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# Keto-sulfoxide derivatives as photoinitiators of polymerization

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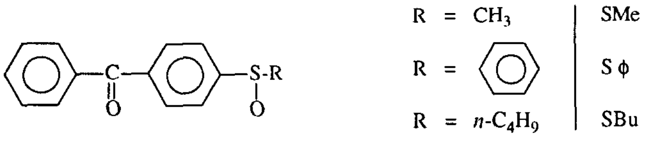
The photolysis of three aryl–alkyl sulfoxide photoinitiators is studied by time-resolved laser spectroscopy. The general diagram of the excited-state process is rather unusual: it shows a dual path of photolysis. Thus, whereas the singlet state cleaves at the S-alkyl bond, the triplet generates aryl and alkyl sulfinyl radicals. The conclusions arrived at are corroborated by product analysis by the coupled gas chromatography–mass spectroscopy technique. The photoinitiated polymerization activity has been checked and compared with that of other well known photoinitiators.

**(Keywords: photoinitiators; keto-sulfoxides; time-resolved spectroscopy)**

## INTRODUCTION

In the past few years, there has been a fresh outbreak of interest in ketones containing C–S bonds. Primary photophysical and photochemical processes have been investigated, including electron transfer in thioxanthones[1-3], C–S bond cleavage in benzoyl diphenylsulfide[4] and *S*-phenyl thiobenzoates[5], $\alpha$ cleavage in $\alpha$-hydroxymethylbenzoin sulfonic esters[2,6], $\beta$ cleavage in sulfonyl[7-9] and oxysulfonyl ketones[10,11], $\beta$ cleavage and competing photoreactions in keto-sulfides[12] and sulfoxides[13]. The present paper is devoted to an investigation of the excited-state processes in (benzoyl-4) phenyl alkyl (or phenyl) sulfoxides:



## EXPERIMENTAL

### *Materials*

The keto-sulfoxides used in this work were prepared according to the procedure described in ref. 14. This reaction involves the oxidation of a thio compound, generally a sulfide. Thus, SMe was obtained through room-temperature oxidation of 4-benzoylthioanisole by 30% $H_2O_2$ in glacial acetic acid. The crude product is recovered by filtration of the precipitate obtained when the reactive mixture is poured onto ice–water. SBu and S$\phi$ were prepared in analogous manner by oxidizing 4-benzoyl butylphenylsulfide and 4-benzoyl diphenylsulfide respectively.

### *Apparatus*

The set-up used for time-resolved laser spectroscopy experiments has been described elsewhere[15]. The light source is a Nd/YAG laser delivering a short pulse (3 ns, $\lambda = 1060$, 530 or 355 nm, 20 mJ in the blue). Both spectral and kinetic information on the transients can be recorded with an overall time resolution of 5 ns.

### *Photoinitiated polymerization experiments in homogeneous solution*

The evaluation of the efficiency of the different systems is done by determining the rate of polymerization $R_p$ of a given monomer in solution under well defined experimental conditions. The irradiation device consists of a high-pressure mercury lamp (HPK 125), an anticaloric filter, a passband filter (centred around 366 nm, $\Delta\lambda = 20$ nm) and a thermostated rectangular cell containing the sample (which is degassed by $N_2$ bubbling). The incident light intensity is about $0.5 \times 10^{16}$ phot cm$^{-2}$s$^{-1}$ ($\lambda = 366$ nm) at the sample and the concentration of the initiator is chosen so as to obtain a fixed value of the optical density at 366 nm (typically 0.1 in order to avoid absorption in homogeneities). Percentage conversions are determined gravimetrically. Quantum

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yields of polymerization can be estimated according to:

$$\Phi_m = R_p/I_{abs}$$

where $R_p$ = rate of polymerization, $\Phi_m$ = number of monomer units per photon absorbed and $I_{abs}$ = initial absorbed energy.

