

## Photoreduction of benzophenone by 2,4,6-trimethyl-1,3,5-trithiane in solution. Laser flash photolysis study

Bronislaw Marciniak<sup>a,\*</sup>, Ewa Andrzejewska<sup>b</sup>, Gordon L. Hug<sup>c,\*</sup>

<sup>a</sup> Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznan, Poland

<sup>b</sup> Institute of Chemical Technology and Engineering, Poznan University of Technology, 60-965 Poznan, Poland

<sup>c</sup> Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA

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### Abstract

The role of 2,4,6-trimethyl-1,3,5-trithiane (TMT) in accelerating the initiation of polymerization induced by benzophenone (BP) was pursued by studying the primary photochemical reactions occurring between BP and TMT. Kinetic aspects of the quenching of the BP triplet by TMT were followed by laser flash photolysis. Triplet quenching rate constants and quantum yields for electron-transfer products were measured. In addition the mechanism of the photoreduction of BP by organic sulfides in acetonitrile and mixed acetonitrile/water solutions is discussed. Photoinitiated polymerizations with a model monomer were carried out with some of the sulfide co-initiators investigated, and the polymerization behavior was correlated with the kinetic results. © 1998 Elsevier Science S.A.

**Keywords:** Benzophenone; 2,4,6-trimethyl-1,3,5-trithiane; Laser flash study

### 1. Introduction

The photoinduced radical polymerization of unsaturated compounds, most often (meth)acrylic monomers, is usually performed in the presence of photoinitiators of the 'cleavage' type (e.g., benzoin derivatives) or H-abstraction type (e.g., aromatic ketones). In the second class of reactions, e.g., with benzophenone (BP), initiation occurs mainly through hydrogen abstraction by <sup>3</sup>BP from the monomer and/or a synergist molecule, such as an ether, alcohol, or amine [1–4]. The initiating radical is derived from the hydrogen-donating molecule, whereas the ketyl radical that is formed participates in the termination process.

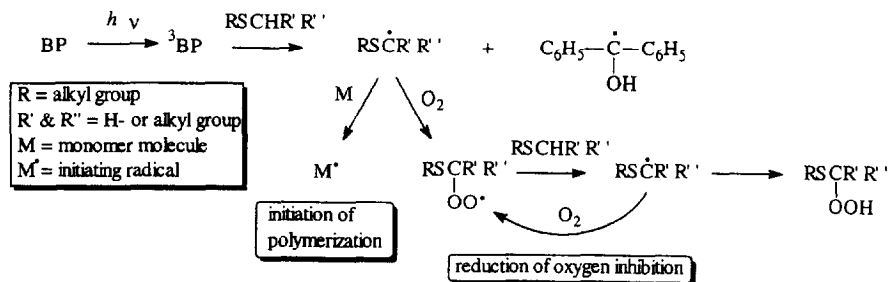
The interaction of <sup>3</sup>BP with aliphatic sulfides in organic solvents leads to efficient quenching and a much less efficient H-abstraction; whereas with aliphatic amines, the efficiencies of the two processes are comparable [5]. Taking into account that the quenching rate constant of <sup>3</sup>BP by ethers is  $\sim 10^6 \text{ M}^{-1} \text{ s}^{-1}$  [3,6], by aliphatic amines  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [6], and by alkyl sulfides  $\sim 10^7 - 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [7–16], one can expect that the activity of sulfides as hydrogen donors during initiation should be intermediate between the activities of ethers and amines.

A number of works has been devoted to the influence of aliphatic sulfides on the polymerization of multi(meth)acrylates both in the presence of photofragmenting initiators [17,18] as well as BP [18,19]. The works showed a deep and rather complicated effect of sulfides on three steps of the polymerization process: initiation, propagation, and termination. The effect of the sulfide group becomes more complex when the thioether linkage is built into the monomer molecule [20–24]. Generally, the effect discussed is a result of retarding and accelerating processes occurring simultaneously, and their relationship depends on the reaction conditions and the sulfide structure [17–19].

