coordination of the monomer to the catalytic center is actually determining in the stereoregulation. Poly(*p*-methoxystyrene) is stereoirregular (see Figure 3a). PMOS polymerizes even in the absence of titanium compounds and in the presence of anisole which inhibits syndiotactic polymerization of S. As previously observed S and PMOS do not copolymerize to each other and in the $^{13}C$ NMR spectrum of this sample (see Figure 5) the quaternary carbons $C_1$ of S and PMOS are multiplets diagnostic of stereoirregular environments. Probably PMOS polymerizes by a completely different mechanism and deactivates the catalytic complexes syndiotactic specific for styrene polymerization.

**Acknowledgment.** Financial support by CNR and MPI is gratefully acknowledged.

**Registry No.** S, 100-42-5; PMS, 622-97-9; MMS, 100-80-1; PMOS, 637-69-4; PCS, 1073-67-2; MCS, 2039-85-2; OCS, 2039-87-4; (S)(MS) (copolymer), 26655-84-5; (S)(CS) (copolymer), 62742-92-1; (S)(MOS) (copolymer), 24936-43-4; anisole, 100-66-3; tetrabenzyltitanium, 17520-19-3; polystyrene, 9003-53-6; poly(*p*-methylstyrene), 24936-41-2; poly(*m*-methylstyrene), 25037-62-1; poly(*p*-methoxystyrene), 24936-44-5; poly(*p*-chlorostyrene), 24991-47-7; poly(*m*-chlorostyrene), 26100-04-9; poly(*o*-chlorostyrene), 26125-41-7.

## References and Notes

(1) Ishihara, N.; Kuramoto, M.; Uoi, M. European Patent Application 0210615, A2, 1987.

(2) Ishihara, N.; Kuramoto, M.; Uoi, M. European Patent Application 0224097 A1, 1987.

(3) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277.

(4) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 249.

(5) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035.

(6) Longo, P.; Grassi, A.; Proto, A.; Ammendola, P. *Macromolecules* **1988**, *21*, 24.

(7) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

(8) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.

(9) Fineman, M.; Ross, S. D. *J. Polym. Sci.* **1950**, *5*, 259.

(10) Natta, G.; Danusso, F.; Sianesi, D. *Makromol. Chem.* **1959**, *31*, 238. For S-PMS isotactic copolymerization Natta found $r_1$ = 0.82. For S-PCS $r_1$ = 2.2.

(11) Ammendola, P.; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307.

---

# Water-Soluble Polymerization Initiators Based on the Thioxanthone Structure: A Spectroscopic and Laser Photolysis Study

**D. J. Lougnot,* C. Turck, and J. P. Fouassier**

*Laboratoire de Photochimie Générale, Unité Associée au CNRS no. 431, Ecole Nationale Supérieure de Chimie, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France.*

*Received May 11, 1988*

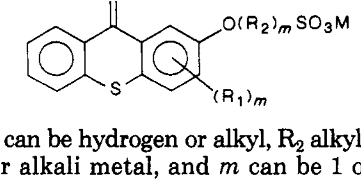
ABSTRACT: This paper reports on the time-resolved and steady-state photochemical study of a new set of water-soluble initiators of polymerization. They exhibit a bell-shaped dependence of the rate of polymerization as a function of the amine concentration. This unusual shape is accounted for by a concurrent quenching of the singlet and triplet states of the initiator by the cosynergist and a pretty good modelization of the polymerization kinetics is achieved. In addition to the study of the initiation ability of these initiators as a function of several chemical parameters, the question of their photochemical properties (fluorescence and triplet quantum yield, quenching constants by electron donnors in the triplet and singlet states, photoreduction quantum yield) is considered with special attention and some structure/reactivity relationships are pointed out.

## I. Introduction

Recently, several types of ketones have acquired importance as photoinitiators of unsaturated hydrocarbon polymerization.[1] The value of some ionic benzophenone and benzil compounds absorbing UV light between 200 and 350 nm has been reported in the literature for the grafting of water-soluble vinylic monomers onto cellulose or wool.[2] Moreover, the high activity of (4-benzoylbenzyl)trimethylammonium chloride or sodium 4-(sulfomethyl)benzophenone for the photopolymerization of acrylamide in aqueous solution,[3] methyl methacrylate in direct lauryl sulfate micelles,[4] or inverse AOT microemulsions[5] was demonstrated.

However, in spite of their high performances, these photoinitiators are only active when irradiated at 365 nm and below in the UV range of the spectrum; therefore, their use in many technical applications which requires illumination in the blue end of the visible spectrum is impossible.

In an effort to overcome these drawbacks, several groups synthesized thioxanthone derivatives that, when used in conjunction with activators, were reported to be specially appropriate for the curing of some coating formulations between 350 and 450 nm. Like in the case of benzophenones or benzils, water-soluble thioxanthones were also developed by introducing ionic substituents in the skeleton of the corresponding oil-soluble compounds. These compounds carry either anionic or cationic solubilizing groups



in which $R_1$ can be hydrogen or alkyl, $R_2$ alkylene, M either hydrogen or alkali metal, and *m* can be 1 or 2[6] or

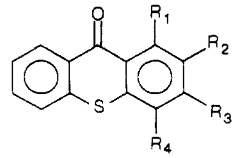
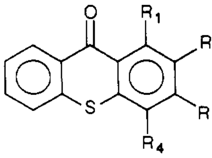


**Table I**
**Formulas of the Water-Soluble TXs**



A = $-OCH_2CH_2CH_2N^+(CH_3)_3$ $SO_3Me^-$
B = $-OCH_2CHOHCH_2N^+(CH_3)_3$ $Cl^-$
C = $-OCH_2COOH$
D = $-OCH_2CH_2CH_2SO_3^-$ $Na^+$

| product | $R_1$ | $R_2$ | $R_3$ | $R_4$ |
|---|---|---|---|---|
| 1 | H | A | H | H |
| 2 | H | B | H | H |
| 3 | H | C | H | H |
| 4 | H | D | H | H |
| 5 | H | B | $CH_3$ | H |
| 6 | H | B | H | $CH_3$ |
| 7 | H | B | $CH_3$ | $CH_3$ |
| 8 | $CH_3$ | B | $CH_3$ | $CH_3$ |
| 9 | H | H | A | H |
| 10 | H | H | B | H |
| 11 | H | H | H | A |
| 12 | H | H | H | B |
| 13 | $CH_3$ | H | H | B |
| 14 | $CH_3$ | $CH_3$ | H | B |
| 15 | $CH_3$ | H | $CH_3$ | B |

wherein one of $R_2$, $R_3$, or $R_4$ is $-OCH_2C(X)HCH_2N^+(CH_3)_3$ $A^-$, in which X is either a hydrogen atom or a hydroxy group and $A^-$ a chloride or methanesulfonate anion.[7] The other R substituents are independently selected as a hydrogen atom or a methyl group (Table I). The synthesis of this second class of compounds is often easier than that of the first one since it requires one less step. Preliminary comparative curing tests have led the investigators to claim a higher efficiency of some of these compounds as compared with other water-soluble initiators.[8]

In this work, the spectroscopic properties as well as the photochemical reactivity of a set of 14 thioxanthones taken from this second series of new water-soluble initiators has been investigated. Also the sodium salt of 2-(3-sulfopropoxy)thioxanthone was tested for comparison purposes. The rates of polymerization of acrylamide in water have been measured so as to compare the initiating efficiencies of these products. The study of the influence of the monomer and amine concentrations upon the rates of polymerization gave an opportunity to test the validity of some assumptions which have been introduced in the kinetic model developed from time-resolved spectroscopy experiments with the objective of predicting the practical efficiencies of this kind of compound.