## RESULTS

### *U.v. absorption: ground-state spectroscopy*

Typical absorption spectra and extinction coefficients of SMe, SΦ and SBu in acetonitrile are reported in *Figure 1*: they exhibit the usual shape of absorption of benzophenone. The sulfoxide group does not seem to modify strongly the energy levels of the carbonyl group: the lowest-energy transition remains of n–$\pi^*$ character and the corresponding shoulder in the region of 310–340 nm is less pronounced than in benzophenone because of the red shift of the $\pi\pi^*$ absorptions. However, the $\pi\pi^*$ transition of SΦ (which carries the phenyl substituent) exhibits a higher degree of charge transfer (CT) than the alkyl-substituted compounds of the series (SMe and SBu). This conclusion is in line with the structureless shape of the absorption band of this compound in the region of 260 nm when dissolved in a non-polar solvent. Moreover, this CT character becomes more pronounced with SMe and SBu when going to more polar solvents. SMe is slightly soluble in water. However, its stability in neutral water and the shelving time do not exceed a few hours.

### *Steady-state photolysis: a g.c.-m.s. investigation*

Typical chromatograms of irradiated solutions of sulfoxides (Ss) in acetonitrile and toluene (HPK 125 W, 366 nm filtered light, exposure time = 30 min) have been recorded. *Schemes 1* and *2*, which summarize the main processes, account for the identified products formed either directly through cleavage and recombination, or through recombination after hydrogen abstraction. In toluene solution, **3** is generated after H abstraction on toluene. Formation of compound **1** could proceed, as suggested in ref. 16, by disproportionation of sulfinyl radicals to sulfonyl and thiyl radicals and recombination[16]. Moreover, sulfonyl radicals can also release $SO_2$ as reported in the photochemistry of sulfonyl ketones[17]. Addition of methylnaphthalene MeN ($5 \times 10^{-2}$ M) to an acetonitrile solution of SMe suppresses completely the formation of **1** and enhances the yield of benzophenone **2**. This is easily accounted for by a cleavage process in the triplet state (*Scheme 3*) and a cleavage process in the singlet state leading to benzophenone (after disproportionation, $SO_2$ release and H abstraction).

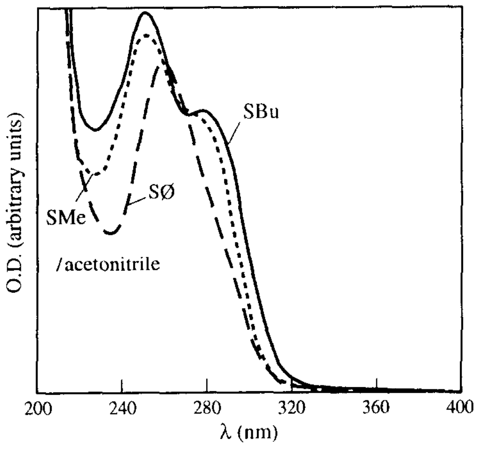
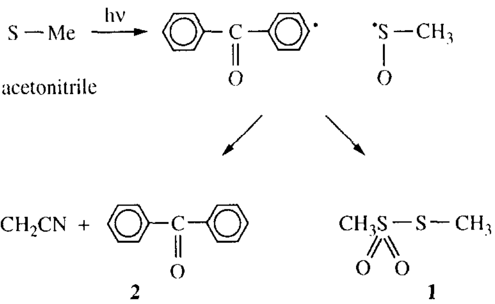


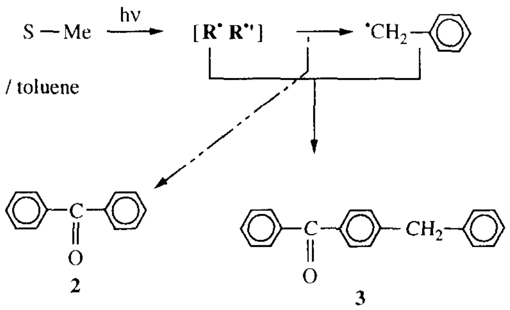
**Figure 1** Typical u.v. spectra of Ss (molar extinction coefficient of SMe in acetonitrile $14000\,M^{-1}\,cm^{-1}$ at $\lambda_{max} = 250$ nm and $88\,M^{-1}\,cm^{-1}$ at $\lambda_{max} = 366$ nm)

