

## PHOTOCHEMISTRY OF THIOXANTHONES—III

### SPECTROSCOPIC AND FLASH PHOTOLYSIS STUDY ON HYDROXY AND METHOXY DERIVATIVES

N. S. ALLEN\*, F. CATALINA† and B. MOGHADDAM

Department of Chemistry, John Dalton Faculty of Technology, Manchester Polytechnic, Chester Street,  
Manchester M1 5GD, U.K.

P. N. GREEN and W. A. GREEN

Ward-Blenkinsop & Company Limited, Halebank Estate, Lower Road, Widnes,  
Cheshire WA8 8NS, U.K.

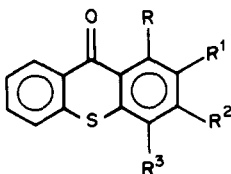
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**Abstract**—The spectroscopic properties of 9 oil soluble hydroxy and methoxy thioxanthone derivatives have been examined in various solvents and the data compared to their photopolymerization efficiency and flash photolysis behaviour in solution. Absorption maxima, extinction coefficients, fluorescence and phosphorescence spectra and quantum yields have been measured. Generally, most of the compounds exhibit low fluorescence and high phosphorescence quantum yields except 1-substituted derivatives where intra-molecular hydrogen bonding is involved. These observations are consistent with the high photo-reactivity of the molecules occurring via the lowest excited triplet state. Photopolymerization rates of *n*-butyl methacrylate, using *N*-diethylmethylamine as co-initiator, correlate to some extent with the absorption maxima and extinction coefficients of the thioxanthenes. Transient formation on micro-second flash photolysis is associated with the ketyl radical formed by the lowest excited triplet state of the thioxanthenes abstracting a hydrogen atom from the solvent. In the presence of a tertiary amine, a new longer wavelength transient absorption is produced and is assigned to a radical-anion formed by the lowest excited triplet state of the thioxanthenes abstracting an electron from the amine. A correlation was observed between the transient absorption due to the radical-anion and the ionisation potential of various amines. Flash photolysis studies in acid and base media confirmed the identity of the radical and radical-ion species. Intra-molecular hydrogen bonding in the  $\alpha$ -position to the carbonyl group deactivates both the lowest excited singlet and triplet states of thioxanthone but has little effect on polymerization efficiency. The latter is associated with competition of the carbonyl group with the amine co-initiator for hydrogen bonding and consequent electron abstraction to give an active radical-anion. This is confirmed using micro-second flash photolysis.

#### INTRODUCTION

Thioxanthenes form an important class of photo-initiators which display high photoinitiation activity when irradiated in the near u.v. with wavelengths up to 400 nm [1]. This feature makes them particularly useful for the photocuring of white pigmented coatings [2, 3]. In earlier papers, we examined the photochemistry of currently available thioxanthone derivatives [4] as well as some novel water soluble types [5]. In both cases we observed a close relationship between the photophysical properties of the substituted thioxanthenes and their activity in initiating photopolymerization. In the former case, initiation involves the lowest excited triplet state of the thioxanthone,

whilst in the latter types the lowest excited singlet state was implicated. In the presence of a tertiary amine co-initiator, both excited states abstract an electron to give a radical-anion whereas in the absence of an amine hydrogen atom abstraction from the solvent is the dominant process. In this paper we have extended our previous studies [4, 5] to the photochemistry and photopolymerization activity of a range of hydroxy and methoxy derivatives of thioxanthone of structures I(a-i). Their photochemical properties are reported here for the first time and, of the derivatives, the 1-hydroxy, 4-hydroxy and 1-methoxythioxanthenes are novel compounds.



- I (a)  $R=OH$ ,  $R(1)=R(2)=R(3)=H$   
(b)  $R(1)=OH$ ,  $R=R(2)=R(3)=H$   
(c)  $R(2)=OH$ ,  $R=R(1)=R(3)=H$   
(d)  $R(3)=OH$ ,  $R=R(1)=R(2)=H$   
(e)  $R=OCH$ ,  $R(1)=R(2)=R(3)=H$   
(f)  $R(1)=OCH$ ,  $R=R(2)=R(3)=H$   
(g)  $R(2)=OCH$ ,  $R=R(1)=R(3)=H$   
(h)  $R(3)=OCH$ ,  $R=R(1)=R(2)=H$   
(i)  $R=CH$ ,  $R(3)=OH$ ,  $R(1)=R(2)=H$

\*Address for correspondence.