When considering the initiation process of the polymerization induced by BP, the use of aliphatic sulfides as synergists assists the reaction by the acceleration of the formation of initiating radicals and, in air, by reduction of oxygen inhibition [18–20]. These reactions are depicted in Scheme 1.

The beneficial effect of the acceleration of initiation is so strong that it exceeds the effect of some retarding processes that occur in later reaction stages. The activity of a sulfide depends strongly on its chemical structure; it was shown that this activity is associated with the hydrogen-donating ability of the sulfide [17,18]. Among the sulfides investigated (linear sulfides, sulfides containing other functionalities, cyclic dithioacetals) an exceptionally strong effect was shown by 2,4,6-trimethyl-1,3,5-trithiane [17,18].

\* Corresponding author.



Scheme 1.

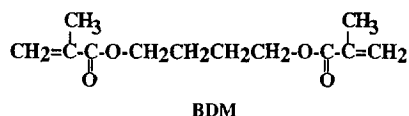
The mechanism of the photoreduction of the BP triplet by dialkyl sulfides proposed in Refs. [7,8] assumed that the initial step was electron transfer to form a charge-transfer (CT) complex between the BP triplet and the sulfide. It was further proposed that this CT complex would decay either by the formation of ketyl and  $\alpha$ -(alkylthio)alkyl radicals or by back electron transfer to regenerate the reactants. Recently, a modified mechanism has been proposed [10,16,25] on the basis of nanosecond laser flash photolysis investigations [10,11,16,25] of the interaction of triplet states of BP and substituted benzophenones with dialkyl sulfides and sulfur-containing amino acids. The initial step in this mechanism is an electron transfer from the sulfur atom of the sulfide to the benzophenone triplet to form a radical ion pair (CT complex). The complex can break up through three competing pathways: (1) proton transfer within the complex  $k_{\text{H}}$  and diffusion apart of the radicals, (2) diffusion apart  $k_{\text{sep}}$  of the radical ions, and (3) back electron transfer  $k_{\text{bt}}$ . The first reaction leads to the formation of ketyl radicals and  $\alpha$ -(alkylthio)alkyl radicals. The second reaction leads to the formation of separated ketyl radical anions and sulfur-centered radical cations that may form  $(\text{S}\cdot\text{S})^+$  dimers with an unoxidized sulfide molecule. The third reaction leads back to the starting materials, i.e. the benzophenones in their ground state and the alkyl sulfides.

Triplet quenching of benzophenones by dimethyl sulfide in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution showed rather low quantum yields of ketyl-radical formation, in addition to very low quantum yields in pure acetonitrile [16]. These results suggest that back electron transfer within the charge-transfer complex to regenerate the reactants is the dominant quenching process [16]. Similar results were obtained for diisopropyl sulfide [8]. Polymerization studies showed rather moderate activity of simple dialkyl sulfides as synergists [17,18].

The very high activity of TMT in accelerating the initiation of polymerization induced by BP was the reason for our interest in the primary photochemical reactions occurring between BP and TMT. This high activity of TMT is confirmed in this work by the differential scanning calorimetry (DSC) method. This work presents some kinetic aspects of the quenching of the BP triplet by TMT. In addition the mechanism of the photoreduction of BP by organic sulfides in acetonitrile solution is discussed.

## 2. Experimental details

Benzophenone and 4-carboxybenzophenone (CB) were obtained from Aldrich as the best available grades and were used without further purification.  $\beta$ -2,4,6 trimethyl-1,3,5-trithiane (TMT, *cis-cis* form) was synthesized from sodium thiosulfate and acetaldehyde according to Ref. [26] and was purified by repeated crystallization. Butane-1,4-diol dimethacrylate (BDM, Fluka) was purified by column chromatography over  $\text{Al}_2\text{O}_3$ . 2,2'-Thiobisethanol (TBE) was purchased from Merck and di-*n*-propyl sulfide ( $\text{Pr}_2\text{S}$ ) from Fluka.



Acetonitrile (Fisher, HPLC grade) was used as received, and water was purified by a Millipore Milli-Q system.