### *Laser study of the sulfoxy compounds*

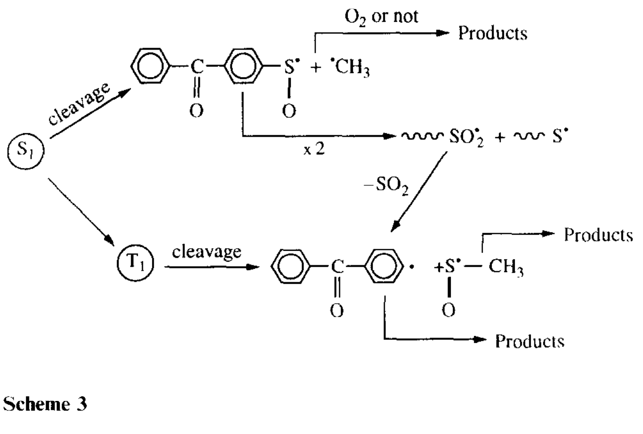
A rapid survey of compounds SMe, SΦ and SBu by time-resolved laser spectroscopy with excitation at 355 nm reveals the presence of three transient absorptions, one in the 10 ns range, the others in the microsecond range. These transient signals have in common a very weak absorbance, which makes it rather difficult to undertake any accurate kinetic studies. The transients detected in compound SΦ are weaker still, so that it does not lend itself to investigations by laser



**Scheme 1**



**Scheme 2**



**Scheme 3**

spectroscopy. SMe and SBu exhibit basically the same general behaviour.

*The triplet state.* The laser excitation of compound SMe induces a very short-lived transient, the absorption spectrum of which is reported in *Figure 2*. Its absorption is not restricted to the visible; however, no transient spectrum can be recorded in the near-u.v. owing to a convolution with other long-lived species. Because of its very short lifetime, this species is insensitive to the presence of dissolved oxygen in the solvent but it is clearly quenched by methylnaphthalene. Since the lifetime of this species is of the order of that of the laser pulse, no classical Stern–Volmer treatment of this quenching process is possible. However, in this case the experimental intensity of the transient absorption ($I$) can be considered to be proportional to the surface ($S$) of the pulse corresponding to the convolution product of the real signal (due to the transient absorption) by the response function of the detection system, that is to the actual lifetime ($\tau$) of the transient species. Therefore, the quantity $\tau_0/\tau$, which is involved in the classical Stern–Volmer treatment, can be replaced by $I_0/I$. This procedure and the results deduced agree well with the quenching of a triplet state. If one assumes the quenching constant to be $5 \times 10^9\,M^{-1}\,s^{-1}$, a triplet lifetime $\tau_0$ of 7.5 ns is arrived at. Interestingly, the general shape of the absorption spectrum of this triplet state and that of unsubstituted benzophenone are very much alike, which denotes a rather weak influence of the SOMe substituent on the electron distribution in this excited state.

*Radicals formed.* As mentioned before, laser excitation of SMe induces, besides the triplet absorption, a weak transient that absorbs from the u.v. up to 600 nm. Its spectrum exhibits a conspicuous band with a sharp maximum at 355 nm and a broad tail that spans the whole visible range (*Figure 3*). This transient absorption (A) decays according to second-order kinetics. In the u.v. range, another transient absorption in the 10 $\mu$s range is also visible with an optical density equal to or weaker than that of the other transient species. This second species B shows first-order decay ($k < 10^4\,s^{-1}$) and arises from the relaxation of A. Its absorption spectrum is centred in the region of 390 nm (*Figure 3*). In agreement with the g.c.-m.s. data, these two transients are attributed to radicals arising from the cleavage of either the singlet or the triplet state of SMe and/or to secondary products of the photolysis (*Scheme 4*).