†Visiting research fellow from: Instituto de Plasticos y Caucho, Madrid 28006, Spain.

Here further evidence is presented to confirm the identity of the radical-anion through an investigation

of amines of varying ionisation potential as well as the effect of pH on transient formation.

### EXPERIMENTAL

#### Materials

Samples of the thioxanthenes [structures I(a-i)] were synthesized and supplied by Ward-Blenkinsop and Company Ltd. All the compounds were chromatographically pure and microanalytical data for the 3 novel compounds are as follows:

4-Hydroxy M.Pt. 284.5–286.5°C				
	C	H	S	O
Calc.	68.39	3.53	14.05	14.02
Found	68.20	3.62	13.89	—

1-Hydroxy M.Pt. 147–148°C				
	C	H	S	O
Calc.	68.39	3.53	14.05	14.02
Found	68.32	3.62	14.18	—

1-Methoxy M.Pt. 133.5–134.5°C				
	C	H	S	O
Calc.	69.39	4.16	13.32	13.20
Found	69.14	4.24	13.21	—

The solvents (2-butanone, toluene, chloroform, 2-propanol, and ethyl acetate) were of "Analar" reagent grade. The amines (diphenylamine, triethylamine, tri-*n*-butylamine, piperidine, diethylamine, dicyclohexylamine and *n*-diethylmethylamine) were obtained from the Aldrich Chemical Company Ltd.

#### Spectroscopic measurements

Absorption spectra were obtained using a Perkin-Elmer Model 554 spectrophotometer. Fluorescence and phosphorescence excitation and emission spectra and quantum yields were obtained using a Perkin-Elmer LS-5 Luminescence spectrometer and were computer corrected via a Perkin-Elmer 3600 data station with appropriate obey files for this purpose. Fluorescence quantum yields were obtained at 300°K using the relative method with quinine sulphate as a standard [6] assuming a quantum yield of 0.55 in 0.1 M H<sub>2</sub>SO<sub>4</sub>. Phosphorescence quantum yields were obtained in the same way using benzophenone as a standard assuming a quantum yield of 0.74 in ethanol glass at 77°K.

#### Flash photolysis

Transient absorption spectra were obtained using a micro-second Kinetic flash photolysis apparatus utilising two 16 KV xenon-filled flash lamps (operated at 10 KV) and a 150 W tungsten-halogen monitoring light source. Transient decay profiles were stored using a Tetrax DM6 storage oscilloscope and were corrected for variations in light intensity.

#### Photopolymerization

Rates of photopolymerization were measured dilatometrically at 30°C utilising 100W tungsten/halogen lamp at a 10 cm distance. *n*-Butyl methacrylate, 50/50 v/v with 2-butanone, was used as the monomer. The initiators were used at 0.5% w/v together with 0.5% w/v of *N*-diethylmethylamine co-initiator.

## RESULTS AND DISCUSSION

#### Photopolymerization efficiency

The initial rates of photopolymerization of *n*-butyl methacrylate in 2-butanone for all 9 thioxanthenone derivatives are compared in Fig. 1. Here the presence of the tertiary amine, *N*-diethylmethylamine, is essential for effective conversion over a short period. All the derivatives examined induced polymerization