UV-visible absorption spectra were recorded using a Cary 219 spectrophotometer and a Hewlett Packard diode array spectrophotometer. The nanosecond laser flash photolysis apparatus ( $\lambda_{\text{ex}} = 337.1 \text{ nm}$ ) has been described elsewhere [27].

Experiments were performed in rectangular quartz cells at room temperature. The concentration of benzophenone was  $2 \times 10^{-3} \text{ M}$  in all experiments. The concentration of TMT was in the range  $10^{-5}$  to  $10^{-3} \text{ M}$  in the quenching experiments. However, the concentration of the quencher was 0.01 M for the quantum yield determinations and for the experiments that involved recording transient absorption spectra in the time range following complete quenching (>98%) of the benzophenone triplet. All solutions (in acetonitrile or a mixed solvent: acetonitrile/water 1:1 v/v) were deoxygenated by bubbling high-purity argon through them.

The polymerization kinetics were monitored under isothermal conditions at  $40 \pm 0.01^\circ\text{C}$  in an argon atmosphere by a differential scanning calorimeter (DSC 605 M, Unipan-Termal, Warsaw), equipped with a lid specially designed for photochemical measurements. The procedure was the same as given in Ref. [21]. Polymerizations were initiated by 0.06 M BP or its mixture with  $\text{Pr}_2\text{S}$ , TBE, or TMT (0.06 M). The incident light (366 nm from a Hg medium pressure lamp) intensity at the sample pan position was  $1.8 \text{ mW cm}^{-2}$ .

For calculations the polymerization heat of 56 kJ/mol per one double bond was used.

### 3. Results and discussion

Solutions containing benzophenone (2–4 mM) and  $\beta$ -2,4,6-trimethyl-1,3,5-trithiane (TMT, 0.01 M) in acetonitrile and acetonitrile/water (1:1 v/v) were first examined spectroscopically for any evidence of ground-state association. The absorption spectra of these mixtures were shown to be equal to those expected by adding the spectra from separate solutions of BP and TMT. No evidence for ground-state association was found under the experimental conditions used.

#### 3.1. Quenching rate constants

Quenching of the benzophenone triplet state by TMT in acetonitrile and acetonitrile/water (1:1 v/v) solutions was studied by means of nanosecond laser flash photolysis. The quenching rate constants,  $k_q$ , were measured by monitoring of the decays of the triplet–triplet absorption of BP at 520 nm. The concentration of BP was held fixed (2 mM) while the concentrations of TMT varied over a range that reduced the lifetime of the triplet. The  $k_q$  values were determined from a linear least-squares fit of  $k_{\text{obs}}$  vs. the quencher concentration plots employing the formula

$$k_{\text{obs}} = (\tau_T)^{-1} + k_q[Q] \quad (1)$$

where  $\tau_T$  is the lifetime of the BP triplet state in the absence of quencher,  $Q$ . The resulting rate constants together with the  $k_q$  values for quenching of benzophenone triplet by dimethyl sulfide (DMS) [16] and other simple alkyl sulfides [7–9] are listed in Table 1.

A comparison of the kinetic data in Table 1 indicates that the rate constants for quenching of the BP triplet by TMT are in the range  $10^8$ – $10^9$   $\text{M}^{-1} \text{s}^{-1}$  and are similar to those obtained for diisopropyl sulfide. As for other organic sulfides,

$k_q$  values for TMT are higher in acetonitrile/water mixture than in acetonitrile solutions. Direct evidence for the participation of an electron-transfer process in the quenching of the benzophenone triplet by TMT was found by the observation of the ketyl radical anion  $\text{BP}^{\cdot-}$  in the transient absorption spectra at 620 nm (vide infra, Fig. 2) in acetonitrile/water solution. Taken together with the large values of  $k_q$  for quenching by TMT, which is in the range of other simple organic sulfides such as DMS, previously established as the electron-transfer quenching [16], this indicates that electron transfer from the sulfur atom to the BP triplet is the mechanism for the quenching of the BP triplet by TMT. The driving force,  $\Delta G_{\text{et}}$  for the quenching by TMT is expected to be similar to that for simple organic sulfides. This would put the quenching rate constant for TMT close to the plateau of the Rehm–Weller plots [11,28] as it has been suggested for DMS [16]. For DMS  $\Delta G_{\text{et}} = -12$  kJ/mol computed from  $E_p = 1.41$  V vs.  $\text{Ag–Ag}^+$  [29] with similar assumptions made in Ref. [11].

