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PHOTOCHEMISTRY OF THIOXANTHONES

VI: A POLYMERIZATION, SPECTROSCOPIC AND FLASH PHOTOLYSIS STUDY ON NOVEL WATER-SOLUBLE SUBSTITUTED 3-(9-OXO-9*H*-THIOXANTHENE-2,3-γ-4-YLOXY)-*N*,*N*,*N*-TRIMETHYL-1-PROPANAMINIUM SALTS

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Summary

The photopolymerization activity and photochemistry of nine novel water-soluble 3-(9-oxo-9*H*-thioxanthene-2,3-γ-4-yloxy)-*N*,*N*,*N*-trimethyl-1-propanaminium salts is examined in water and 2-propanol using absorption, luminescence and conventional microsecond flash photolysis techniques. For both the chloro and the methylsulphonate salts, photopolymerization activity in water follows the order of substitution 4- > 2- > 3-. Methyl substitution in the 1-position deactivates the molecule and this is reflected by a reduction in both the photopolymerization activity and luminescence (fluorescence and phosphorescence) quantum yields and the triplet lifetime. Intramolecular hydrogen-atom abstraction is the main competitive process suppressing photochemical activity. The longest wavelength absorption maxima and extinction coefficients and luminescence quantum yields are similar to those of water-soluble 2-substituted derivatives studied previously, indicating a lowest excited singlet state with strong $\pi\pi^*$ character. On changing the solvent from 2-propanol to water all the fluorescence quantum yields are enhanced and this is consistent with a strong degree of charge transfer character in the lowest excited singlet state. From conventional microsecond flash photolysis results, transient absorptions below 400 nm are associated with the intermediate ketyl radical formed by the lowest excited singlet/triplet states of the thioxanthene molecule abstracting a hydrogen atom from the amine synergist (used in photopolymerization) while absorptions above 400 nm are associated with the radical anion intermediate formed by a concurrent electron abstraction process from the

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amine. The latter is confirmed through a detailed study on the effect of pH and amine concentration on transient production, as well as the effect of various amines of increasing ionization potential. Transient formation is only partly reduced in aerobic conditions and is consistent with our earlier findings and conclusions that photopolymerization activity is associated, in the main, with electron abstraction by the lowest excited singlet state of the thioxanthone molecule from the tertiary amine synergist. This is confirmed by a correlation between the photopolymerization activity and the ionization potential of different amines.

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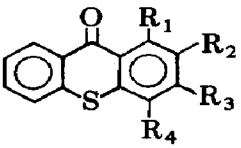
1. Introduction

Parts II and V of this series concentrated on the photochemistry of novel 2-substituted water-soluble derivatives of thioxanthone [1, 2]. These molecules have, as a result of their extended absorption up to 400 nm, widespread applications as photoinitiators in white pigmented coatings and particularly water-based inks and silk screen photoemulsions [3, 4]. Generally, the photoactivity of a thioxanthone initiator depends on its structure. The oil-soluble structures [5, 6] have been found, for example, to operate by a primary photochemical process of electron abstraction by the lowest excited triplet state of the initiator while the water-soluble structures operate through the lowest excited singlet state. In the latter case both hydrogen abstraction and electron abstraction appear to be operative. In Part V of this series, for example, we examined the photochemistry of novel methyl-substituted 3-(9-oxo-9*H*-thioxanthene-2-yloxy)-*N*,*N*,*N*-trimethyl-1-propanaminium salts (see structure IV below). Compounds of this structure where X ≡ OH also displayed strong evidence of intramolecular hydrogen-atom abstraction from the hydroxy group.

In this article we have extended our research activities to include a range of novel water-soluble 3- and 4-substituted chloro and methylsulphonate *N*,*N*,*N*-trimethyl-1-propanaminium salts (I - VI), including the effect of methyl substitution on the 4-substituted chloro salt (VI - IX). This study will enable us to determine on a wider basis the relationship between structure and photochemical activity of this interesting molecule in order to develop more effective water-soluble photoinitiators for radiation-curable resins. Information on compounds II and IV has been published previously [1, 2] but is included again for completeness.



