Phosphorescence (2-propanol)		
	$\lambda_{\text{max}}$	Log $\epsilon^a$	$\lambda_{\text{max}}$	$\phi_f$	$\lambda_{\text{max}}$	$\phi_p$	$\tau^{0b}$
H	392	3.70	468	0.51	460	0.20	197
Methyl	392	3.72	495	0.11	465	0.07	10
Ethyl	393	3.74	494	0.30	—	—	—
Fluorine	392	3.75	489	0.44	464	0.24	203
Chlorine	394	3.74	483	0.32	470	0.45	169

<sup>a</sup>  $\epsilon$ , Extinction coefficient

<sup>b</sup>  $\tau^0$ , Triplet lifetime

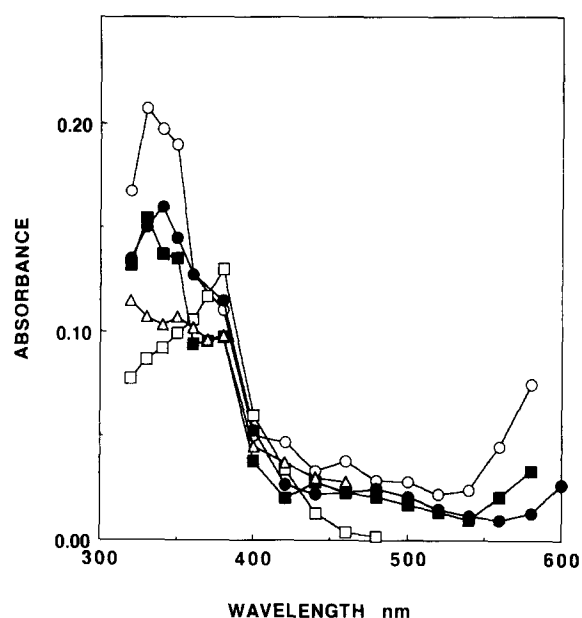
**Table 2** Photoreduction quantum yields of water soluble 1-substituted thioxanthenes in 2-propanol ( $10^{-5}$  M) with 1% w/w *N,N'*-dimethylaniline

R =	Quantum yield
H	0.29
Methyl	0.12
Ethyl	0.13
Fluorine	0.14
Chlorine	0.05

*Photoreduction and flash photolysis*

The photoreduction quantum yields for all the five initiators in deoxygenated water and in the absence of a hydrogen atom donor were low ( $<10^{-4}$ ). The photoreduction quantum yields were therefore measured in 2-propanol in the presence of a tertiary amine, *N,N*-dimethylaniline and data are shown in Table 2. The quantum yields are seen to be significantly lower for all four 1-substituted derivatives compared with that of the unsubstituted derivative. In the case of the alkyl derivatives intramolecular hydrogen atom transfer would account for their reduced activity and this is consistent with the reduced activity of the lowest excited triplet state. In the case of the halogen derivatives there is also reduced activity and this may be associated with steric hindrance of the carbonyl group in forming an exciplex with the amine for effective photoreduction.

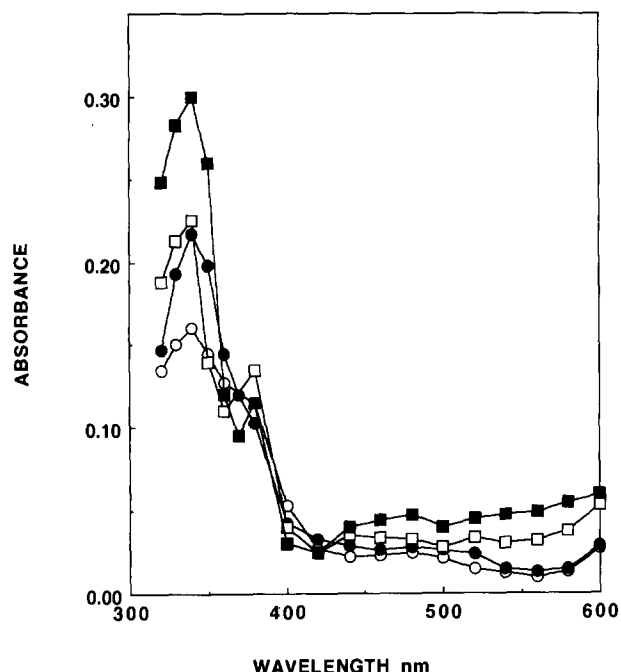
End-of-pulse transient absorption spectra of all five photoinitiators in 50:50 v/v 2-propanol-water produced on microsecond flash photolysis are shown in Figure 1. Absorption maxima in the absence and presence of oxygen are summarized in Table 3. All the initiators possess broad absorption maxima in the region 300–400 nm which are associated with the formation of a semiquinone radical produced by the lowest excited triplet state of the thioxanthone chromophore abstracting a hydrogen atom from the solvent<sup>4–7</sup>. A weak broad absorption is also observed above 400 nm except for the ethyl derivative which is due to the formation of the radical anion species produced by electron abstraction from the solvent. In 2-propanol the lowest excited triplet state appears to be the more active state, unlike that found previously in water alone, since oxygen has a strong quenching effect on transient formation (Table 3). Deactivation by 1-substitution however, is also evident with regard to free radical formation on flash photolysis. The data in Table 3 show that transient absorbance is markedly reduced in the case of all four derivatives compared with that produced for the unsubstituted derivative. The results are consistent with the presence of a low lying less active triplet  $\pi-\pi^*$  excited state for the 1-substituted derivatives. The effect of adding a tertiary amine namely, tri-*n*-butylamine, on transient formation for one of the derivatives (compound II) is shown in Figure 2 and the maxima are summarized in Table 4. It is seen that with increasing amounts of amine both the semi-quinone radical and radical anion species are enhanced probably through triplet exciplex formation between the thioxanthone and the amine. This would also account for the notable synergistic effect of amines on the rate of photopolymerization induced by thioxanthenes<sup>4–7</sup>.