*Influence of amines on the primary processes.* In the presence of an amine, the transient absorption due to species B increases significantly. This observation is supported by the fact that the absorption spectrum of the transient species created by this photochemical process is identical to that of B (*Figure 3*) and also exhibits second-order decay. Since the triplet state T and the radical B absorb in the same wavelength range, it is impossible to conduct any experiment in which the extent of the quenching of T by an amine would be expressed in terms of the quencher concentration. In order to circumvent this difficulty, the quenching of T by methylnaphthalene (MeN) has been conducted under the same experimental conditions, successively in the absence and in the presence of TEA (triethylamine), and the optical density

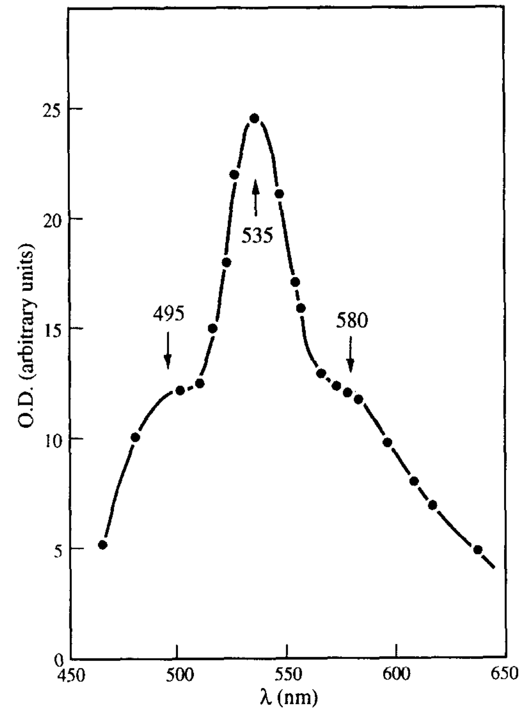


**Figure 2** Triplet–triplet spectrum of SMe in acetonitrile

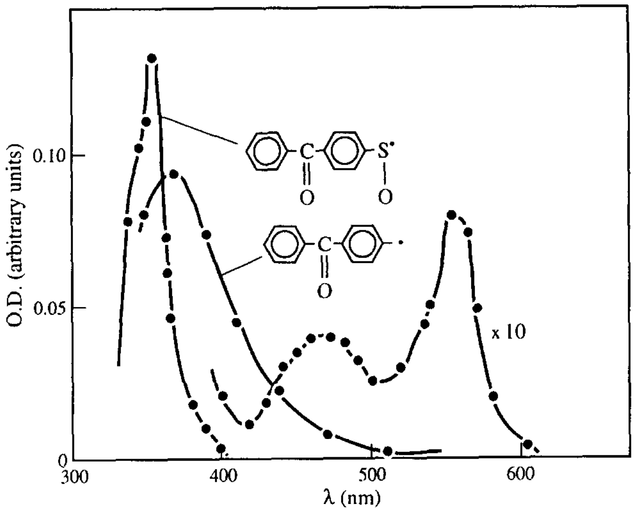
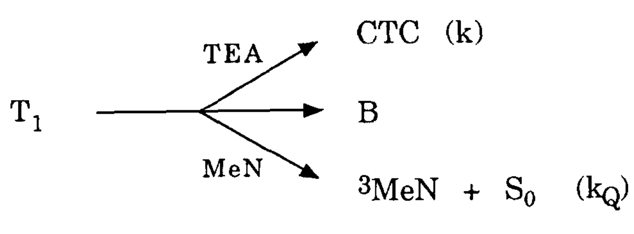


**Figure 3** Absorption spectra formed under photolysis of SMe. The spectrum ×10 is also due to species A

$$\text{SMe} \xrightarrow{h\nu} \text{A} \longrightarrow \text{B} \qquad \text{with: } \text{B} = \text{BP}^\bullet, \; \text{A} = \text{BPS}^\bullet\text{O}$$

**Scheme 4**



**Scheme 5**

due to the absorption of $^3$MeN populated by energy transfer has been measured (*Scheme 5*).