#### 3.2. Transient absorption spectra of intermediates, and quantum yields of ketyl radical and ketyl radical anion

Flash excitation of the solution of BP (2 mM) and TMT (0.01 M) in acetonitrile or acetonitrile/water solutions resulted in the appearance of the absorption corresponding to various transients depending on the time delay and the solvent used. A high concentration of quencher was used to rapidly quench more than 98% of the BP triplet.

The time-resolved spectra were generated from the sets of individual kinetic traces collected at 10 nm intervals, choosing appropriate time delays and appropriate time windows. Then the spectra were resolved into component species by a linear regression technique using known spectra of the appropriate components. Further details of this method have been described elsewhere [11]. The spectra of the benzophenone triplet state, the ketyl radical ( $\text{BPH}^{\cdot}$ ) and the ketyl radical anion ( $\text{BP}^{\cdot-}$ ) in acetonitrile and acetonitrile/water solutions were measured from the appropriate solutions in this work.

Table 1

Rate constants for quenching of the BP triplet and quantum yields of photoproducts formation during photoreduction of BP by TMT and dialkyl sulfides in solution

Quencher	$k_q \times 10^{-9}$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$\Phi_{\text{BPH}^{\cdot}}$ <sup>a</sup>	$\Phi_{\text{BP}^{\cdot-}}$ <sup>a</sup>	$\Phi_{\text{total}}$ <sup>b</sup>
TMT in $\text{CH}_3\text{CN}$	$0.47 \pm 0.03$	0.62	<0.01 <sup>c</sup>	0.62
TMT in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v)	$1.5 \pm 0.3$	0.51	0.13	0.64
$(\text{CH}_3)_2\text{S}$ in $\text{CH}_3\text{CN}$	$2.5 \pm 0.1^d$	<0.01 <sup>d</sup>	<0.01 <sup>d</sup>	<0.01 <sup>d</sup>
$(\text{CH}_3)_2\text{S}$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1 v/v)	$4.6 \pm 0.1^d$	0.14 <sup>d</sup>	0.02 <sup>d</sup>	0.16 <sup>d</sup>
<i>(iso-C}_3\text{H}_7)_2\text{S} in <math>\text{CH}_3\text{CN}</math></i>	$0.59^e$	<0.05 <sup>c</sup>		
<i>(iso-C}_3\text{H}_7)_2\text{S} in <math>\text{CH}_3\text{CN}/\text{H}_2\text{O}</math> (1:1 v/v)</i>	3.1 <sup>c</sup>	<0.05 <sup>c</sup>		

<sup>a</sup>Estimated error  $\pm 10\%$ .

<sup>b</sup>Total quantum yield for reduction equal to the sum of the quantum yields of ketyl radical anion ( $\text{BP}^{\cdot-}$ ) and ketyl radical ( $\text{BPH}^{\cdot}$ ).

<sup>c</sup>Estimate is based on the concentration of the  $\text{BP}^{\cdot-}$  component in the resolved spectrum.

<sup>d</sup>Ref. [16].

<sup>e</sup>Ref. [8].

<sup>f</sup>With  $(n\text{-C}_4\text{H}_9)_2\text{S}$ ,  $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [7],  $2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [9] and with  $(t\text{-C}_4\text{H}_9)_2\text{S}$ ,  $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [7].