I: $R_2 \equiv OCH_2CH_2CH_2\overset{+}{N}(CH_3)_3S\bar{O}_3Me$; $R_1 \equiv R_3 \equiv R_4 \equiv H$

II: $R_3 \equiv OCH_2CH_2CH_2\overset{+}{N}(CH_3)_3S\bar{O}_3Me$; $R_1 \equiv R_2 \equiv R_4 \equiv H$

III: $R_4 \equiv OCH_2CH_2CH_2\overset{+}{N}(CH_3)_3S\bar{O}_3Me$; $R_1 \equiv R_2 \equiv R_3 \equiv H$

IV: $R_2 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv R_3 \equiv R_4 \equiv H$
V: $R_3 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv R_2 \equiv R_4 \equiv H$
VI: $R_4 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv R_2 \equiv R_3 \equiv H$
VII: $R_4 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv Me$; $R_2 \equiv R_3 \equiv H$
VIII: $R_4 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv R_2$ F Me; $R_3 \equiv H$
IX: $R_4 \equiv OCH_2CH(OH)CH_2\overset{+}{N}(CH_3)_3\bar{Cl}$; $R_1 \equiv R_3 \equiv Me$; $R_2 \equiv H$

Photoinitiation activity is a maximum for the 4-substituted structures and is associated with a primary photochemical process of electron abstraction from the amine synergist used in resin formulations, particularly at high amine concentration where the conditions for this mechanism are more likely to be favoured.

2. Experimental details

2.1. Materials

Samples of the nine thioxanthenes I - IX were supplied by Ward–Blenkinsop and Co. Ltd. and Patent cover is pending. Microanalytical data together with the melting points of the compounds are shown in Table 1. The water used in this study was double distilled and the nitrous oxide was obtained from Air Products Ltd., U.K. The amines *N*-diethylmethylamine, diphenylamine, tri-*n*-butylamine, triethylamine, diethylamine, dicyclohexylamine and piperidine were obtained from the Aldrich Chemical Company Ltd. The 2-propanol (AnalaR grade) was obtained from Fisons Ltd.

TABLE 1

Microanalytical data on novel 3-(9-oxo-9*H*-thioxanthene-2,3-γ-4-yloxy)-*N*,*N*,*N*-trimethylpropanaminium salts

Compound	*Melting point* (°C)	*Elemental composition (%)*									
		Calculated					*Found*				
		C	*H*	*N*	*Cl*	*S*	*C*	*H*	*N*	*Cl*	*S*
I	227.5 - 229.5	55.53	6.06	3.24	—	14.83	55.23	6.12	3.15	—	14.60
II	265.5 - 266.5	56.72	5.95	3.31	—	15.15	56.64	5.93	3.28	—	15.22
III	213 - 214.5	54.40	6.16	3.17	—	14.52	54.68	6.14	3.17	—	14.77
IV	245 - 246.5	57.35	6.08	3.32	8.91	8.06	57.73	6.01	3.40	8.77	8.02
V	226.5 - 228	59.32	5.90	3.64	9.2	8.34	59.41	6.17	3.46	9.04	8.02
VI	268.5 - 269.2	59.36	5.90	3.64	9.22	8.34	59.53	5.76	3.63	9.48	8.40
VII	271 - 272	60.98	6.14	3.56	9.00	8.14	60.70	6.15	3.48	9.01	8.13
VIII	267 - 268	59.82	6.58	3.36	8.41	7.61	59.88	6.55	3.32	8.52	7.66
IX	239 - 240	61.13	6.48	3.40	8.60	7.77	60.92	6.62	3.32	8.24	7.46

2.2. Spectroscopic measurements

Absorption spectra were obtained using a Perkin–Elmer Model 554 spectrophotometer and fluorescence and phosphorescence data were obtained using a Perkin–Elmer LS-5 luminescence spectrometer coupled to a 3600 data station. Fluorescence and phosphorescence quantum yields were both obtained by the relative method using quinine sulphate ($\phi_F = 0.55$ in 0.1 M sulphuric acid) and benzophenone ($\phi_p = 0.74$ in ethanol glass at 77 K) as standards [7].

2.3. *Flash photolysis*

Transient absorption spectra were recorded using a microsecond kinetic flash photolysis apparatus utilizing two 16 kV xenon-filled flash lamps (operated at 10 kV) and a 150 W tungsten–halogen monitoring source. Transient decay profiles were stored using a Tetronix DM6 storage oscilloscope.

2.4. *Photopolymerization*

Photopolymerization efficiencies were determined gravimetrically by irradiating 1 cm quartz cells containing 2 cm^3 2-hydroxyethyl methacrylate, 1 cm^3 water, 0.3% w/v of initiator and 1.5% w/v of amine for 15 min in a Microscal unit (this unit utilizes a 500 W high pressure Hg–W fluorescent lamp (temperature, about 50 °C) and the sample distance is 18 cm) with constant stirring using a mino-wire stirrer. After irradiation, the whole mixture was poured into ethanol for precipitation, and this was followed by centrifuging, filtration and drying to constant weight in an air oven at 60 °C.