The kinetic treatment of this problem leads to the following expression:

$$\frac{1}{OD_{\mathrm{Men}}} \propto 1 + \frac{1}{k_Q\tau_0[\mathrm{MeN}]}$$

Thus a plot of $1/OD_{\mathrm{MeN}}$ as a function of 1/[MeN] leads to the product $k_Q\tau_0$ of the quenching constant (of T by MeN) by the lifetime of T in the absence of MeN. This product $k_Q\tau_0$ is also known as $K^{\circ}_{SV}$. When the experiment is conducted in the presence of a certain amount of TEA, the only change is the replacement of $1/\tau_0$ by $1/\tau$ with:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k[\mathrm{TEA}]$$

Doing so, $K_{SV}$ and $K^{\circ}_{SV}$ lead to $k_Q$, which cannot be measured directly:

$$K^{\mathrm{o}}_{SV} = k_Q\tau_0$$

$$K_{SV} = k_Q\tau = \frac{k_Q}{1/\tau_0 + k[\mathrm{TEA}]}$$

and

$$\frac{1}{K_{SV}} = \frac{1}{K^{\mathrm{o}}_{SV}} + \frac{k[\mathrm{TEA}]}{k_Q}$$

The experimental results obtained via this procedure are reported in *Figure 4*. They lead finally to $k = 1.6 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$, a result that is in line with the values generally reported for the quenching of benzophenone derivatives by amines with low ionization potentials. Should the quenching by amine affect exclusively the triplet state, the addition of MeN would be detrimental to the formation of the species B through this channel. In reality, this process seems to be entirely insensitive to the presence of MeN and supports the view of a cleavage of SMe in its singlet state as proposed in the g.c.-m.s. experiments. Moreover, chemical reaction of the amine with this state takes place (enhancement of the B formation) besides the classical reaction with the triplet state (*Scheme 6*).

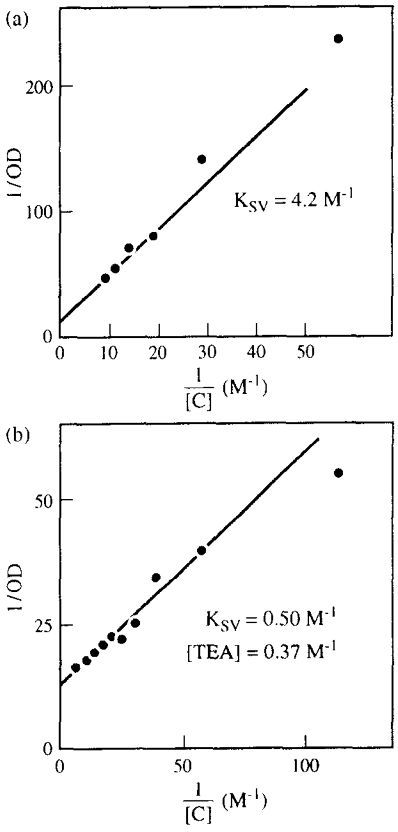
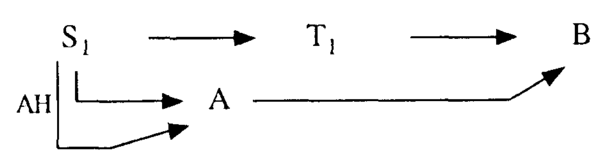