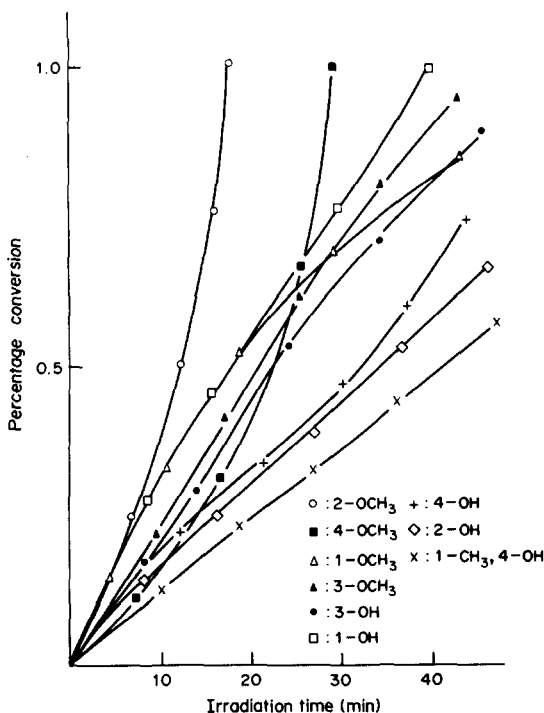


Fig. 1. Rate of initial photopolymerization of *n*-butyl methacrylate (50:50 v/v) in 2-butanone for  $\Delta$ : 1-methoxy,  $\circ$ : 2-methoxy,  $\blacktriangle$ : 3-methoxy,  $\blacksquare$ : 4-methoxy,  $\square$ : 1-hydroxy,  $\diamond$ : 2-hydroxy,  $\bullet$ : 3-hydroxy,  $+$ : 4-hydroxy and  $\times$ : 1-methyl, 4-hydroxy substituted thioxanthenes at 0.5% w/v with 0.5% w/v of *N*-diethylmethylamine. % conversion is a measure of the total volume change in a calibrated dilatometer set at 30°C.

but at various rates. The most effective initiator was the 2-methoxy derivative followed by 4-methoxy and 1-hydroxy, 3-methoxy, 3-hydroxy, 1-methoxy, 4-hydroxy, 2-hydroxy and then finally the 1-methyl, 4-hydroxy derivative. The interesting feature of the results is the high initiation activity of the 1-hydroxy derivative despite possible deactivation via intramolecular hydrogen bonding with the carbonyl group. Here hydrogen bonding with the amine probably reduces the strength of the intra-molecular hydrogen bond and induces reaction with the amine via electron abstraction as will be seen later.

#### Spectroscopic properties

The longest wavelength absorption maxima and corresponding extinction coefficients for all the 9 thioxanthenone derivatives are shown in Table 1. Blank spaces indicate difficulty in measurement. In general the extinction coefficients appear to be little affected by solvent polarity and all appear to range between 3.6 and 4.0. The longest wavelength absorption maxima are also little affected by solvent polarity and apart from chloroform there is more of a blue shift in 2-propanol. Thus, the longest wavelength absorption band may be assigned to an  $n\pi^*$  transition although in some cases its insensitivity to solvent polarity could imply some  $\pi$ -character also, offsetting any blue shift. Excluding the one substituted derivatives for the moment, the high rate of photopolymerization by the 2-methoxy derivative is

Table 1. Absorption maxima (longest) (nm)/extinction coefficients of hydroxy and methoxy substituted thioxanthenes ( $10^{-4}$  M)

Thioxanthone	Toluene		Chloroform		Ethyl acetate		2-Propanol	
	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$	$\lambda_{\max}$	$\log \epsilon$
1-Hydroxy	405	3.96	405	3.93	400	3.76	382	3.71
2-Hydroxy	400	—	403	—	400	—	402	3.73
3-Hydroxy	370	—	365	—	380	3.74	360	3.70
4-Hydroxy	384	—	385	—	385	—	387	3.74
1-Methoxy	370	3.83	380	3.86	370	3.81	374	3.81
2-Methoxy	396	3.78	400	3.82	395	3.77	395	3.82
3-Methoxy	365	3.88	370	3.92	363	3.82	365	3.74
4-Methoxy	385	3.85	375	3.92	387	3.88	385	3.94
1-Methyl-4-hydroxy	390	—	380	—	380	3.73	387	3.64

certainly accounted for on the basis of its long-wavelength absorption maximum at 395 nm in ethyl acetate i.e. it is capable of absorbing a greater amount of the total light intensity. The 4-methoxy derivative is also efficient particularly at longer irradiation times, followed by the 3-methoxy derivative. All the hydroxy derivatives were difficult to examine due to solubility problems and no clear comparisons could be made. The latter are certainly less effective than the methoxy derivatives apart from one notable exception viz 1-hydroxythioxanthone which exhibits a long wavelength absorption at 400 nm and a high rate of polymerization (Fig. 1). The 1-methoxy derivative is also highly effective initially but the conversion slows down at longer irradiation times and this may be associated with its shorter wavelength maximum at 370 nm in ethyl acetate. Intra-molecular hydrogen bonding is certainly expected to suppress photochemical activity as is the case of the 1-methyl, 4-hydroxy derivative. However, in a polar environment, particularly in the presence of an amine, intra-molecular hydrogen bonding could easily be disrupted and weakened. In the case of the 1-methoxy derivative, the photostability of the

methyl group could be an important deciding factor and may be a labile entity. Further study is necessary on this point although it is worth mentioning that all the derivatives examined here were found to be relatively photostable in 2-propanol solution after 1 hr of irradiation.