More generally, this type of work is carried out with the aim of pointing out some relationships between structure and photochemical properties in the series. Such relationships are useful for several reasons: they provide the organic chemists with pieces of information that orient their new synthesis and above all they contribute to the elaboration of general models of the basic processes involved in the photochemistry of carbonyl compounds.

## II. Experimental Section

The water-soluble thioxanthones were obtained from Ward Blenkinsop and were used as received. A blank test showed that no further purification was necessary when electrophoresis grade acrylamide from Aldrich was used. In steady-state experiments, the polymerizable mixtures were prepared by dissolving appropriate amounts of acrylamide AA and methyldiethanolamine MDEA (0.7 and 0.05 M, respectively, unless otherwise stated) in bidistilled water; the initiator concentration was adjusted so that the optical density was about 0.1 at 365 nm. The rates of polymerization were determined gravimetrically as the slope of the initial straight portion of the percent conversion vs irradiation time curve. Unless otherwise mentioned, the incident light intensity was $0.5 \times 10^{16}$ photons $cm^{-2}$ $s^{-1}$. The techniques used in laser spectroscopy experiments were described previously.[9] The spectroscopic determinations were made on a Beckmann DU-7 spectrophotometer and on a Jobin-Yvon Beam spectrofluorimeter. The fluorescence lifetimes were measured by using the third harmonic of a Nd-YAG Quantel laser as the excitation source, an ultrafast photodiode—RTC XA 1002—associated with the appropriate set of pass-band glass filters, and a 250-MHz fast-memory scope; the rise time of this system is lower than 2 ns. In some cases when the lifetimes were too short, they were determined by the single photon counting technique. The molecules were then excited by the harmonics of a Kiton Red dye laser pumped by a pulsed argon ion laser. The time resolution was less than 1 ns.

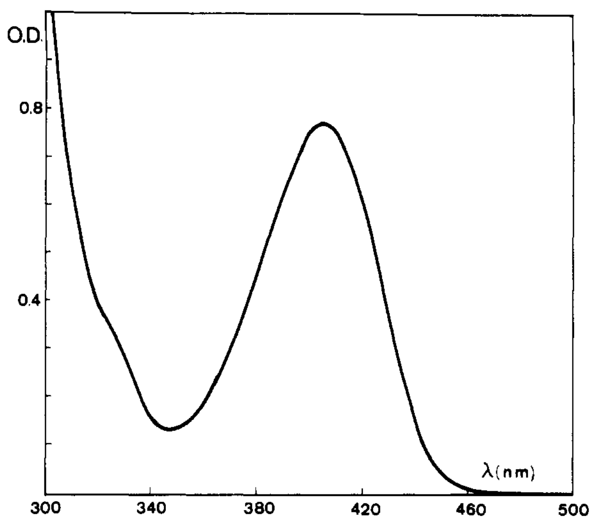


**Figure 1.** Typical absorption spectrum of an ionic thioxanthone ([7] = $6 \times 10^{-5}$ M in water).

**Table II**
**Absorption Maximum and Extinction Coefficient of the Ground-State Absorption of TXs**

| product | $\lambda_{max}^{abs\,a}$ | $\log \epsilon_{max}{}^{b}$ | product | $\lambda_{max}^{abs\,a}$ | $\log \epsilon_{max}{}^{b}$ |
|---|---|---|---|---|---|
| 1 | 406 | 3.75 | 8 | 392 | 3.85 |
| 3[c] | 408 | 3.45 | 10 | 376 | 3.70 |
| 4 | 407 | 3.80 | 11 | 393 | 3.70 |
| 5 | 402 | 3.80 | 12 | 393 | 3.90 |
| 6 | 407 | 3.70 | 14 | 393 | 3.70 |
| 7 | 404 | 3.80 | | | |

[a] ±1 nm. [b] ±0.1. [c] Insoluble in pure water; dissolved at pH 9.2.

## III. The Ground State

The absorption spectra of the series of water-soluble thioxanthones do not basically differ from that of unsubstituted thioxanthone or of 2-, 3-, or 4-methoxythioxanthone which can be regarded as the generic molecules in this series.[10] By way of example the absorption spectrum of 7 is shown on Figure 1. The introduction of methyl substituents at some of the unoccupied positions of the benzene ring carrying the ionic substituent has only a weak effect on the position of the absorption maximum and on the extinction coefficient of the first singlet–singlet transition. The corresponding experimental results are reported in Table II. It can be seen from this table that the blue shift which results from methyl substitution is consistent with an approach taking into consideration only the inductive effect introduced by the methyl substituents. Likewise, the extinction coefficient of the $S_0 \rightarrow S_1$ transition is weakly affected by increasing the degree of substitution. However, it is important to notice that the extinction coefficients at 365 nm—the wavelength used in the photopolymerization experiments—significantly differ in the series (see Table II).

**Table III**
**Fluorescence Maximum, Quantum Yield, and Singlet Lifetime of TXs**

| product | $\lambda_{max}^{fluo\,a}$ | $\phi_F^b$ | $\tau_F^c$ |
|---|---|---|---|
| **1** | 483 | 0.42 | 14.7 |
| **2** | 474 | 0.47 | 14.0 |
| **3** | 470 | 0.45 | 14.0 |
| **4**[d] | 482 | 0.52 | 15.2 |
| **5** | 464 | 0.63 | 13.7 |
| **6** | 480 | 0.33 | 14.2 |
| **7** | 471 | 0.38 | 13.0 |
| **8** | 479 | 0.12 | 9.0 |
| **9** | 436 | 0.17 | 3.6 |
| **10** | 436 | 0.19 | 4.0 |
| **11** | 472 | 0.24 | 12.3 |
| **12** | 470 | 0.29 | 11.3 |
| **13** | 495 | 0.09 | 9.0 |
| **14** | 507 | 0.05 | |
| **15** | 463 | 0.17 | |

[a] ±2 nm. [b] ±10%. [c] ±0.5 ns. [d] Dissolved at pH 9.2.

**Table IV**
**Stern–Volmer Constants and Quenching Rates of the Singlet State of TXs by MDEA**

| product | $K_{SV}$,[a] $M^{-1}$ | $k_Q^S$, $10^9$ $M^{-1}\,s^{-1}$ | product | $K_{SV}$,[a] $M^{-1}$ | $k_Q^S$, $10^9$ $M^{-1}\,s^{-1}$ |
|---|---|---|---|---|---|
| **1** | 34.6 | 2.4 | **8** | 23.9 | 2.7 |
| **2** | 32.4 | 2.3 | **9** | 16.7 | 4.6 |
| **3**[b] | 24.7 | 1.8 | **10** | 16.6 | 4.2 |
| **4** | 37.0 | 2.4 | **11** | 27.6 | 2.3 |
| **5** | 40.9 | 2.9 | **12** | 31.9 | 2.8 |
| **6** | 36.6 | 2.6 | **13** | 14.5 | 1.6 |
| **7** | 40.0 | 3.1 | | | |

[a] ±5%. [b] Dissolved at pH 9.2.

## IV. The First Singlet State

**1. Emission Spectrum and Quantum Yield.** The emission spectra of the thioxanthones (TXs) under study generally image the corresponding absorption and the stockes shift is almost constant over the series (ca. 4000–4300 $cm^{-1}$) (Table III). Only **13** seems to depart from this general behavior: the Stockes shift comes to ca. 5600 $cm^{-1}$. This singularity could be related to the presence of a methyl substituent in the ortho position with respect to the carbonyl chromophore. Owing to the closeness of these groups, a very fast keto enol tautomerism affecting the structure of the emitting species could well take place.