**Figure 4** Stern–Volmer plot in presence and absence of TEA (see text)



**Scheme 6**

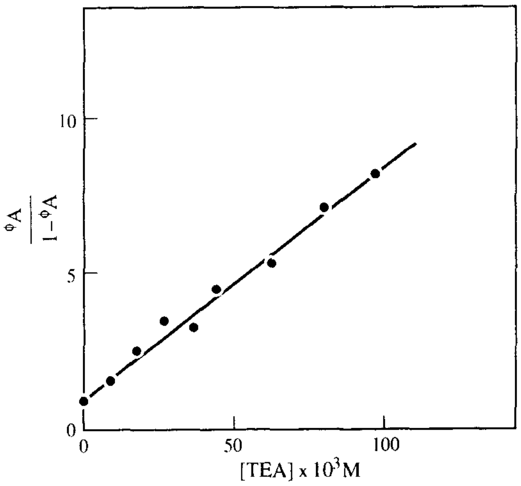


**Figure 5** Plot corresponding to equation (1) (see text)

The kinetic treatment of this process is the following:

$$\Phi_A = \frac{k_A + k_e[\mathrm{TEA}]}{\sum k + k_e[\mathrm{TEA}]}$$

with $\Phi_A$ = quantum yield corresponding to the formation of A; $k_A$ = rate constant of the quenching of SMe in its singlet state by TEA to generate A; and $\Sigma k$ = inverse of the singlet lifetime in the absence of amine ($\Sigma_k = k_{ST} + k_A$). Thus:

$$\frac{\Phi_A}{1 - \Phi_A} = \frac{k_A}{k_{ST}} + \frac{k_e[\mathrm{TEA}]}{k_{ST}} \qquad (1)$$

This equation fits the experimental points quite well (*Figure 5*). The plot of $\Phi_A/(1 - \Phi_A)$ leads to the ratio $k_A/k_{ST}$ (intercept) and $k_e/k_{ST}$ (slope), from which the ratio $k_e/k_A$ can be deduced. If a rate constant of $6 \times 10^9\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ is assumed for $k_e$, the experimental results lead to $k_A = 8.2 \times 10^7\ \mathrm{s}^{-1}$. In the absence of TEA, the intercept $k_A/k_{ST}$ leads to $k_{ST} = 2.5 \times 10^8\ \mathrm{s}^{-1}$ and to a singlet-state lifetime of 3 ns. Thus, the postulated mechanism is acceptable and supports the view of both $S_1$ and $T_1$ pathways for the radical cleavage of sulfoxides.

*Rate of polymerization.* The rate of polymerization $R_p$ is calculated from the linear part of the percentage

**Table 1** Rates of polymerization of MMA with Ss ([MMA] = 7 M; solvent, toluene; $\lambda = 366$ nm; $I_0 = 5 \times 10^{15}$ phot cm$^{-2}$ s$^{-1}$ = $8 \times 10^{-6}$ E l$^{-1}$ s$^{-1}$; $OD_{366} = 0.1$)

| | Relative $R_p$ | |
|---|---|---|
| | Without amine | [MDEA] = 0.05 m |
| SΦ | 6 | 29 |
| SMe | 28 | 33 |
| SBu | 33 | 42 |
| Benzophenone | – | 32 |
| DMPA[a] | 82 | – |
| TMPK[b] | 66 | – |
| BMS[c] | 16 | 32[d] |

[a] 2,2-Dimethoxy-2-phenyl acetophenone
[b] Methylthiophenyl morpholinopropanone
[c] *p*-Thiophenyl benzophenone
[d] [MDEA] = 0.1 M