The fluorescence excitation and emission spectra and quantum yields and corresponding phosphorescence data are shown in Tables 2 and 3 respectively. The first and most interesting feature of the results is the generally low fluorescence quantum yields compared with the very high phosphorescence quantum yields. As found earlier, this indicates some element of  $\pi$ -character in the lowest excited singlet state. Solvent polarity appears to have a strong influence on the fluorescence emission wavelength maxima and quantum yields. The data in Table 2 show an overall red shift in emission wavelength maxima and an increase in the quantum yield with increasing solvent polarity. Thus, in more polar solvents the lowest excited singlet state acquires more  $\pi$ -character due to a bathochromic shift in the singlet  $\pi\pi^*$  excited state. The absence of any fluorescence in the case of the 1-hydroxy derivative is certainly

Table 2. Fluorescence properties of hydroxy and methoxy-substituted thioxanthenes

Thioxanthone	Toluene		Chloroform		Ethyl acetate		2-Propanol	
	$E_m\lambda_{\max}^*$	$\phi_F$	$E_m\lambda_{\max}$	$\phi_F$	$E_m\lambda_{\max}$	$\phi_F$	$E_m\lambda_{\max}$	$\phi_F$
1-Hydroxy	NO		NO		NO		NO	
2-Hydroxy	430	0.015	450	0.02	430	0.03	460	0.12
3-Hydroxy	NO		404	0.003	NO		412	0.006
4-Hydroxy	419	$7 \times 10^{-4}$	445	0.042	425	$2 \times 10^{-4}$	467	0.01
1-Methoxy	NO		NO		NO		445	0.003
2-Methoxy	430	0.022	440	0.54	425	0.035	460	0.58
3-Methoxy	NO		406	0.003	NO		415	0.02
4-Methoxy	416	0.001	434	0.034	412	0.002	447	0.15
1-Methyl-4-hydroxy	NO		362	0.015	437	$3 \times 10^{-4}$	489	0.013

NO = Not observed.

\*In nm.

Table 3. Phosphorescence properties of hydroxy and methoxy substituted thioxanthenes

Thioxanthone	Toluene		Chloroform		Ethyl acetate		2-Propanol	
	$E_m\lambda_{\max}^*$	$\phi_p$	$E_m\lambda_{\max}$	$\phi_p$	$E_m\lambda_{\max}$	$\phi_p$	$E_m\lambda_{\max}$	$\phi_p$
1-Hydroxy	457	0.064	459	0.005	NO		440	0.068
2-Hydroxy	500	0.16	520	0.27	500	0.77	500	0.27
3-Hydroxy	445	0.58	447	0.47	435	0.84	447	0.63
4-Hydroxy	476	0.12	511	0.05	486	0.20	480	0.20
1-Methoxy	449	0.19	471	0.08	471	0.16	461	0.11
2-Methoxy	495	0.24	495	0.11	495	0.76	491	0.37
3-Methoxy	466	0.18	451	0.26	440	0.017	439	0.36
4-Methoxy	467	0.50	493	0.27	469	0.45	465	0.14
1-Methyl-4-hydroxy	459	0.032	NO		NO		445	0.092

NO = Not observed.

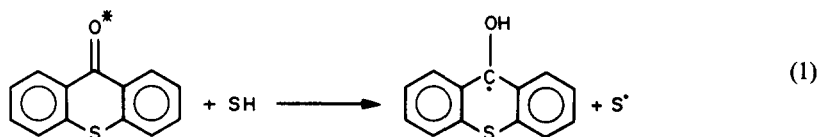
\*In nm.

associated with deactivation of the lowest excited singlet state by intra-molecular hydrogen bonding. In the case of the 1-methoxy and 1-methyl derivatives, the fluorescence was also either not observed or very weak and it again associated with intra-molecular hydrogen bonding but certainly weaker than in the case of the 1-hydroxy derivative.