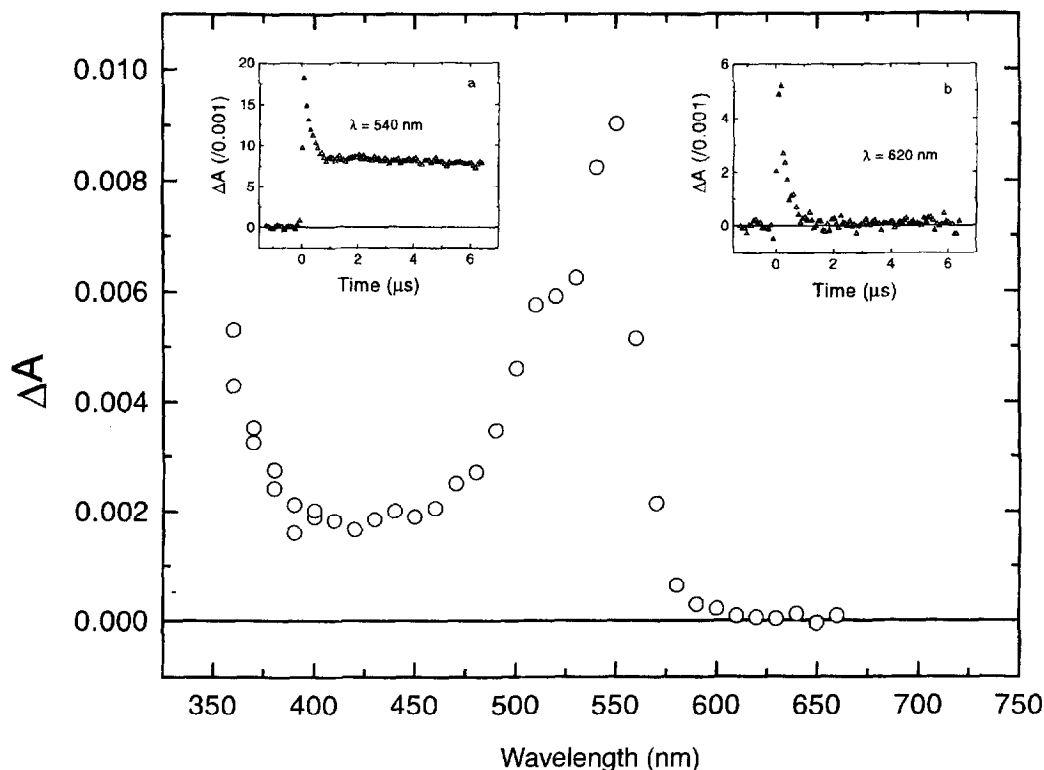


Fig. 1. Transient absorption spectrum following quenching of the BP triplet state by TMT (0.01 M) in acetonitrile taken 2  $\mu$ s after the flash. Insets: kinetic traces at 540 nm (a) and at 620 nm (b).

The BPH<sup>•</sup> spectrum in acetonitrile/water was taken by quenching the BP triplet state with 1 M 2-propanol, and the analogous experiment with the addition of 1 mM NaOH gave the BP<sup>•-</sup> after a time delay of 50 to 60  $\mu$ s after the flash. The molar absorption coefficients [16,30] were taken from the literature ( $\epsilon_{520} = 6500 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{545} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{625} = 6000 \text{ M}^{-1} \text{ cm}^{-1}$  for the BP triplet, BPH<sup>•</sup>, and BP<sup>•-</sup>, respectively).

For flash excitation of acetonitrile solutions of benzophenone in the presence of TMT (0.01 M), the transient spectra had spectral features reminiscent of the BP triplet and the ketyl radical depending on the time delay. A typical spectrum of this type obtained 2  $\mu$ s after the flash is presented in Fig. 1 which shows the characteristic band of the ketyl radical [30] at 545 nm with a shoulder around 520 nm (see Fig. 2 for reference spectrum of the ketyl radical). This spectrum, together with the kinetic traces measured at 540 nm and 620 nm (insets in Fig. 1), clearly indicates that the ketyl radical is the only transient observed after the decay of the triplet state. The absence of BP<sup>•-</sup> is indicated by the lack of long-lived absorption at 620 nm (inset b) which is its absorption maximum (see Fig. 2 for reference spectrum of the ketyl radical anion). The rapidly decaying transient at 620 nm in inset b is that of the triplet state. Its decay is also seen as the fast decay component at 540 nm in inset a of Fig. 1. The long-lived absorption at 540 nm is the ketyl radical whose lifetime is 10s of microseconds.