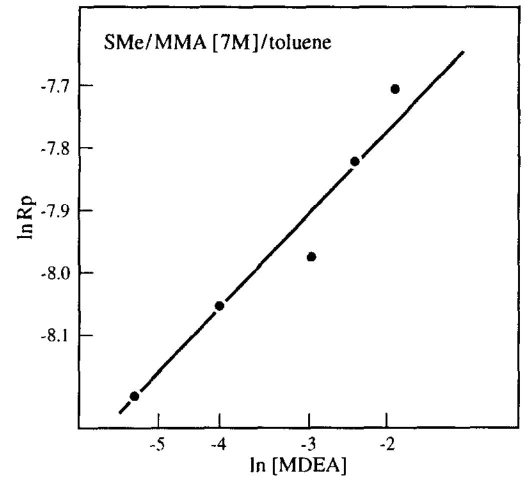
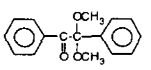
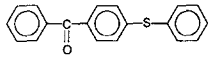


**Figure 6** Log–log plot of $R_p$ vs. [MMA]

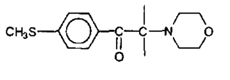
conversion vs. time curve. The results of the polymerization of 7 M MMA in toluene in the presence of Ss and other different photoinitiators (BMS, TMPK, DMPA) are reported in *Table 1*.



DMPA



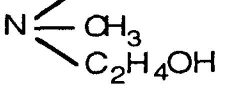
BMS



TMKP

In agreement with the singlet and triplet cleavage mechanism, addition of 0.5 M MeN almost suppresses the initiation reaction ($R_p$ drops from $28 \times 10^{-5}$ to $2 \times 10^{-5}$ M s$^{-1}$); moreover, the singlet mechanism is weakly efficient.

In the presence of amine (*N*-methyldiethanolamine, MDEA) the rates increase in the order SMe < SBu < SΦ.



MDEA

**Table 2** Influence of the basicity of the amine on $R_p$

| SBu | Relative $R_p$ | p*K* |
|---|---|---|
| MDEA | 42 | 8.5 |
| TeOH[a] | 36 | 7.8 |
| TEA | 30 | 10.7 |

[a] Triethanolamine

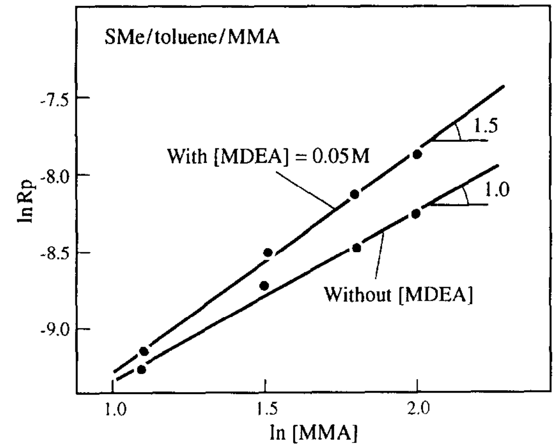
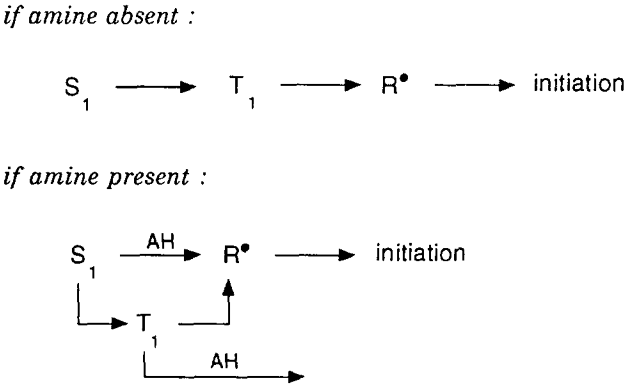


**Figure 7** Log–log plot of $R_p$ vs. [MDEA]



**Scheme 7**

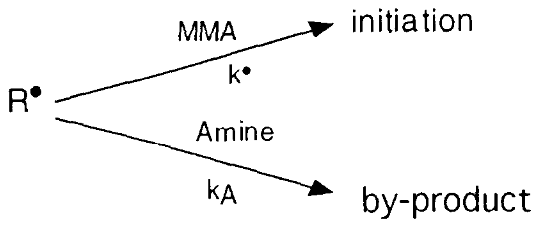
The evolution of $R_p$ was followed as a function of [MDEA] (*Figure 6*) and [MMA] (*Figure 7*). The following dependences are observed from *Figure 6*:

$$R_p = K[\mathrm{MDEA}]^{\alpha}$$

with $\alpha \approx 0.1$(SΦ), 0.12 (SMe) and 0.025 (SBu).