The quantum yields of fluorescence were determined by the relative method using thioxanthone in methanol as the standard.[11] The experimental results are reported in Table III.

**2. Fluorescence Lifetimes.** The experimental data are reported in Table III which show that the fluorescence lifetimes are significantly affected by increasing the degree of methyl substitution in a subseries characterized by a constant position of the ionic substituent (**1**, **5**, **7**, and **8**). Likewise, a very important change is noticed when going from substitution in position 2 or 4 to substitution in position 3. Finally, the replacement of the methanesulfonate counterion by a chloride anion has no significant effect on the singlet lifetimes. This observation agrees with the fact that in water, the ionic thioxanthones are almost completely dissociated.

**3. Quenching by Amines.** Contrary to benzophenones,[12] thioxanthones are known to strongly interact in their first excited singlet state, with many electron donors. The quenching constant $k^s_Q$ of **6** by MDEA was measured to be 2.6 × $10^9$ $M^{-1}\,s^{-1}$. The experimental results of a thorough study of the singlet state deactivation of the complete set of TXs, by steady-state fluorescence quenching, are collected in Table IV along with the values of $k^s_Q$ calculated from the corresponding $\tau_f$s when available.

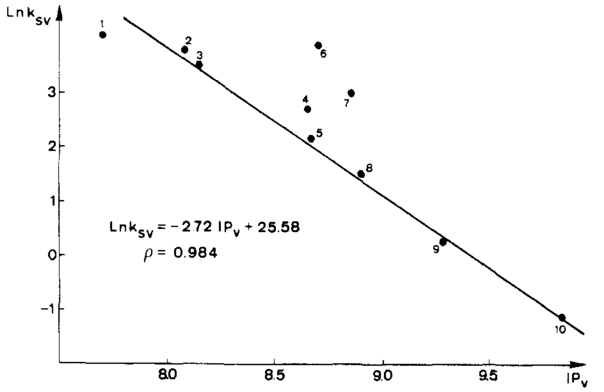


**Figure 2.** Correlation between the vertical ionization potential of different amines and the Stern–Volmer constant of the quenching of fluorescence of **4** ($\lambda_{excitation}$ = 400 nm, $\lambda_{detection}$ = 480 nm, OD at 400 nm = 0.02).

**Table V**
**Stern–Volmer Constants Corresponding to the Singlet Quenching of 4 by a Series of Amines with Various Ionization Potentials**

| amine | $K_{SV}$ | PI | ref |
|---|---|---|---|
| A. diazabicyclooctane | 59.5 | 7.52 | 13 |
| B. triethylamine | 44.6 | 8.08 | 14 |
| C. dimethylbenzylamine | 34.1 | 8.14 | 15 |
| D. ethylbenzylamine | 15.5 | 8.65 | 15 |
| E. diethylamine | 8.7 | 8.67 | 14 |
| F. triethanolamine | 45.8 | 8.70 | 15 |
| G. dimethylethanolamine | 20.0 | 8.85 | 15 |
| H. morpholine | 4.5 | 8.90 | 13 |
| I. *n*-butylamine | 0.75 | 9.29 | 14 |
| J. ethanolamine | 0.32 | 9.85 | 15 |

It is to be noticed that these rate constants are almost indifferent to both the degree of substitution and the branching position. Since the energy of the first excited state is weakly affected by these factors, this result is not surprising.

The dependance of the Stern–Volmer constant on the ionization potential of the donor used to quench the fluorescence of substituted thioxanthone was studied in the case of **4**. Since the simple *N*,*N*,*N*-trimethyl-1-propanaminium salt **1** was recognized to be weakly mutagenic the corresponding 2-(3-sulfopropoxy) salt **4** was preferred. This compound is the only 2-monosubstituted thioxanthone carrying the propoxy substituent to the exclusion of other substituent or side hydroxy groups which could give rise to deleterious quenching processes (i.e., intramolecular hydrogen abstraction or acid–base equilibrium).

The results of this study are collected in Table V and Figure 2. They show a clear correlation between the Stern–Volmer constant and the vertical ionization potential of the donor over a more than two-unit range of ionization potentials. This result is in good agreement with the findings of many authors who studied the quenching of the excited states of ketones in organic solvents by electron donors.[16] Only the hydroxy amines seem to a slight extent to depart from the correlation, a fact which could be due to strong hydrogen bonding in a polar solvent.

**4. pH Effects on the Fluorescence Quenching.** Since this work deals with a series of molecules to be utilized as photoinitiators for the polymerization of water-soluble monomers, the question of the influence of pH on the elementary processes involved in the initiation mechanism must be considered with particular attention. MDEA has been chosen as the standard cosynergist

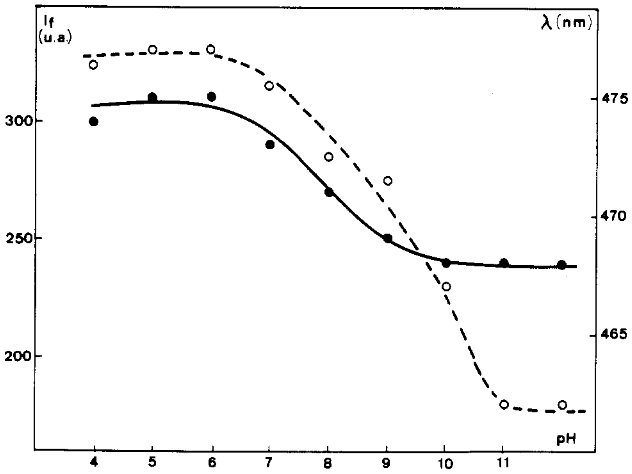


**Figure 3.** Influence of the pH on the fluorescence properties of 7.

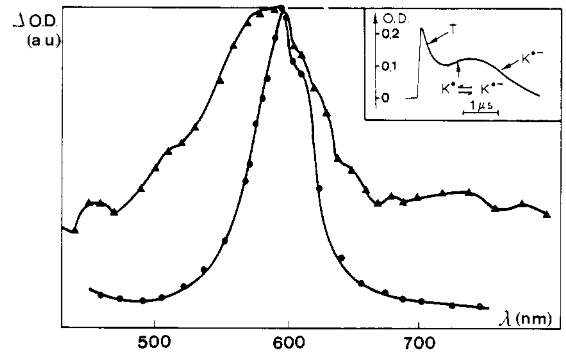


**Figure 4.** Triplet-triplet absorption spectra of 7 in pure water (▲) and of thioxanthone in methanol (●). Insert: Typical oscillogram recorded at 600 nm with 14 in the presence of [MDEA] = 8 × $10^{-2}$ M. T, K•, and K•− correspond to the contributions due to triplet, ketyl, and ketyl anion, respectively.

throughout this study because this amine is reputedly one of the best adapted electron donors for water-soluble systems. The p*K* of this rather strong base was measured to be ca. 10.7 in water.

The quenching of TXs fluorescence by MDEA was observed to critically depend on the pH of the water solution: the rate constant of this process is indifferent to pH changes beyond 8.5, whereas it becomes insignificant in acidic or neutral medium, that is, when the amine is present in the system in its protonated form.

Moreover, the basicity of the amine causes the pH to increase from 7 to about 9.5 throughout these quenching experiments. In the case of substituted thioxanthones carrying a 2-hydroxy-*N*,*N*,*N*-trimethyl-1-propanaminium side chain, an unexpected secondary effect of the pH change is observed: the emitting species undergoes an acid-base equilibrium, the consequence of which is a weak change of the emission wavelength and a more pronounced change (i.e., a decrease) of the emission quantum yield (Figure 3).