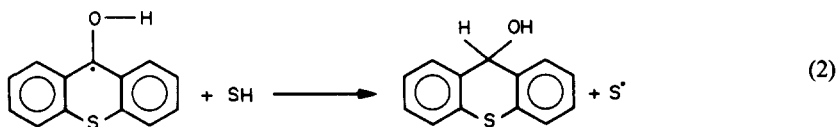
The high phosphorescence quantum yields are typical of aromatic carbonyl compounds but there is no trend with solvent polarity. Overall there is a general shift in the emission wavelength maxima to shorter wavelengths indicating that the lowest excited triplet state is  $\pi\pi^*$  in character and this is consistent with the observation of high phosphorescence quantum yields, particularly in ethyl acetate which is obviously related to the monomer in terms of any polarity effect. The results here are consistent with our earlier finding [4, 5] on other derivatives of thioxanthone and indicate a high probability of reactivity e.g. hydrogen atom abstraction via the lowest excited triplet state. The 3 1-substituted derivatives exhibit low phosphorescence quantum yields, particularly the 1-hydroxy and 1-methyl thioxanthenes, again associated with deactivation of the lowest excited triplet state via intra-molecular hydrogen bonding. Hydrogen bonding is, as expected, weaker in the case of the 1-methoxy derivative, hence the somewhat higher quantum yields.

#### Flash photolysis

End-of-pulse transient absorption spectra in 2-propanol of all 9 derivatives are shown in Figs 2–5. As postulated earlier [4, 5], transient absorption in the absence of amine is associated with the ketyl radical produced by the lowest excited triplet state of the thioxanthone abstracting a hydrogen atom from the solvent, viz 2-propanol, since in non-hydrogen atom donating solvents no transient was observed.



Similar spectra were recorded here with absorption maxima between 340 and 420 nm for the 1-methoxy, 3-methoxy and 2-methoxy derivatives (Fig. 2), 2-hydroxy and 4-methoxy derivatives (Fig. 3) and the 4-hydroxy derivative (Fig. 4). Decay kinetics were difficult to measure but were found statistically to be first-order indicating that the ketyl radical in reaction (1) is decaying via a pseudo-hydrogen atom abstraction process thus:



It is interesting to note that the 3-hydroxy, 1-methyl, 4-hydroxy (Fig. 5) and 1-hydroxy (Fig. 4) derivatives exhibit no transient formation in 2-propanol due to the ketyl radical. This would

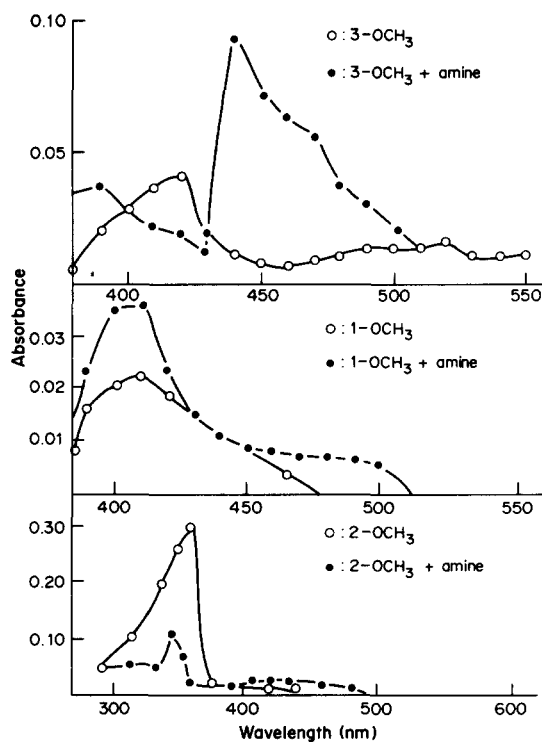


Fig. 2. End-of-pulse transient absorption spectra produced on flash photolysis of 3-methoxy, 1-methoxy and 2-methoxy thioxanthone in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in the (○) absence and (●) presence of *N*-diethylmethylamine ( $\sim 5 \times 10^{-5}$  M).

certainly be expected in the case of the first 2 but not the latter.

The presence of the tertiary amine, *N*-diethylmethylamine, has a variable effect on transient

formation but overall gives rise to a new longer wavelength absorption above 400 nm previously assigned to the radical-anion formed by the lowest excited triplet state of the thioxanthone abstracting an electron from the amine. This is evident for the 3-methoxy, 1-methoxy and 2-methoxy derivatives (Fig. 2), 2-hydroxy and 4-methoxy derivatives (Fig. 3), 3-methoxy derivative (Fig. 4) and the 1-hydroxy

and 1-methyl, 4-hydroxy derivatives in Fig. 5. In the case of the 1-methoxy, 4-methoxy and 4-hydroxy derivatives, an enhancement in the ketyl radical absorption below 400 nm is also observed due to