3. Results and discussion

3.1. *Photopolymerization activity*

The photopolymerization activities of all nine thioxanthene compounds, measured gravimetrically for the conversion of 2-hydroxyethyl methacrylate monomer, are compared in Table 2. These results show a number of interesting features. For both the methylsulphonate and the chloro salts, substitution in the 4-position of the molecule gives the greatest photochemical activity whilst substitution in the 3-position gives the lowest activity. In the case of the 4-chloro salt, photopolymerization was very rapid and after a period of 15 min the monomer gelled making precipitation and isolation of any polymer very difficult. Substitution of a methyl group in position 1 of the 4-chloro salt is seen to cause a reduction in photopolymerization activity, probably because of deactivation of the excited states of the thioxanthene molecule by intramolecular hydrogen bonding, and this is reflected by the spectroscopic data below. The introduction of other methyl groups in positions 2 and 3 decreases the activity of the molecule further.

The data in Table 3 demonstrate that the ionization potential of the amine co-synergist used in the photopolymerization is an important factor in controlling the efficiency of the initiator. In this case, for compound III, which is one of the most active of the 4-substituted thioxanthenes studied,

TABLE 2

Photopolymerization of 2-hydroxyethyl methacrylate in water by novel water-soluble 2,3-γ-4-substituted thioxanthenes[a]

Thioxanthene	*Percentage conversion (15 min)*
I (2-SO_3^-Me)	1.13
II (3-SO_3^-Me)	0.70
III (4-SO_3^-Me)	4.23
IV (2-Cl^-)	1.57
V (3-Cl^-)	0.71
VI (4-Cl^-)	Gelation
VII (1-Me, 4-Cl^-)	3.60
VIII (1,2-diMe, 4-Cl^-)	2.23
IX (1,3-diMe, 4-Cl^-)	1.66

[a] 0.3% w/v + 1.5% w/v *N,N*-diethylmethylamine.

TABLE 3

Photopolymerization of 2-hydroxyethyl methacrylate in water by compound III[a] in the presence of various tertiary amines

Amine[b]	*Ionization potential*	*Percentage conversion (15 min)*
Tri-*n*-butylamine	7.40	Gelation
Triethylamine	7.85	≈ 5.5 ± 0.5%
N-Diethylmethylamine	8.10	4.23
Diethylamine	8.40	1.13
Dicyclohexylamine	9.20	0.80

[a] 0.3% w/v.
[b] 1.5% w/v.

there is a good correlation between the ionization potential of the amine and the percentage conversion on photopolymerization of 2-hydroxyethyl methacrylate monomer in water. Thus, the lower the ionization potential of the amine the more effective is the conversion, confirming the involvement of electron abstraction by the lowest excited singlet/triplet states of the thioxanthone molecule.

3.2. Spectroscopic properties

The absorption and emission properties of the thioxanthenes are compared in Table 4 for water and 2-propanol only. Phosphorescence measurements were carried out in the latter solvent only for the reason that water had a frequent tendency to cause the quartz tubes, used as cells, to crack during freezing and thawing cycles. The results show a number of interesting features. First, the absorption maxima of all the compounds studied here occur between 370 and 400 nm with little difference in terms of their extinction coefficients (between 3.70 and 3.90) and do not differ signifi-

TABLE 4

Spectroscopic properties of novel water-soluble 2,3-γ-4-substituted thioxanthenes

Thioxanthene	*Absorbance in water*		*Fluorescence*				*Phosphorescence in 2-propanol*		
			In water		*In 2-propanol*				
	λ_{max}	log ϵ_{max}	λ_{max}(em) (nm)	ϕ_F	λ_{max}(em) (nm)	ϕ_F	λ_{max}(em) (nm)	ϕ_F	ζ (ns)
I	400	3.79	486	0.30	455	0.28	491	0.12	134
II	373	3.76	439	0.10	416	0.02	438	0.45	66
III	388	3.75	480	0.36	443	0.27	465	0.30	50
IV	400	3.74	481	0.50	454	0.33	490	0.30	73
V	375	3.75	439	0.19	414	0.04	438	0.38	65
VI	390	3.86	475	0.16	445	0.06	465	0.20	51
VII	390	3.71	503	0.11	454	0.04	474	0.017	10
VIII	397	3.69	522	0.05	471	0.04	513	0.006	32
IX	390	3.74	473	0.08	443	0.014	466	0.015	21