## V. The Triplet State

**The T-T Absorption Spectrum.** The T-T absorption spectrum of TX 7 in water is reported in Figure 4. Its general shape does not basically differ from that of unsubstituted thioxanthone except the red tail is both more pronounced and spreads far beyond 800 nm.[17] The maximum is blue-shifted to 587 nm as compared with that of thioxanthone in polar solvents (605 in methanol[18]) due to both substituent and solvent effects. This blue shift was attributed to a strong decrease in dipole moment on excitation.[19] The inversion of the n$\pi^*$ and $\pi\pi^*$ levels could also play a part in this question.[20] Moreover, in water the T-T absorption spectra of TXs are markedly broadened because of the strong solvent-solute interactions which prevail in highly polar solvents.

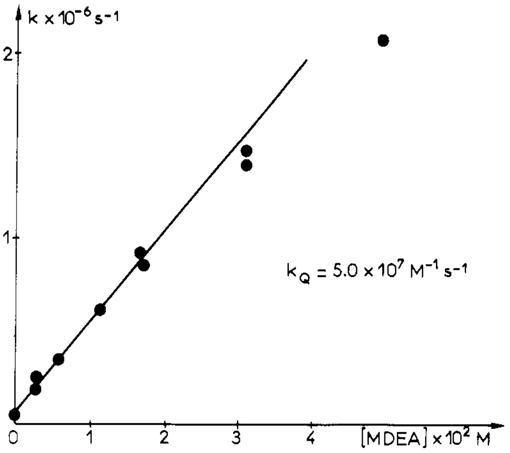


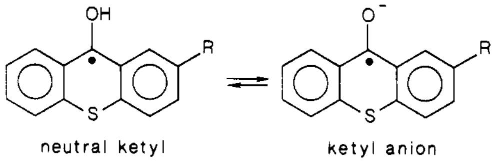
**Figure 5.** Decay rate constant of the triplet of 5 as a function of the quencher concentration.

Table VI
**Quenching Constants of the Triplet of TXs by MDEA**[a]

| product | $k_Q^T$, $10^7$ $M^{-1}$ $s^{-1}$ [a] | product | $k_Q^T$, $10^7$ $M^{-1}$ $s^{-1}$ [a] |
|---|---|---|---|
| **1** | 3.2 | **6** | 3.2 |
| **3** | 6.5 | **7** | 3.0 |
| **4** | 4.4 | **10** | 3.7 |
| **5** | 5.0 | **14** | 7.8 |

[a] The lifetimes were determined with an optical density of the ground state of 0.5 per cm at 355 nm (i.e., (~3-5) × $10^{-4}$ M).

**Quenching by MDEA.** Due to the absence of detectable phosphorescence at room temperature the only available technique to determine the quenching constant of the triplet state of TXs by amines is laser spectroscopy. However, this determination is made rather problematical because of the almost complete overlapping of the transient absorption spectra of the triplet, the ketyl radical, and the anion radical. Since the p$K_a$ of the equilibrium lies in the same range as the p*K* of MDEA, these radicals equilibrate immediately after triplet quenching as a function of the pH of the medium. As a consequence, the decay of the triplet absorption convolutes with the equilibration between the two forms of the ketyl radical and with the relaxation of the ketyl anion radical (Figure 4). This behavior makes it difficult to determine the triplet lifetime with precision and prevents any analysis of the transient optical density due to ketyl radical as a function of the amount of MDEA added.



However, the perturbation introduced by the acid-base equilibrium of the ketyl radical is more or less pronounced, depending on its p*K* relative to that of MDEA. Figure 5 shows the Stern-Volmer treatment of the triplet decay rate of **5**, and the quenching rate constants of some of the TXs that lend themselves to this usual Stern-Volmer treatment are collected in Table VI.

Though this treatment cannot be extended to all the members of the series, a qualitative investigation shows that no dramatic changes in the efficiency of this process are to be expected with the other TXs. As a general rule,

**Table VII**
**Quenching Rate Constants of the Triplet of 4 by a Series of Amines with Various Ionization Potentials**

| product[a] | $k_Q^T$, $10^6$ $M^{-1}$ $s^{-1}$ | $PI_v$ | product[a] | $k_Q^T$, $10^6$ $M^{-1}$ $s^{-1}$ | $PI_v$ |
|---|---|---|---|---|---|
| B | 51 | 8.08 | H | 1.3 | 8.90 |
| D | 32 | 8.65 | J | 0.6 | 9.85 |
| E | 14 | 8.67 | | | |

[a] The names of the amines are given in Table V.

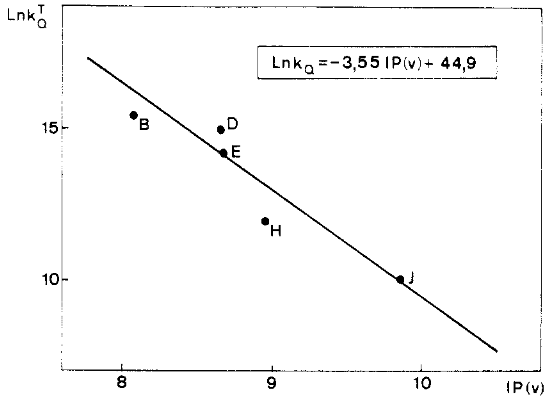


**Figure 6.** Correlation between the vertical ionization potential of different amines and the quenching constant of 4.

**Table VIII**
**Rates of Polymerization of Acrylamide in the Presence and in the Absence of Amine**

| product | [MDEA], M | $10^5R_p$, M $s^{-1}$ [a] | product | [MDEA], M | $10^5R_p$, M $s^{-1}$ [a] |
|---|---|---|---|---|---|
| **3** | 0 | 21 | **7** | 0 | 25 |
| | 0.05 | 136 | | 0.05 | 154 |
| **4** | 0 | 23 | **10** | 0 | |
| | 0.05 | 117 | | 0.05 | 313 |

[a] $I_0 = 0.5 \times 10^{16}$ photons cm$^{-2}$, $OD_{366} = 0.1$, and [AA] = 0.7 M.

**Table IX**
**Rates of Polymerization of Acrylamide in Aqueous Solutions by TXs**

| product | $10^5R_p$, M $s^{-1}$ [a] | $\phi_m$ | product | $10^5R_p$, M $s^{-1}$ [a] | $\phi_m$ |
|---|---|---|---|---|---|
| **1** | 129 | 675 | **9** | 287 | 1502 |
| **2** | 136 | 712 | **10** | 313 | 1640 |
| **3** | 136 | 712 | **11** | 217 | 1140 |
| **4** | 117 | 612 | **12** | 229 | 1200 |
| **5** | 151 | 790 | **13** | 235 | 1230 |
| **6** | 177 | 926 | **14** | 230 | 1203 |
| **7** | 156 | 816 | **15** | 272 | 1423 |
| **8** | 344 | 1800 | | | |

[a] As in Table VIII with [MDEA] = 0.05 M.

all the quenching rate constants by MDEA lie in the range (3-7) × $10^7$ $M^{-1}$ $s^{-1}$.

As was observed with the singlet state, the quenching constants of the triplet state by amines correlate linearly with the vertical ionization potential of the electron donor. However, the number of amines used here is limited by their basicity: their p*K* must not exceed 9 so as to prevent the ketyl radical from undergoing acid-base equilibration. The experimental results are collected in Table VII and the linear correlation is shown in Figure 6. The slope of the straight line indicates a slightly higher degree of charge transfer in the triplet exciplex as compared to the same species in the singlet state.