**Figure 1** End of pulse transient absorption spectra of water soluble thioxanthenes (○) I, (●) II, (□) III, (■) IV and (△) V produced on microsecond flash photolysis in a deoxygenated 2-propanol-water mixture (50:50 v/v)**Table 3** Transient absorption properties of thioxanthenes in 50:50 propan-2-ol-water

R =	Anaerobic $\lambda_{\max}$ (nm)	Absorbance	Aerobic $\lambda_{\max}$ (nm)	Absorbance
H	310	0.270	310	0.030
	380 (s)	0.110		
	420 (s)	0.047		
Fluorine	330	0.155	330	0.033
	380 (s)	0.097		
	440 (s)	0.027		
Chlorine	320	0.115	320	0.024
	380 (s)	0.097		
	440 (s)	0.029		
Methyl	340	0.160	340	0.034
	380 (s)	0.114		
	480 (s)	0.025		
Ethyl	340 (s)	0.092	380	0.015
	380	0.130		

**Table 4** Influence of tri-*n*-butylamine on the transient absorption properties of 1-methyl substituted thioxanthone in 50:50 propan-2-ol-water

Amine concentration (M)	Anaerobic $\lambda_{\max}$ (nm)	Absorbance	Aerobic $\lambda_{\max}$ (nm)	Absorbance
None	340	0.160	340	0.034
	380 (s)	0.114		
	480 (s)	0.025		
$10^{-4}$	340	0.216	340	0.046
	380 (s)	0.103		
	480 (s)	0.029		
$5 \times 10^{-4}$	340	0.225	340	0.050
	380 (s)	0.133		
	480 (s)	0.033		
$10^{-3}$	340	0.300	340	0.059
	380 (s)	0.115		
	480 (s)	0.047		



**Figure 2** End of pulse transient absorption spectra of water soluble thioxanthone (II) in the presence of (O) no amine, (●)  $10^{-4}$  M, (□)  $5 \times 10^{-4}$  M and (■)  $10^{-3}$  M tri-*n*-butylamine produced on microsecond flash photolysis in a deoxygenated 2-propanol-water mixture (50:50 v/v)

**Table 5** Photopolymerization rates ( $R_p$ ), quantum yields of monomer conversion ( $\phi_m$ ) and photoinitiation rates ( $\phi_i$ ) as measured by photocalorimetry for acrylamide in aerobic water (20% w/w) at 365 nm irradiation in the presence of water soluble 1-substituted thioxanthenes ( $10^{-3}$  M) with *N,N'*-diethylaminoethanol ( $10^{-2}$  M)

R =	$R_p (\times 10^2)$ ( $M s^{-1}$ )	$\phi_m$	$\phi_i$
H	2.2	162	0.0017
Methyl	1.9	137	0.0013
Ethyl	1.7	124	0.0010
Fluorine	1.8	135	0.0012
Chlorine	1.8	131	0.0012

**Table 6** Percentage photoconversion (at  $812\text{cm}^{-1}$ ) as measured by FTi.r. spectroscopy for a water miscible acrylated prepolymer RCP 2492 with 5% w/w water induced by 1% w/w 1-substituted thioxanthenes after 30 s irradiation with a 100 W high pressure mercury lamp

R =	Photoconversion (%)
H	82
Methyl	51
Ethyl	41
Fluorine	76
Chlorine	54

### Photopolymerization

The photopolymerization rates of acrylamide in aerobic water, quantum yield of monomer conversion and photoinitiation rates as measured by photocalorimetry are shown in Table 5. The tertiary amine, *N,N*-diethylaminoethanol, was present in all cases. Despite the presence of oxygen the quantum yields for monomer

conversion were all high. This effect may well be due to the presence of the amine scavenging the oxygen via alkylamino radicals produced by the lowest excited triplet state of the thioxanthone abstracting a hydrogen atom from the amine. The rates of photopolymerization are all in the range  $1.7 \times 10^2$ – $1.9 \times 10^2 M s^{-1}$  and are much lower than that measured for the unsubstituted initiator ( $2.2 \times 10^2 M s^{-1}$ ). In order to cross-check the efficiencies of these photoinitiators the photocuring of a water miscible commercial acrylic prepolymer was also examined using FTi.r. spectroscopy. Here the degree of photoconversion of the vinyl absorption at  $812\text{cm}^{-1}$  after 30 min of u.v. exposure is shown by the data in Table 6. In agreement with the acrylamide data in Table 5 it is seen that all the substituted derivatives are less effective than that observed for the unsubstituted compound with the ethyl derivative being the least effective. Thus, the lower photopolymerization activities of all four 1-substituted derivatives is associated with the presence of less active low lying triplet excited states and this is reflected in the luminescence data and low yields of radical formation on microsecond flash photolysis.

### CONCLUSIONS

The substitution of alkyl and halogen groups in the 1-position of a thioxanthone chromophore containing a water solubilizing 4-substituted 2-hydroxy-*N,N,N*-trimethylammonium propoxy group deactivates the lowest excited singlet and triplet states of the molecule and hence its overall activity as an initiator of photopolymerization. This is reflected by a reduction in both their photoreduction quantum yields and free radical formation on microsecond flash photolysis. Alkyl groups appear to deactivate the lowest excited triplet state by intramolecular hydrogen atom transfer with the quinone carbonyl group while the presence of halogen atoms increases the degree of  $\pi$ - $\pi^*$  character of the lowest excited singlet and triplet states.

### ACKNOWLEDGEMENT

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