cantly from the values of substituted thioxanthones studied earlier [1, 2, 5, 6]. Thus, marked differences in terms of photopolymerization activity cannot be related to this particular property. The fluorescence emission maxima in water and 2-propanol vary markedly but all show a pronounced hyperchromic shift in the former, indicating a high degree of charge transfer character in the lowest excited singlet state. Concurrent with this trend is an increase in the fluorescence quantum yields and this is consistent with our earlier results for compound I [1] which showed that the phosphorescence quantum yields in water were negligible. Correlations of photopolymerization activity with luminescence quantum yields are apparent to some extent and are consistent with our earlier conclusions [1] on the involvement of the lowest excited singlet state. Thus, for the methylsulphonate series the photoactivity decreased in the order III > I > II, and this corresponds to decreasing fluorescence quantum yields in water. A similar effect is seen for the 4-chloro salt and the corresponding effect of methyl substitution where the order of photopolymerization conversion is VI > VII > VIII > IX, and this is consistent with a decrease in the fluorescence quantum yields. In the latter series, 1-methyl substitution will deactivate the lowest excited singlet state, and for that matter the triplet state, of the molecule through intramolecular hydrogen bonding. As mentioned above no significant phosphorescence was observed in our earlier work [1] on compound I and other 2-substituted thioxanthones which may, at first, suggest a high degree of photoactivity from the lowest excited triplet state. However, the flash photolysis data in aerobic conditions, as shown below, indicate that this is not primarily the case.

Phosphorescence half-lives were measured for all the compounds and are also compared in Table 4. It is interesting to note that for both the chloro series and the methylsulphonate series the most photoactive 4-substituted compounds exhibit similar lifetimes and are the shortest of the two series (excluding the effect of methyl substitution). Thus, a shorter triplet lifetime appears to be consistent with higher photoactivity which may suggest either greater $n-\pi^*$ character or a lower rate of intersystem crossing. In the case of 1-methyl substitution in compound VII the triplet half-life is significantly reduced and is evidently associated with intramolecular hydrogen bonding. Methyl substitution in either the 2- or the 3-position increases the degree of charge transfer character in the molecule and consequently enhances the triplet half-life and suppresses photoactivity (Table 2).

3.3. *Flash photolysis*

End-of-pulse transient absorption spectra of the compounds in water exhibited features similar to those obtained earlier [1, 2, 5, 6] with other thioxanthone molecules. In the presence of the amine *N*-diethylmethylamine two transients were observed, one below 400 nm and located at 340 nm resulting from the ketyl radicals formed by hydrogen-atom abstraction and the other at about 400 nm with absorption maxima located between 400 and 550 nm resulting from the radical anions formed by electron abstraction. In water alone only the former was observed to a much lesser extent and may well be associated with some intermolecular hydrogen-atom abstraction between the molecules themselves or possibly some intramolecular hydrogen-atom abstraction in the case of the 2-substituted derivatives. Hydrogen-atom abstraction from water by the photoexcited thioxanthone molecules is expected to be very inefficient. A typical spectrum is shown in Fig. 1 for compound III in the absence and the presence of the tertiary amine while Fig. 2 shows typical spectra for compounds VI and VIII in the presence of the tertiary amine. Confirmation of the identity of the transients is shown by the results in Fig. 3 for compound II and these agree with our earlier preliminary findings on the effect of the two extremes of pH on other thioxanthone molecules [6]. In this particular case, varying the pH from acid (pH 2) to alkali (pH 12) conditions results in a change from high transient absorption below 400 nm to a spectral red shift

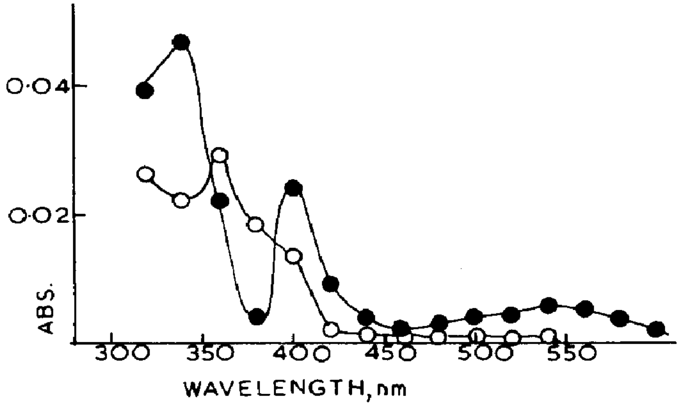


Fig. 1. End-of-pulse transient absorption spectra of compound III in the absence (○) and the presence (●) of N-diethylmethylamine (5×10^{-5} M each) in N_2-saturated water.