**Quenching by Acrylamide.** In many instances,[21] this type of interaction has been observed to play a detrimental part in the efficiency of many photoinitiating systems. In point of fact, the physical quenching of the triplet state by a monomer which does not contribute in the generation of active radicals consumes the triplet excited states of the photoinitiator.

The case of TXs is somewhat different: the quenching rate constant of the triplet of **13** by acrylamide was measured to be 8 × $10^4$ $M^{-1}$ $s^{-1}$ and the other TXs are deactivated with rate constants of the same order of magnitude as that of the reference compound [(5-12) × $10^4$ $M^{-1}$ $s^{-1}$].

## VI. Steady-State Photopolymerization

**Comparative Reactivity.** The photopolymerization activities of all 15 thioxanthone compounds measured gravimetrically for the conversion of acrylamide under usual conditions are compared in Tables VIII and IX. These results show a number of interesting and attractive features. For both the methanesulfonate and chloro salts, the introduction of the ionic substituent onto the thioxanthone skeleton leads to very high rates of polymerization. Further substitution of methyl groups in the available position of the benzene ring carrying the ionic substituent is seen to cause perceptible changes of reactivity but the general trend is toward a high initiating activity in the series. The performances of **8** and **13**, which carry a methyl in position 1 and which were suspected to undergo keto enol tautomerism in their excited states,[22] do not seem to be lessened by such an intramolecular deactivating process.

The results shown in Table VIII indicate a weak initiating activity of the TXs in the absence of a cosynergist (electron donor) for the polymerization of acrylamide. Though the question of the origin of this activity has not received any definitive answer yet, the participation of an exciplex between an excited state of the initiator and the monomer was postulated before, to account for the weak activity of some ionic benzophenones under similar experimental conditions.[4]

**Influence of the Amine Concentration on the $R_p$s.** Since the amine cosynergist was observed to interact with both the singlet and triplet states, it was important to determine the dependence of the rates of polymerization as a function of the amine concentration. However, in order to get rid of the specific pH effects which appear upon increasing the amine concentration (vide infra), the solutions used in this study were buffered at pH 9.2 by using the suitable amount of mineral buffer tablets. The inertness of this chemical toward the polymerizable system was controlled by conducting in parallel two polymerization experiments in which the pH was adjusted with these buffer tablets and with hydrochloric acid. The concordance of the $R_p$s measured in these experiments can be regarded as positive proof of the inert character of the mineral buffer.

The experimental curve showing the dependence of $R_p$ as a function of the amine concentration in the case of **4** is reported on Figure 7. The general shape of this curve is quite unusual and it merits some comments: first, the rate of polymerization increases with the amine concentration, [MDEA] < 0.05% w/v, then reaches a maximum, and finally decreases and becomes very low at high amine concentration, [MDEA] > 2.5% w/v.

The same type of behavior was observed with **7** and also with **11**, a thioxanthone carrying the ionic substituent in position 4; however, in this case, the maximum was observed at a lower concentration, [MDEA] ~ 0.005 M, which makes it difficult to obtain precise experimental data at lower amine concentration (Figure 7). Moreover, though not investigated so extensively, all the other thioxanthones exhibit the same typical behavior with a rate of polymerization reaching its maximum for a amine

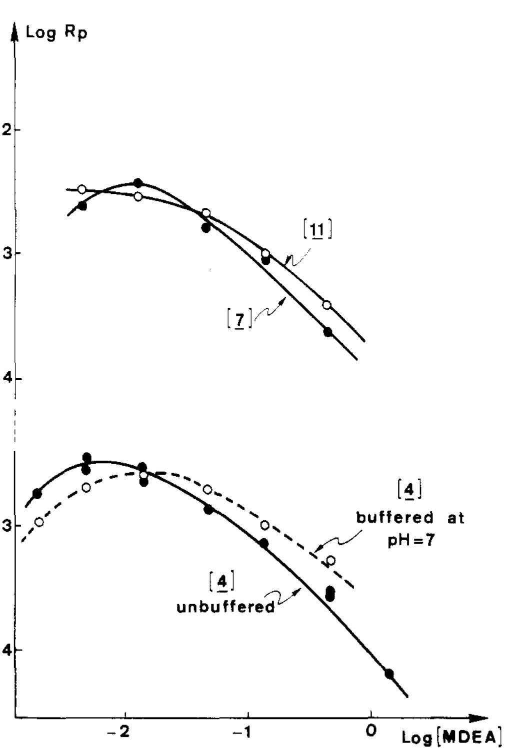


**Figure 7.** Dependence of the rate of polymerization of **4**, **7**, and **11** vs the synergist concentration. Experimental conditions as in Table VIII.

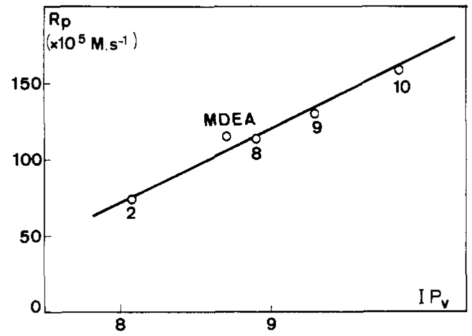


**Figure 8.** Correlation between the vertical ionization potential of the synergist and $R_p$ for compound **4**. [Amine] = 0.05 M; other experimental conditions as in Table VIII.

concentration between 0.005 and 0.01 M and becoming very weak beyond 0.25 M.

This unusual shape must be considered as an indication of concurrent quenching processes affecting both the excited singlet and triplet states, the efficiencies of which in producing active initiating radicals can also be very different. Moreover, for a sufficiently high concentration of MDEA (0.05 M), the rate of polymerization is experimentally observed to increase with the ionization potential of the cosynergist (Figure 8). These questions will be debated in the general discussion with a view to introducing a kinetic scheme which could apply to all the 15 compounds studied.

**Influence of the Monomer Concentration.** This study has been conducted on systems containing a constant amount of amine—[MDEA] = 0.05 M—in the presence of **7**. The results are shown in Figure 9. The slope of the straight line obtained is about 1.5, a result which is also arrived at in the case of **3**.

This type of monomer dependence denotes an expression of the rate of polymerization in which the concentration of the monomer exercises an influence not only on the propagation term but also on the initiation efficiency. Such a general behavior was already reported in the case of deoxybenzoin, for instance, where it was interpreted by postulating an efficiency of the initiating radicals toward MMA, linearly increasing with the monomer concentration.[23]

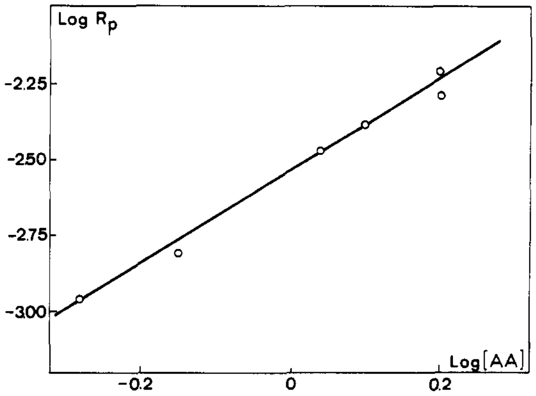


**Figure 9.** Rate of polymerization of **7** vs monomer concentration. Experimental conditions as in Table VIII.

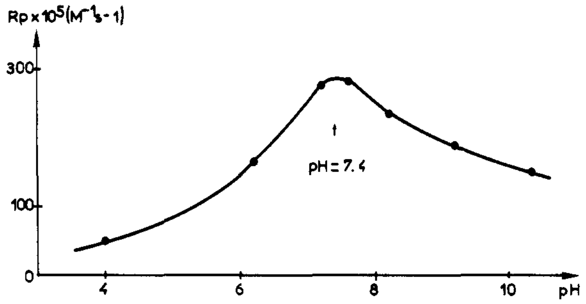
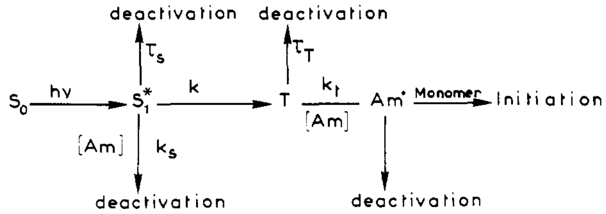