The quantum yields of the transients were determined for concentrations of TMT large enough that the BP triplet state

was almost totally quenched. To measure the quantum yield, the relative actinometry method [31] was used. The experiments were carried out in matched optically flat cells having identical absorbance at 337 nm due to benzophenone or 4-carboxybenzophenone (CB). An acetonitrile solution of BP (2 mM) with no quencher present or an aqueous solution of CB was used as an actinometer. The quantum yields were calculated according to

$$\Phi = \Delta A_p \epsilon_T / (\Delta A_T \epsilon_p) \quad (2)$$

where  $\Delta A_p$  is the product's absorption change extrapolated to the 'end of pulse' under the conditions of nearly complete quenching,  $\Delta A_T$  is the absorption change in the actinometer immediately after the flash due to the BP (at 520 nm) or the CB triplet (at 545 nm) under conditions of no quenching,  $\epsilon_p$  and  $\epsilon_T$  are the corresponding molar absorption coefficients of the product and the BP (or CB) triplet state, respectively. The values of molar absorption coefficients for the actinometers were taken from Refs. [30,32] as  $\epsilon_{520} = 6500 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{535} = 6250 \text{ M}^{-1} \text{ cm}^{-1}$  for the BP and the CB actinometers, respectively. In cases where overlapping of the absorption spectra of some transients occurred, the absorption changes at  $\lambda_{\text{max}}$  of a particular species were corrected to remove the contribution from the remaining transients.

Using this procedure, the quantum yield of ketyl radical formation for the photoreduction of benzophenone by TMT in acetonitrile was determined to be  $\Phi_{\text{BPH}^{\bullet}} = 0.62$ , and the quantum yield of ketyl radical anion formation ( $\Phi_{\text{BP}^{\bullet-}}$ ) was