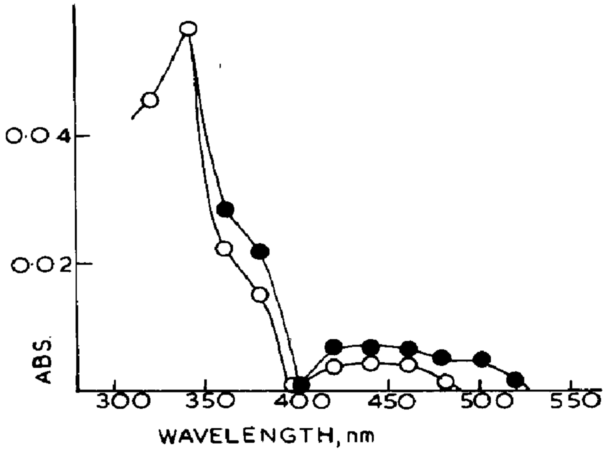


Fig. 2. End-of-pulse transient absorption spectra of compounds VIII (○) and VI (●) (5×10^{-5} M) in N_2-saturated water in the presence of N-diethylmethylamine (5×10^{-5} M).

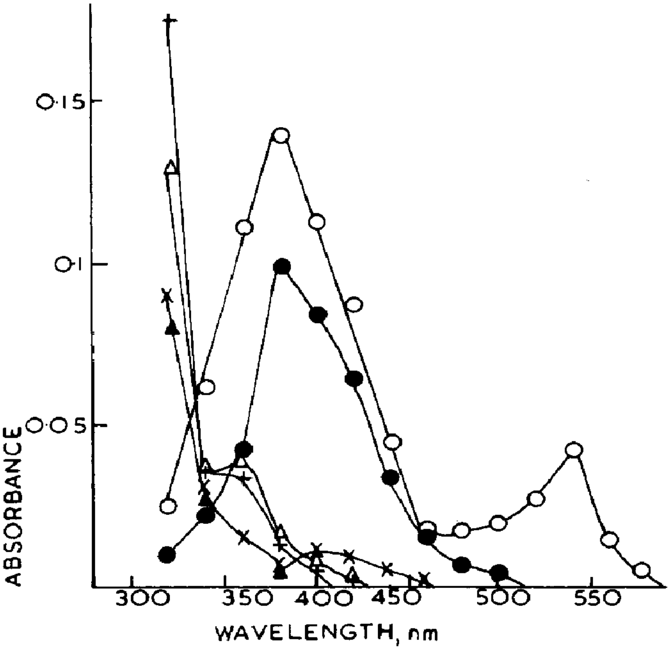


Fig. 3. End-of-pulse transient absorption spectra of compound II (5×10^{-5} M) in N_2-saturated water at the following pH (obtained using HCl and NaOH): +, 2; △, 4; ▲, 6; ×, 8; ●, 10; ○, 12.

and high transient absorption at 400 nm together with further extended absorption at 540 nm at pH 12. Thus, under low pH (acid) conditions hydrogen-atom abstraction appears to be more favourable while under high pH (basic) conditions electron abstraction will dominate.

In a further attempt to identify the radical anion and also implicate its importance in photopolymerization we examined the effect of various amines of differing ionization potential [8] on transient absorption and the spectra are shown in Fig. 4. Here it is seen that amines with a low ionization potential, *e.g.* diphenylamine and tri-*n*-butylamine, give strong transient absorptions below and above 400 nm from both the ketyl radical and the radical anion whereas amines with a high ionization potential, such as dicyclohexylamine, give an overall low transient intensity in both spectral regions. A plot of the ionization potential of the amine *vs.* transient absorption at 400 nm for compound V is shown in Fig. 5 and shows a reasonable linear relationship, confirming again the identity and importance of the radical anion intermediate. These results also correlate well with our findings on photopolymerization conversion in Table 3 which shows that amines with a high ionization potential are the least efficient initiators and vice versa. Hydrogen-atom abstraction from either diethylamine or dicyclohexylamine by the photoexcited thioxanthone is evidently not important, as shown by the low transient intensity at 340 nm.