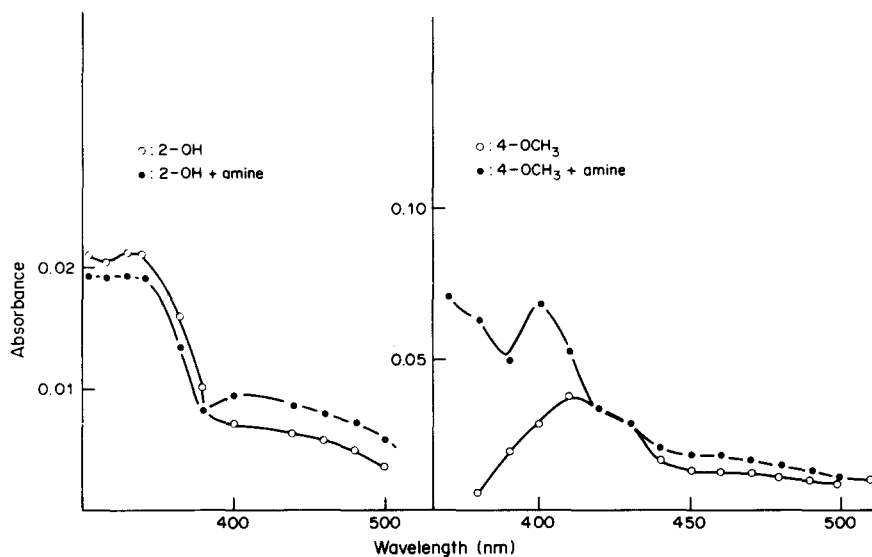
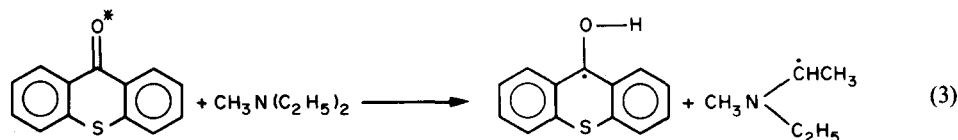


Fig. 3. End-of-pulse transient absorption spectra produced on-flash photolysis of 2-hydroxy and 4-methoxy thioxanthenes in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in the (○) absence and (●) presence of *N*-diethylmethylamine ( $\sim 5 \times 10^{-5}$  M).

hydrogen atom abstraction from the amine thus:



In the case of the 2 and 3-methoxy derivatives, ketyl radical formation is significantly reduced (Fig. 2). Transient absorption maxima and absorbances are summarized in Table 4.

Further evidence in favour of electron abstraction is provided by the results shown in Fig. 6. This shows the effect of various amines on transient formation

for the most effective initiator 2-methoxythioxanthenes. In all cases radical-anion absorption is observed above 400 nm but of various absorbances. Figure 7 shows that these transient absorbances correlate reasonably well with the ionisation potential of the amines [7] thus confirming the theory of electron abstraction by the initiator. In this case,

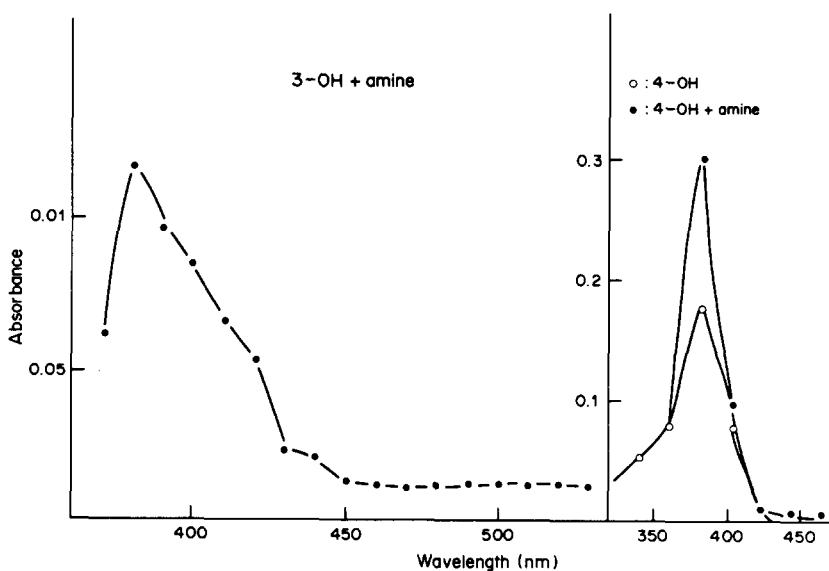


Fig. 4. End-of-pulse transient absorption spectra produced on-flash photolysis of 3-hydroxy and 4-hydroxy thioxanthenes in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in the (○) absence and (●) presence of *N*-diethylmethylamine ( $\sim 5 \times 10^{-5}$  M).