**Figure 10.** Rate of polymerization of **7** vs pH. Experimental conditions as in Table VIII.

**Scheme I**



**Influence of the pH.** The question of the influence of the pH on the polymerizable mixture was invoked in many instances to try to explain some irregularities in the polymerization kinetics of other ionic initiators (benzophenones or benzils[24]). A direct influence of the pH on the photooxidizable character of the amine cosynergist is often put forward and the possibility of a direct participation of either the ketyl or ketyl anion radicals in the termination process was also considered.[25]

Figure 10 shows the influence of pH in the case of **7** in the presence of [MDEA] = 0.05 M and [acrylamide] = 7 M. The bell-shaped curve which is obtained shows a maximum in the range pH 7.4. The loss of activity observed in acidic media is certainly due to the protonation of the amine, which prevents the charge transfer from taking place. When going to strongly alkaline media, the decrease is less pronounced and no definite statement is available yet to account for this effect. The possible part played by the ketyl radical in the termination process which was invoked has still to be substantiated.

Finally, it is to be noticed that the initiating activity of all the thioxanthones of the series as deduced from a simplified study is pH sensitive. The same general behavior is observed: a maximum efficiency in neutral to weakly alkaline media, almost no activity in acidic media, and a

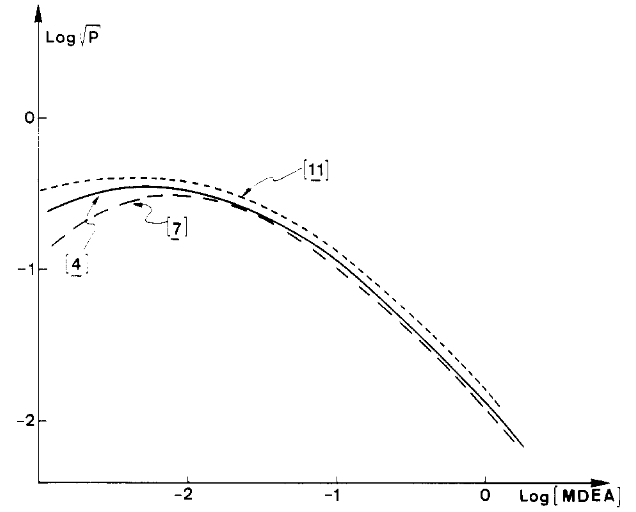


**Figure 11.** Calculated values of log $P^{1/2}$ as a function of log [MDEA].

weakening of the initiating properties as the medium becomes more and more alkaline.

## VII. Discussion of the Kinetic Model

The general diagram summarizing the different elementary steps which play a part in the photoinitiating process by ionic thioxanthones is reported on Scheme I.

In a first approach, this diagram takes account of a physical quenching of the singlet state ($k_S$) and of a chemical quenching of the triplet state ($k_T$) by the amine. In consideration of its very low rate constant, the quenching by the monomer is disregarded. The actual lifetimes of $S_1$ and T in the absence of quencher are $\tau_s$ and $\tau_T$, respectively, and the rate constant for intersystem crossing is represented by $\phi_{ST}$. Finally, the efficiency of the initiating process itself is expressed by

$$\rho = (\text{number of polymer chains created})/(\text{number of initiating radicals available})$$

The rate of a polymerization obeying this general scheme can be expressed as

$$R_p^2 = 2.3\frac{k_p^2}{k_t}[M]^2 OD I_0 \rho \frac{\phi_{ST}}{\tau_s k_s[Am] + 1} \frac{\alpha k_T[Am]}{k_T[Am] + 1/\tau_T} \tag{1}$$

where [M] stands for the monomer concentration, OD for the optical density of the initiator, $I_0$ for the intensity of the source, and $\alpha$ for the quantum efficiency of the photoreduction of the triplet state by the amine.

Since $\rho$, $\alpha$, and $\phi_{ST}$ are not experimentally known, the absolute rates of polymerization cannot be calculated. However, in order to test this model, we have estimated from the available experimental data the value of

$$P = \frac{1}{1 + k_s\tau_s[Am]} \frac{k_T[Am]}{1 + k_T\tau_T[Am]} \tag{2}$$

which is proportional to $R_p^2$ provided that the parameters $\phi_{ST}$, $\alpha$, and $\rho$ are effectively constant when the concentration of the synergist increases.

The results of this calculation are shown on Figure 11 for compound 4. It is very interesting to compare this curve with that reported on Figure 7 and to observe that they go through a maximum for the same amine concentration (~0.005 M) and that they exhibit the same general shape. In connection with this observation, it must be pointed out that the existence of a maximum in the experimental curve is corroborative evidence for the absence of an efficient chemical reaction between the excited singlet state of the initiator and the amine. Should this reaction contribute importantly to the production of initiating species, the rate of polymerization would increase continuously with increasing amine concentration, as can be demonstrated by kinetic analysis: if one considers the possibility of an active amine-derived radical (Am•) generated either by singlet or triplet quenching, its quantum yield would be expressed by the following relationship:

$$\phi_{Am\bullet} = \frac{1}{k_s[Am] + 1/\tau_s}\left[k_s[AM] + \frac{k_{ST}k_T[Am]}{1/\tau_T + k_T[Am]}\right] \tag{3}$$

which shows that $\phi_{Am\bullet}$ must reach unity for high amine concentration.

The results obtained with compounds 7 and 11, which carry the cationic substituent in position 2 and 4, respectively, suggest the same conclusion. With these molecules, the graphs exhibit a maximum for amine concentrations ranging between $1 \times 10^{-3}$ and $5 \times 10^{-3}$ M and their general shape compares well with that of the curve refering to compound 4.

The kinetic study of the monomer dependence of the $R_p$s obtained with this series of thioxanthones is also very informative. The data reported in section IV.3 show a cubic dependence of the $R_p$s as a function of the square of the monomer concentration in the case of two ionic compounds taken as examples. By analogy with the case of deoxybenzoin, which exhibits the same behavior, we suggest an indirect influence of the monomer upon the efficiency factor $\rho$ which can be expressed as follows:

$$\rho = \frac{k_i[M]}{k_i[M] + \sum k}$$

In this expression $k_i$ stands for the rate of the initiating step itself and $\sum k$ for the sum of the other rate constants contributing to the decay of the active species. If the efficiency factor is low ($\rho \leqslant 0.1$) its expression reduces to

$$\rho \approx \frac{k_i}{\sum k}[M]$$

where $k_i/\sum k$ is an intrinsic parameter characterizing the active species.