The effect of amine concentration on transient formation is shown for compound III in Fig. 6. In this case, transient formation is enhanced for both the ketyl radical and the radical anion. At high amine concentration the

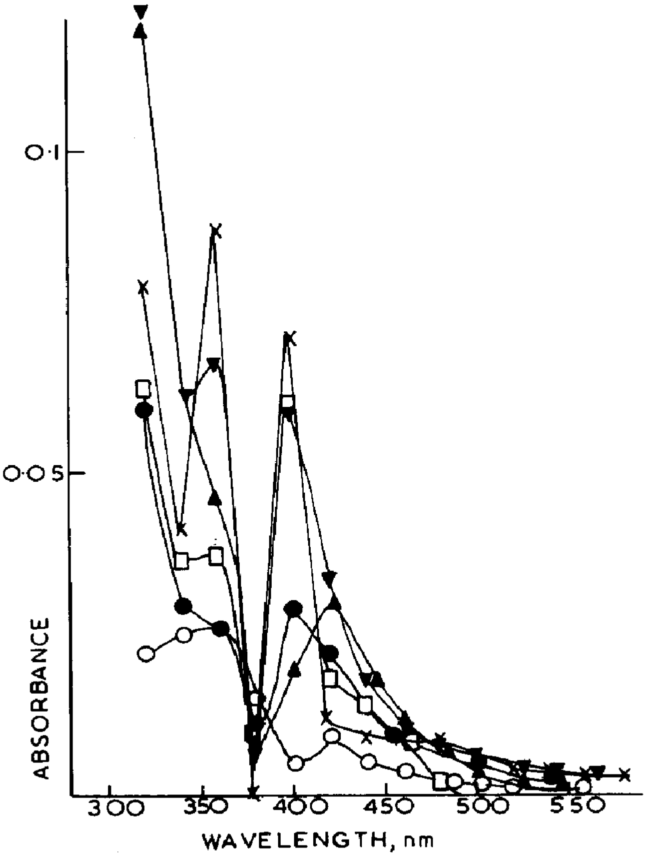


Fig. 4. End-of-pulse transient absorption spectra of compound V (5×10^{-5} M) in the presence of diphenylamine (×), tri-*n*-butylamine (□), triethylamine (▼), diethylamine (▲), *N*-diethylmethylamine (●) or dicyclohexylamine (○) (each 5×10^{-5} M), in N_2-saturated water.

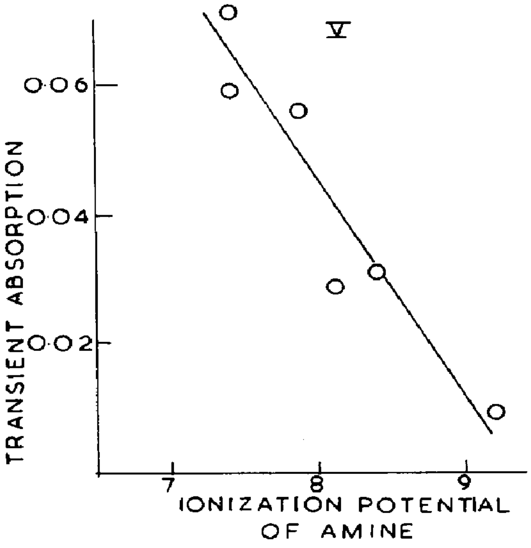


Fig. 5. End-of-pulse transient absorption at 400 nm for compound V (5×10^{-5} M) *vs.* the ionization potential of the amines (5×10^{-5} M) in Fig. 4.

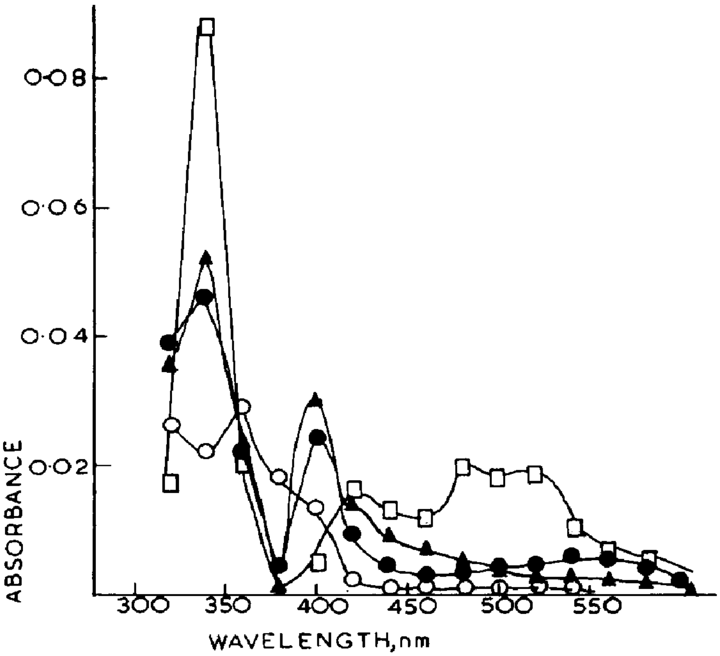


Fig. 6. End-of-pulse transient absorption spectra of compound III in the presence of 0 M (○), 5 × 10^{-5} M (●), 1.5 × 10^{-4} M (▲) or 2.5 × 10^{-4} M (□) *N*-diethylmethylamine in N_2-saturated water.