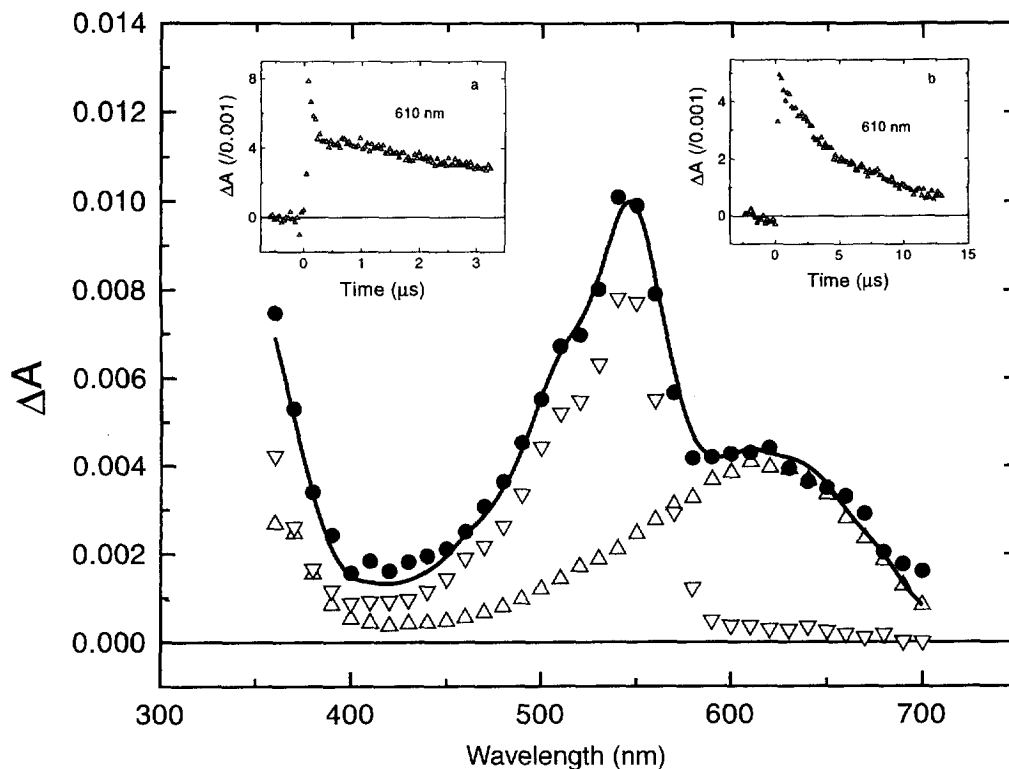


Fig. 2. The spectral resolution (solid line) of the transient absorption spectrum (solid circles) following quenching of the BP triplet state by TMT (0.01 M) in acetonitrile / water (1:1 v/v) solution. Spectrum was taken 1.5  $\mu$ s after the flash. Reference spectra (see text) for the spectral resolution were the BP\* spectrum (upward-pointing triangles) and the BPH\* spectrum (downward-pointing triangles). Insets: kinetic traces at 610 nm.

estimated to be lower than 0.01 (Table 1). The large yield of the ketyl radical formation for the quencher TMT differs from the results for other simple alkyl sulfides in acetonitrile such as dimethyl sulfide and diisopropyl sulfide where the BPH\* radicals were not formed (Table 1). Competition between the reactions of ketyl radical formation and back electron transfer can explain those differences (vide infra).

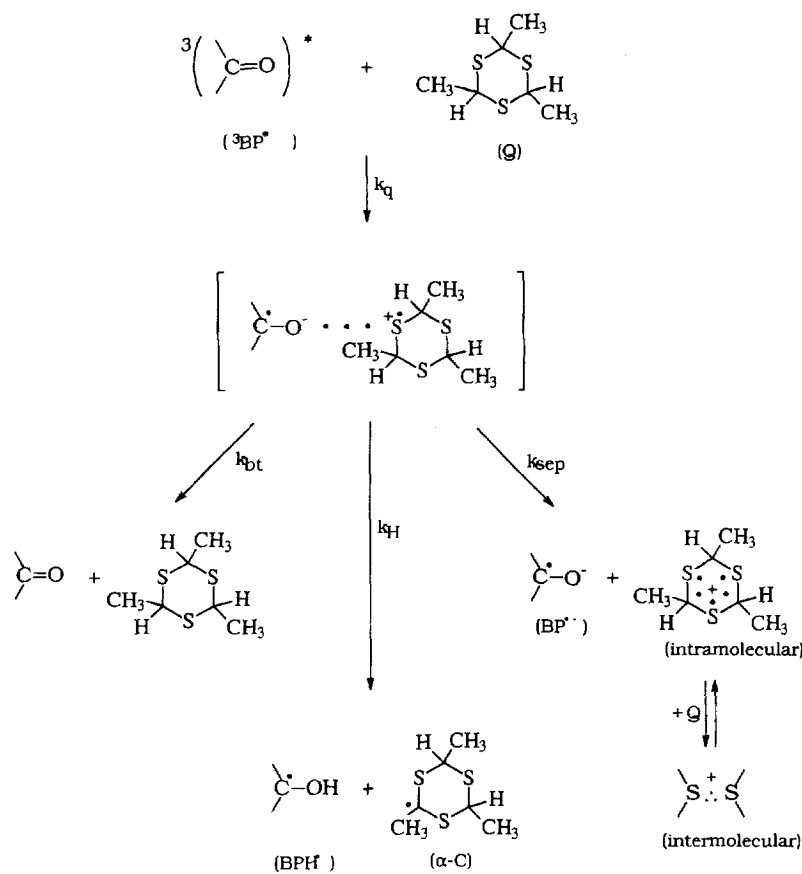
The transient absorption spectra obtained in the flash excitation of the BP acetonitrile/water (1:1 v/v) solution in the presence of TMT (0.01 M) are more complex than those for acetonitrile solution. After the initial decay of the BP triplet (see inset a in Fig. 2), the spectrum obtained on the microsecond time scale is reminiscent of the ketyl radical (with  $\lambda_{\max} = 545$  nm) and the ketyl radical anion with a long-wavelength band around 620 nm. The quantitative resolution of the spectrum, using the procedure mentioned above, is presented in Fig. 2. Inset b in Fig. 2 shows the decay of BP\*<sup>-</sup>. The species is relatively long-lived with an observed first-order rate constant of  $k_d = 1.7 \times 10^5$  s<sup>-1</sup>.