With such an approach, the equation can be rewritten

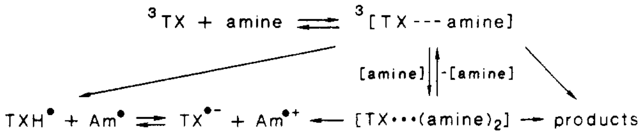
$$R_p^2 = 2.3\frac{k_p^2}{k_t} OD I_0 \frac{\phi_{ST}}{\tau_s k_s[Am] + 1} \frac{\alpha k_T[Am]}{k_T[Am]} \frac{k_i}{\sum k}[M]^3 \tag{4}$$

When the monomer concentration is a variable and $R_p$ a function, the following general relationship is deduced:

$$R_p^2 = A[M]^3$$

This result is important since it must be considered as the sign of a modest initiating efficiency of the amide-derived radical; in point of fact, should this efficiency approach unity, $R_p$ would linearly depend on the monomer concentration.

In the case of unsubstituted thioxanthone, Schuster and co-workers,[1] basing their argument on Davidson's works,[26] have suggested the possible participation of triplexes in the decomposition of the exciplex which arises from the interaction between the triplet state of the carbonyl and the electron donor. The following reaction scheme was postulated:



The intermediacy of such triplexes in the photoinitiation process considered in this work can be probed for by examining the effect of amine concentration on the ketyl radical yield. In fact, if the triplex plays a part in the production of the ketyl radical, the corresponding rate constant ought to be different to that of the "normal" pathway (which involves only the exciplex) since the constants could only be equal by coincidence. Unfortunately, several experimental difficulties make this treatment rather problematic in the case of our ionic derivatives as compared with what was reported by Schuster for unsubstituted thioxanthones. First, due to pH changes which go together with increasing the electron donor concentration, the ketyl radical is more or less converted to its corresponding anion, hence the necessity to buffer the solution at a sufficiently low pH to prevent the neutral ketyl from equilibrating but not too low to avoid protonation of the free amine at the nitrogen. Second, the wavelength window in which the neutral ketyl radical of TXs is usually monitored ($\lambda \sim 430$ nm) is much less favorable in the case of ionic derivatives because of solvent and substituent effects which induce the absorptions due to this transient species and to the ground state to overlapp. On that account, the transient optical density due to the ketyl of TXs in water can only be recorded in the region 550–600 nm, where the determination is much less accurate. Nevertheless, the experiments were conducted in the region of the T–T absorption maximum with several TXs of the series, **4**, **5**, **9**, and **11**, and with three different amines (triethylamine, methyldiethanolamine, and diethanolamine), and the experimental results were analyzed as follows:

$$\mathrm{OD}_\infty = \mathrm{OD}_0 \frac{\epsilon_\mathrm{K}}{\epsilon_\mathrm{T}} \frac{k_\mathrm{Q}{}^\mathrm{T}[\mathrm{Q}]}{\sum k^\mathrm{T} + k_\mathrm{Q}{}^\mathrm{T}[\mathrm{Q}]}$$

$$\frac{\mathrm{OD}_0}{\mathrm{OD}_\infty} = \frac{\epsilon_\mathrm{T}}{\epsilon_\mathrm{K}}\left(1 + \frac{\sum k^\mathrm{T}}{k_\mathrm{Q}{}^\mathrm{T}[\mathrm{Q}]}\right)$$

$\mathrm{OD}_0$ and $\mathrm{OD}_\infty$ represent the transient optical densities just after the laser pulse and after complete relaxation of the triplet ($t = 40\ \mu$s); $\epsilon_\mathrm{T}$ and $\epsilon_\mathrm{K}$ are the extinction coefficients of the triplet and of the ketyl radical at the probe wavelength. Since $k_\mathrm{Q}{}^\mathrm{S}$ is higher than $k_\mathrm{Q}{}^\mathrm{T}$ by almost 2 orders of magnitude, the time required to populate the triplet state is by far shorter than the rise time of the detection. Thus $\mathrm{OD}_0$ represents the initial optical density of the triplet.

Surprisingly, the behavior of all four compounds is normal in the presence of triethylamine or diethanolamine whereas the quenching by methyldiethanolamine shows some singularities. The triplet quenching constants which are deduced from the study of $\mathrm{OD}_0/\mathrm{OD}_\infty$ as a function of the inverse of the quencher concentration are consistent with the value derived from the direct Stern–Volmer analysis of TEA and DEA. In contrast with MDEA, the constants are systematically lower than those obtained from Stern–Volmer treatment (see Table X).

This interesting behavior seems to exclude the participation of any three-center species in the reaction process generating the amide-derived radical. Moreover, it points out the fact that MDEA, which undergoes rapid electron transfer in the presence of water-soluble thioxanthones, leads only to partial subsequent proton transfer and consequently to a modest photoreduction yield.

This conclusion can be put together with the fact that the quenching constants of either singlet or triplet TXs by hydroxyamines were observed to deviate from the general correlation with the ionization potentials. This behavior is probably related to the presence of the hydroxy groups which induce specific interactions in polar hydroxylated solvents.

**Table X**
**Comparison of the Rate Constants $k_0$ Derived from the Triplet Decay Rates and from the Ratio $\mathrm{OD}_0/\mathrm{OD}_\infty$**

| TX/amine | $k_\mathrm{Q}$, $10^6/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ from $k_\mathrm{T}$ | $k_\mathrm{Q}$, $10^6/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$ from $\mathrm{OD}_0/\mathrm{OD}_\infty$ |
|---|---|---|
| 4/TEA | 4.2 | 4.1 |
| 4/DEA | 1.25 | 1.4 |
| 4/MDEA | 49 | 5.5 |
| 5/MDEA | 49 | 7.0 |

The last point to be elucidated refers to the initiating activity of our ionic TXs in the absence of electron or hydrogen donor. Though the quenching rate constant of the triplet state of TXs by acrylamide ($k_\mathrm{Q}{}^\mathrm{AA}$) is on the order of $10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$—that is, the products $k_\mathrm{Q}{}^\mathrm{AA}[\mathrm{AA}]$ and $k_\mathrm{SQ}[\mathrm{TX}]$ are comparable in the experimental conditions of a photopolymerization—a direct photoreduction of acrylamide is not likely to occur in this system. This property could be related rather to the propensity of thioxanthones to undergo para coupling to "light-absorbing transients" (LATs) of the type previously reported by several authors in the case of benzophenone.[27] High yields of LATs have precedents in the works of Schuster et al.[1] or Scaiano et al.,[28] who noticed the enhancement of their formation in high polar environments and in aqueous micellar solutions. For instance, with compound **9**, the self-quenching constant is measured to be $3.6 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$. All other 14 compounds of the series also show efficient self-quenching with rate constants lying in the region (2–4) $\times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

In other respects, such high values of the self-quenching constants may introduce some confusion in the understanding of photochemical properties of TXs and even induce misleading conclusions. For instance, in the study of the interaction of their triplet with amines, as the rate constant of the photoreduction is always low ($10^5$ to $10^8$) compared to that of the self-quenching process, care must be taken to adjust the respective concentrations of the TX and of the amine so that the yield of the ketyl radical produced by the photoreduction exceeds by far that of the deleterious process involving the bimolecular interaction between the triplet and the ground state. Owing to their not having considered this fact, some authors reached questionable conclusions in a recent series of papers devoted to functionalized thioxanthones.[22,29] The system they were dealing with was a $5 \times 10^{-5}$ M solution of TX containing $5 \times 10^{-5}$ M of amine, so that the quantum yield of the process leading to LATs exceeded by far that of the photoreduction. Moreover, the possible effect of pH was completely disregarded. For those reasons, it is no surprise that some of our conclusions could be at variance with theirs.