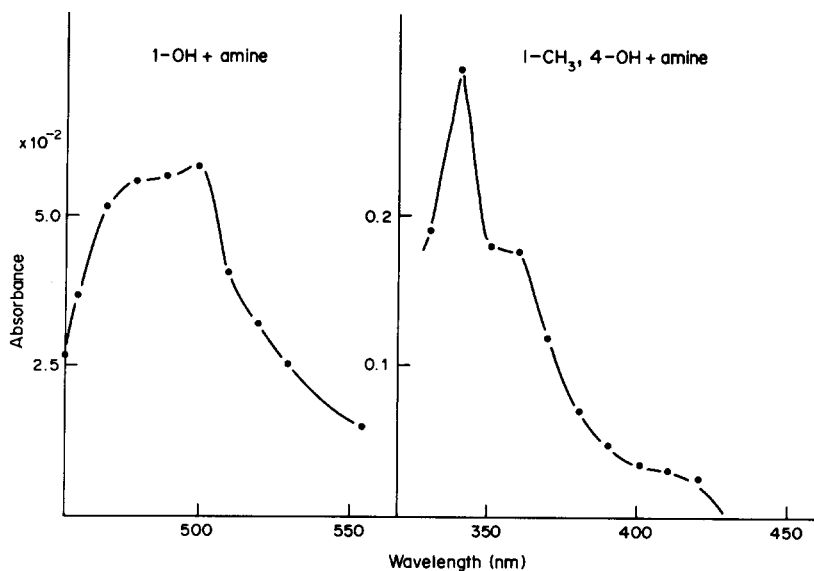


Fig. 5. End-of-pulse transient absorption spectra produced on flash photolysis of 1-hydroxy and 1-methyl, 4-hydroxy thioxanthone in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in (○) absence and (●) presence of *N*-diethylmethylamine ( $\sim 5 \times 10^{-5}$  M).

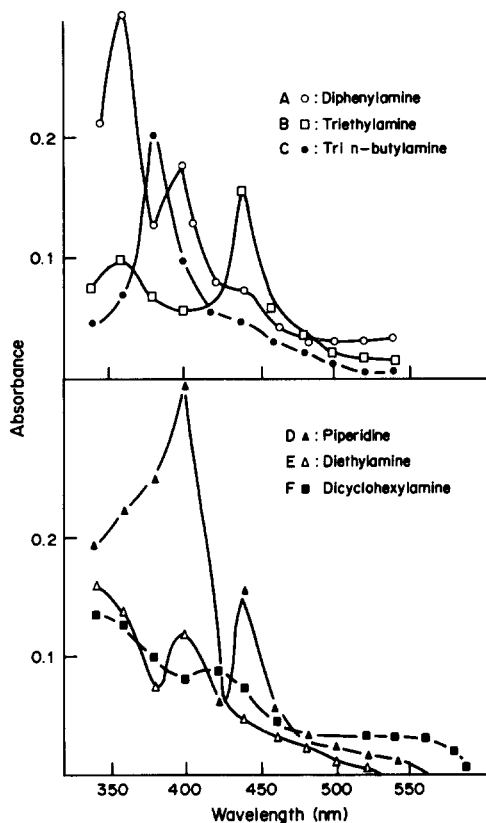


Fig. 6. End-of-pulse transient absorption spectra produced on flash photolysis of 2-methoxythioxanthone in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in the presence of ○: diphenylamine, □: triethylamine, ●: tri-*n*-butylamine, ▲: piperidine, Δ: diethylamine and ■: dicyclohexylamine ( $\sim 5 \times 10^{-5}$  M). (Ionisation Potential for the amines A to F are given in Fig. 7).

amines with a low ionisation potential give rise to higher concentrations of the radical anion and on this basis more effective polymerization. This will be the subject of future studies. Final confirmation of the identity and absorption regions of the ketyl radical and radical-anion is demonstrated by the results in

Table 4. Transient absorbances of hydroxy and methoxy thioxanthenes in 2-propanol

Thioxanthone	Radical		Radical-anion	
	$\lambda_{\max}$	ABS	$\lambda_{\max}$	ABS
1-Hydroxy	NO		500	0.06
2-Hydroxy	340	0.022	400	0.01
3-Hydroxy	NO		440	0.022
4-Hydroxy	385	0.16	420(s)	0.01
1-Methoxy	412	0.022	460(s)	0.008
2-Methoxy	370	0.31	425	0.03
3-Methoxy	430	0.041	440	0.093
4-Methoxy	410	0.040	425	0.035
1-Methyl-4-hydroxy	NO		400	0.030

NO = Not observed.  
(s) = Shoulder.