These observations suggest that the photoreduction process involving the amine is not directly responsible for the initiation. In this kind of experiment conducted in homogeneous solution, the amine-derived radical resulting from the reduction would not be the most active species.

In order to clarify the role played by the amine partner in the initiation mechanism, several polymerization experiments were conducted with a series of amines with very different basicities (*Table 2*). The results show only a weak sensitivity of the rate of polymerization on this parameter. The conclusion is also in line with the fact that the fate of the radicals arising either from the direct



**Scheme 8**

cleavage of the excited states or from their interaction with an amine is almost unaffected by the basicity of this amine.

These observations lead to the conclusion that the amines in this system play essentially a limited role in the initiation mechanism. However, the sensitivity of the mixture to the amine concentration suggests that the species could participate either directly or indirectly in the termination process or in the initiation through the singlet state.

The study of the dependence of $R_p$ as a function of [MMA]:

$$R_p = K[\text{MMA}]^{\beta}$$

leads to $\beta \approx 1$ and 1.5 in the absence and presence of amine, respectively (*Figure 7*).

In the absence of amine, several radicals are generated by different processes. Their stationary concentration $[R^\bullet]$ is directly related to their relative quantum yield of formation (from their precursor):

$$\Phi_{R^\bullet} = \frac{k^\bullet}{k^\bullet + \sum k}$$

where $k^\bullet$ stands for the rate constant of the cleavage process leading to $R^\bullet$ and $\Sigma k$ for the sum of the rate constants of the other processes contributing to the deactivation of the precursor of $R^\bullet$.

The most probable processes for the initiation of the photoinitiated polymerization have been discussed. Several types of radicals can be responsible for the initiation. A simplified view may be written as in *Scheme 7*.

The rate of a radical-photoinitiated polymerization is given by:

$$R_p^2 = \frac{k_p^2}{k_t}[\text{M}]^2(2.3\Phi_i \times OD \times I_0)$$

where $k_p$ and $k_t$ are rate constants of the propagation and termination processes. This expression shows a linear relationship between $R_p$ and [M] (in agreement with what was experimentally observed) if $R^\bullet$ reacts exclusively with MMA.

In the presence of amine, the analytical problem becomes more complex: the linear dependence of $R_p^2$ as a function of $[\text{M}]^3$ can only be accounted for by introducing an efficiency factor of the active initiating radical ($\rho$) depending linearly on the monomer concentration. Such an approach would be in line with an initiating process in which the active radical could be efficiently deactivated in the presence of amine (*Scheme 8*). Thus:

$$\rho = \frac{k^\bullet[\text{MMA}]}{k^\bullet[\text{MMA}] + k_A[\text{Amine}]}$$

Should the quenching by amine be much more efficient than the interaction with MMA, this factor would depend almost linearly on the concentration of the monomer. With such an approach the expression of $R_p$ becomes:

$$R_p^2 \propto \frac{k_p^2}{k_t}(2.3I_0 \times OD)\frac{k^\bullet}{k_A[\text{Amine}]}[\text{MMA}]^3 f([\text{Amine}])$$

where $f$ [Amine] stands for the other photoprocesses involving the amine, e.g. in the singlet or the triplet state, which is again in agreement with our experimental observations (*Figure 7*).

## CONCLUSION

This study shows the interest of such investigations for the knowledge of excited-state processes and the understanding of photochemical reactivity. Other recent papers show how these studies[18] are useful for the design of efficient photoinitiating systems in u.v. curing and laser imaging[19] and in holographic recording[20].

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