The idea that amine-derived radicals are the most important initiators in the systems containing an amine electron donor is supported by the absence of chemical reaction between olefins and the triplet state of the carbonyl compound and the lack of detectable quenching of either the ketyl radicals or the corresponding ketyl anions by olefins. However, due to the high rate of the self-quenching process, the participation of some radicals arising in the course of LATs generation (even macroradicals) in the photoinitiation process cannot be disregarded at low concentration of amine synergist.

Finally, the effect of pH on the rates of polymerization could be an indication for the involvement of some pH-sensitive species in the propagation or termination steps. Regardless of the identity of the species responsible for this effect, the curve reported on Figure 11 suggests that the p$K$ of pH-sensitive species must be in the region 7–8, in line with the deprotonation of the ketyl radical of thioxanthones in water.[30]

## VIII. Conclusion

This work has demonstrated that the photochemical behavior of thioxanthones carrying ionic groups which introduce some water solubility does not basically differ from that of their unsubstituted parent compound. They are efficiently quenched by electron donors in both their singlet and triplet state with a rate constant in inverse ratio to the ionization potential of the donor. This quenching process gives rise to an efficient photoreduction only in the triplet state.

The results of polymerization experiments carried out on this series show that maximum efficiency is achieved through monosubstitution in position 3, regardless of the nature of the solubilizing group. The introduction of additional methyl groups at the other positions of the ring carrying the ionic group has a favorable effect on the initiation efficiency.

In conclusion, these TXs compare fiarly well with other classes of water-soluble initiators based on the benzophenone structure, with the decisive advantage of a photosensitivity range extending up to about 450 nm. Moreover, the indifference of the initiating characteristics to the nature of the ionic group introducing water solubility is in favor of the development of the products requiring the simplest synthetic procedure.

**Acknowledgment.** Drs. P. N. Green and W. A. Green (Ward Blenkinsop Ltd.) are gratefully acknowledged for providing us with the samples of the water-soluble TXs studied in this work and for stimulating discussions. Our thanks extend also to Dr. J. C. Andre for permission to use the single photon counting equipment at the University of Nancy.

**Registry No.** 1, 102790-16-9; 2, 103430-19-9; 3, 84434-05-9; 4, 86691-30-7; 5, 103430-20-2; 6, 103430-21-3; 7, 103430-24-6; 8, 103430-25-7; 9, 103430-27-9; 10, 103430-28-0; 11, 103580-15-0; 12, 103430-29-1; 13, 103430-30-4; 14, 103430-31-5; 15, 103430-32-6; B, 121-44-8; D, 14321-27-8; E, 109-89-7; H, 110-91-8; J, 141-43-5; MDEA, 105-59-9; acrylamide, 79-06-1.

## References and Notes

(1) Amirzadeh, G.; Schnabel, W. *Makormol. Chem.* **1981**, *182*, 2821. Davidson, R. S.; Goodin, J. W. *Eur. Polym. J.* **1982**, *18*, 597. Sandner, M. R.; Osborn, C. L.; Trecker, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *108*, 3173. Fouassier, J. P. *J. Chim. Phys.* **1983**, *80*, 339. Yates, S. F.; Schuster, G. B. *J. Org. Chem.* **1984**, *49*, 3349.

(2) Bottom, R. A.; Guthrie, J. T. *Polym. Photochem.* **1985**, *6*, 111. Guthrie, J. T.; Barker, P. S.; Bottom, R. A.; Green, P. N. *Spectrosc. Chem.* **1985**, *5*, 4.

(3) Fouassier, J. P.; Lougnot, D. J.; Zuchowicz, I.; Green, P. N.; Timpe, H. J.; Kronfeld, K. P.; Mueller, Ü. *J. Photochem.* **1987**, *36*, 347.

(4) Fouassier, J. P.; Lougnot, D. J. *J. Appl. Polym. Sci.* **1986**, *32*, 6209.

(5) Fouassier, J. P.; Lougnot, D. J.; Zuchowicz, I. *Eur. Polym. J.* **1986**, *22*, 933.

(6) Curtis, J. R. Eur. Pat. 81280, 1981.

(7) Gwane, G.; Green, P. N.; Green, W. A. Eur. Pat. 0224967, 1986. Green, P. N. *Polym. Paint Resins* **1985**, *175*, 246.

(8) Davis, M. J.; Gawne, G.; Green, P. N.; Green, W. A. *Proceedings Radcure Baltimore*; Sept 1986.

(9) Faure, J.; Fouassier, J. P.; Lougnot, D. J.; Salvin, R. *Nouv. J. Chim.* **1977**, *1*, 15. Fouassier, J. P.; Lougnot, D. J.; Payerne, A.; Wieder, F. *Chem. Phys. Lett.* **1987**, *135*, 30.

(10) Lai, T.; Lim, E. C. *Chem. Phys. Lett.* **1980**, *73*, 244. Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *Eur. Polym. J.* **1986**, *22*, 793.

(11) Dalton, J. C.; Montgomery, F. C. *J. Am. Chem. Soc.* **1974**, *96*, 6230.

(12) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973**, *73*, 141.

(13) Alder, R. W.; Arrowsmith, R. J.; Casson, A.; Sessions, R. B.; Heibronner, E.; Kovac, B.; Huber, H.; Taagepera, M. *J. Am. Chem. Soc.* **1981**, *103*, 6137.

(14) Aue, D. H.; Weeb, H. H.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311.

(15) Pfister-Guillouzo, G.; Jacques, P., unpublished results.

(16) Guttenplan, J. B.; Cohen, S. G. *J. Am. Chem. Soc.* **1972**, *94*, 4040. Loutfy, R. O.; Yip, R. W.; Dogra, S. L. *Tetrahedron Lett.* **1977**, *33*, 2843.

(17) Yip, R. W.; Szabo, A. G.; Tolg, P. K. *J. Am. Chem. Soc.* **1973**, *95*, 4471.

(18) Garner, A.; Wilkinson, F. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1010.

(19) Abdullah, K. A.; Kemp, T. J. *J. Photochem.* **1986**, *32*, 49.

(20) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

(21) Lougnot, D. J.; Fouassier, J. P. *J. Polym. Sci.* **1988**, *26*, 1021.

(22) Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *J. Photochem.* **1987**, *36*, 112.

(23) Merlin, A.; Fouassier, J. P. *J. Chim. Phys.* **1981**, *78*, 267.

(24) Lougnot, D. J.; Jacques, P.; Fouassier, J. P.; Casal, H. L.; Kim-Thuan, N.; Scaiano, J. C. *Canad. J. Chem.* **1985**, *63*, 3001. Bonamy, A.; Fouassier, J. P.; Lougnot, D. J.; Green, P. N. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 315.

(25) Merlin, A.; Fouassier, J. P.; Lougnot, D. J. *Eur. Polym. J.* **1981**, *17*, 755.

(26) Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *18*, 1.

(27) Lemire, A.; Mar, A.; Maharaj, U.; Dong, D. C.; Cheung, S. T.; Winnik, M. J. *Photochemistry* **1980**, *14*, 265. Chilton, J.; Giering, L.; Steel, C. *J. Am. Chem. Soc.* **1976**, *98*, 1865.

(28) Scaiano, J. C.; Abuin, E. B.; Steward, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.

(29) Allen, N. S.; Catalina, F.; Green, P. N.; Green, W. A. *Eur. Polym. J.* **1986**, *22*, 871.

(30) Lougnot, D. J.; Floret-David, D.; Jacques, P.; Fouassier, J. P. *J. Chim. Phys.* **1985**, *82*, 505.