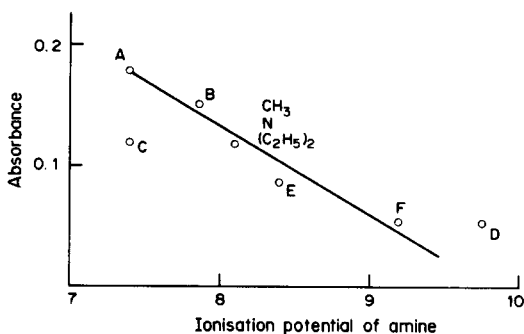


Fig. 7. Plot of transient absorbance due to the radical-anion of 2-methoxythioxanthone and the ionisation potential of the amine.

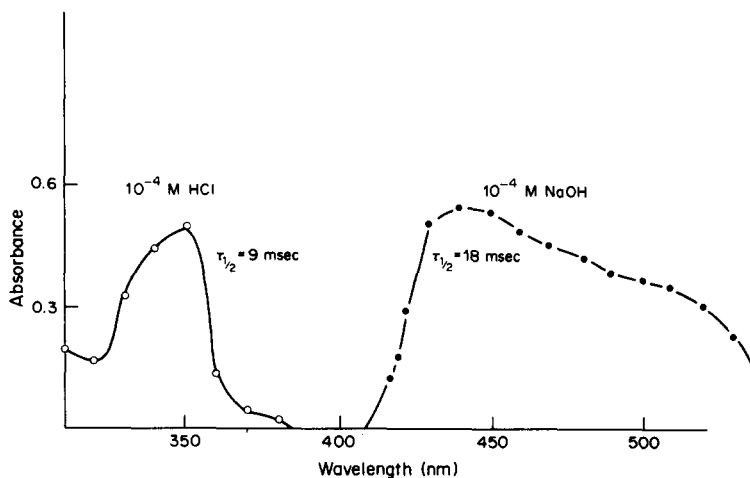


Fig. 8. End-of-pulse transient absorption spectra produced on flash photolysis of 2-methoxythioxanthone in 2-propanol ( $\sim 5 \times 10^{-5}$  M) in the presence of (O):  $10^{-4}$  M HCl and (●):  $10^{-4}$  M NaOH.

Fig. 8 and follows an earlier approach of Porter and co-workers [8, 9]. In the presence of  $10^{-4}$  M HCl in 2-propanol, absorption below 400 nm is observed for 2-methoxythioxanthone and is also enhanced when compared with that in 2-propanol alone (Fig. 2). On the other hand in the presence of  $10^{-4}$  M NaOH, no ketyl radical formation is observed. In this case only the radical-anion is observed above 400 nm with a typical broad structureless absorption extending above 500 nm. Lifetime measurements indicate that the ketyl radical is shorter-lived with a half-life of 9 msec compared with 18 msec for the radical-anion and is consistent with lifetime measurements in the presence of the amine coinitiator. Similar results were obtained when the other derivatives were examined in the presence of acid and base.

One interesting result is the high transient absorption due to the radical-anion for the 1-hydroxy and 1-methyl, 4-hydroxy derivatives in the presence of *N*-diethylmethylamine. Both initiators induce polymerization of the monomer and evidently this must occur through a process of electron abstraction from the amine. The intra-molecular hydrogen bonding must, in these cases, be weakened by the presence of the amine competing with the carbonyl group for the  $\alpha$ -hydrogen atoms on the initiator.

#### CONCLUSIONS

The photochemical properties of 9 derivatives of thioxanthone are presented together with their poly-

merization efficiencies. Photoinitiation of polymerization of acrylate monomers in the presence of a tertiary amine co-initiator is primarily associated with electron abstraction from the amine by the lowest excited triplet  $n\pi^*$  state of the thioxanthone initiator to give a radical-anion. The radical-anion/radical-cation pairs will then initiate polymerization; this will be the subject of future investigations.

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