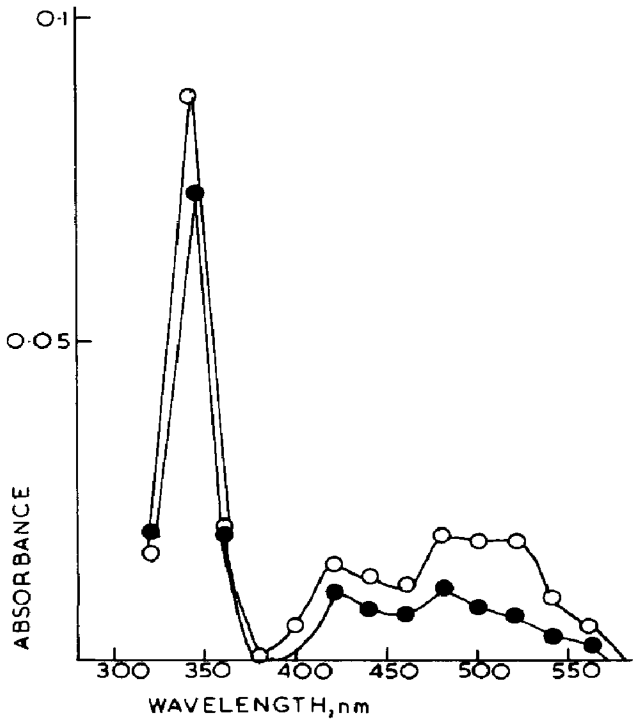


Fig. 7. End-of-pulse transient absorption spectra of compound III (5 × 10^{-5} M) in the presence of 2.5 × 10^{-4}M *N*-diethylmethylamine in N_2-saturated (○) or N_2O-saturated (●) water.

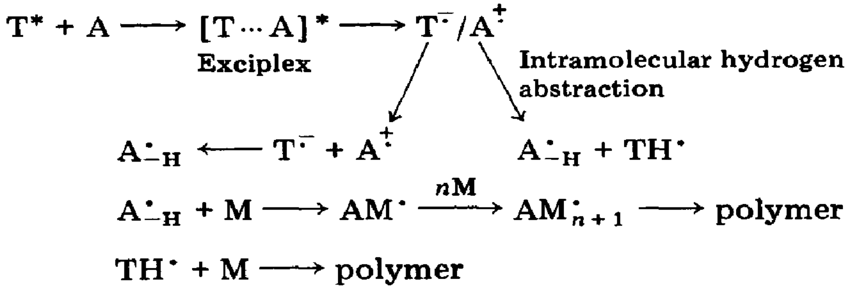
spectra of both intermediates are very much in evidence, particularly the latter. The addition of an electron trap such as acetone [9, 10] quenched transient formation in both regions. Another very efficient electron trap, nitrous oxide [9, 10], also quenched transient formation in both regions, particularly the radical anion, and this effect is shown in Fig. 7. The absence of complete quenching here may be associated with the low solubility of nitrous oxide in water, particularly when compared with the high concentration of the *N*-methyldiethylamine used (2.5×10^{-4} M). Transient absorption maxima for all the compounds are summarized and compared in Table 5 for both anaerobic and aerobic conditions. Here it is seen that, in the presence of oxygen, transient formation due to either the ketyl radical or the radical anion is only partly reduced in aerobic conditions and this agrees well with our earlier findings on water-soluble thioxanthone initiators [1]. In the case of the oil-soluble structures [5] transient formation was strongly quenched. Thus, these results would appear to be consistent with the involvement of the lowest excited singlet state of the thioxanthone in abstracting an electron or hydrogen atom from the amine co-synergist; Scheme 1 depicts the various mechanistic pathways involved. It is well known [11, 12]

TABLE 5

Flash photolysis behaviour of novel water-soluble 2,3-γ-4-substituted thioxanthenes in water in the presence of *N*-diethylmethylamine (5×10^{-5} M)

Thioxanthene *(5×10^{-5} M)*	*Transient absorption*		
	Anaerobic		*Aerobic*
	λ_{max}	ABS	ABS
I (2-SO_3^-Me)	340	0.14	0.097
	480	0.06	0.05
II (3-SO_3^-Me)	320	0.058	0.010
	400	0.033	0.050
III (4-SO_3^-Me)	340	0.046	0.008
	400	0.024	0.004
IV (2-Cl^-)	320	0.031	0.02
	520	0.0035	0.003
V (3-Cl^-)	320	0.06	0.025
	400	0.028	0.010
VI (4-Cl^-)	340	0.056	0.028
	420	0.007	0.004
VII (1-Me, 4-Cl^-)	340	0.085	0.060
	430	0.0065	0.004
VIII (1,2-diMe, 4-Cl^-)	340	0.065	0.040
	440	0.004	0.003
IX (1,3-diMe, 4-Cl^-)	320	0.062	0.040
	400	0.007	0.005

that carbonyl–amine systems react in this way via a single exciplex intermediate to produce corresponding carbonyl radical anion and amine radical cation species. These are capable of further reaction as shown to give a semiquinone or ketyl radical and an alkylamino radical. Both the thioxanthone ketyl radical and the radical anion have been identified in our present study and are confirmed by the pH results in Fig. 3 and the amine concentration dependence of the spectra in Fig. 6. The exact role of each of these intermediates in initiating polymerization is unclear and the subject of much discussion. Thioxanthones alone are not very effective photoinitiators and this has led many workers to suppose that neither the ketyl radical nor the radical anion are directly involved with the monomer [12]. The synergistic effect of amines is certainly argument enough in favour of the alkylamino radical adding on to the monomer as shown in Scheme 1. A further in-depth pH study on polymerization activity may clarify this point. If the transients were insensitive to oxygen, this would clearly give rise to a more efficient photoinitiator system and the elimination of nitrogen blanketing in the UV curing process. The effect of 1-methyl substitution is interesting since in this case reduced excited state activity, as indicated by the luminescence data, may be expected to reduce transient production. However, the results in Table 5 show high transient production, particularly for the ketyl radical, which essentially confirms the predominance of intramolecular hydrogen-atom abstraction from the 1-methyl substituent. The transient kinetics of decay were complex and no meaningful results could be obtained in this particular case.



T ≡ thioxanthone; TH• ≡ ketyl radical; $T^{\cdot -}$ ≡ radical anion; A ≡ amine; $A^{\cdot}_{-H}$ ≡ α-amino radical; M ≡ monomer.

Scheme 1.

4. Conclusions

The results clearly demonstrate that the maximum photopolymerization efficiency for the thioxanthone molecule is achieved through the substitution of effective solubilizing groups in position 4. Is should be pointed out that thioxanthone itself is ineffective as an initiator for two main reasons. The first is a low absorption coefficient at about 350 nm and the second is its poor solubility, hence the use of long side-chain substituents. The luminescence and flash photolysis results clearly show that the photopolymerization activity of water-soluble thioxanthones is associated with the ability of the lowest excited singlet state (and to a lesser extent the triplet state) to abstract an electron from the tertiary amine co-synergist via an intermediate exciplex.

References

1 N. S. Allen, F. Catalina, P. N. Green and W. A. Green, *Eur. Polym. J., 22* (1986) 347.
2 N. S. Allen, F. Catalina, P. N. Green and W. A. Green, *Eur. Polym. J.*, in the press.
3 P. N. Green, *Polym. Paint Resins, 175* (1985) 246.
4 M. J. Davis, G. Garne, P. N. Green and W. A. Green, *Chemspec. BACS Symp.*, (1986) 9.
5 N. S. Allen, F. Catalina, P. N. Green and W. A. Green, *Eur. Polym. J., 22* (1986) 49.
6 N. S. Allen, F. Catalina, P. N. Green, W. A. Green and B. M. Moghaddam, *Eur. Polym. J., 22* (1986) 691.
7 J. N. Demas and G. A. Crosby, *J. Phys. Chem., 75* (1971) 91.
8 V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev and Ye. L. Frankevich, *Bond Energies, Ionisation Potentials and Electron Affinities*, Edward Arnold, London, 1962, p. 151.
9 J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966.
10 N. S. Allen, B. Mohajerani and J. T. Richards, *Dyes Pigm., 2* (1981) 31.
11 M. Gordon and W. R. Ware (eds.), *The Exciplex*, Academic Press, New York, 1975.
12 V. D. McGinniss, in N. S. Allen (ed.), *Developments in Polymer Photochemistry*, Vol. 3, Applied Science, London, 1982, Chapter 1, p. 1.