The presence of the BP\*<sup>-</sup> radical anions, products of the electron-transfer process, require the formation of sulfur-centered TMT radical cations. The latter can exist either as the intramolecular S:·S-bonded radical cation absorbing at about 610 nm [33] or, for high concentrations of TMT, as intermolecular S:·S-bonded dimers with a broad absorption band in the range of 500–1000 nm [34]. Low values for the molar absorption coefficients of both intra and intermolecular S:·S-bonded radical cations of TMT ( $\epsilon_{\max}$ S in the range of 700

M<sup>-1</sup> s<sup>-1</sup> [33,34]) and relatively short half-lifetime of those species (hundreds of ns [34]) can explain the apparent absence of TMT radical cations from the spectrum presented in Fig. 2.

The assignment of the 545 nm band to the BPH\* radical and that of the 620 nm band to the BP\*<sup>-</sup> radical anion allowed the calculation of appropriate quantum yields of the products' formation according to Eq. (2) or in combination with spectral resolutions. The results of such treatments are summarized in Table 1 together with appropriate  $\Phi$  values for dimethyl and diisopropyl sulfides taken from Refs. [16,8].

The detection of benzophenone ketyl radical anions in acetonitrile/water solutions can be taken as direct proof for the involvement of the electron-transfer mechanism for the quenching of the BP triplet state by TMT. The above mentioned experimental observations and an analogy to the photoreduction of BP by dimethyl sulfide [16] allowed us to propose a mechanism for the quenching of the benzophenone triplet state by TMT in solution (Scheme 2). This reaction scheme is similar to the ones previously described for thioethers [16] and other sulfur containing organic compounds [10,11,15,25]. The initial step is an electron transfer from the sulfur atom to the BP triplet state to form a radical-ion pair. The latter can disappear by any of the three following processes: (1) back electron transfer,  $k_{bt}$ , to regenerate the reactants (this process requires the intersystem crossing within the ion-radical pair), (2) intramolecular proton transfer within the radical-ion pair,  $k_{it}$ , leading to the formation of



ketyl radicals and  $\alpha$ -(alkylthio)alkyl radicals, and (3) diffusion apart of the radical-ion pair,  $k_{sep}$ , to form ketyl radical anions and sulfur-centered radical cations (intramolecularly S:S-bonded radical cations). For large concentrations of TMT one would expect formation of the intermolecularly bonded S:S dimer as in the case of other alkyl sulfides [16].

Scheme 2 allows us to explain all the observed characteristic features for quenching of the BP triplet state by TMT in acetonitrile and acetonitrile/water solutions summarized in Table 1. In the case of acetonitrile solutions, the  $k_{sep}$  channel can be neglected for TMT and dimethyl sulfide since  $BP^{\cdot-}$  radical anions were not formed. However, the quantum yield of BPH' formation in acetonitrile was large (0.62) for TMT in contrast to other organic sulfides where BPH' was not observed. This indicates that the proton-transfer reaction  $k_H$  can compete (62%) with the back electron transfer reaction  $k_{bt}$  (38%) for TMT in acetonitrile. Whereas, back electron transfer is the only reaction channel for dimethyl and diisopropyl sulfides in acetonitrile.

These results in acetonitrile solutions can be explained by a much larger ratio of  $k_H/k_{bt}$  for TMT than the other sulfides discussed. Reasons for this larger ratio are as follows: (1) A lower  $k_{bt}$  in the case of TMT, in comparison to DMS and diisopropyl sulfide, could result from the developing positive charge of its radical cation being stabilized by the formation of intramolecular (S:S)<sup>+</sup>-bonds for TMT. (Oxidized trithia compounds are preferentially stabilized by such a coordina-

tion of two of the sulfur atoms; participation of a third sulfur atom cannot be completely excluded, but generally seems to be slight [34]). This coordination should lead to more stable radical-ion pairs for TMT, compared to the other two sulfides considered, and hence facilitate subsequent chemical reactions, i.e., proton transfer  $k_H$ . (2) Larger  $k_H$  values are reasonable for TMT, compared to the other sulfides, due to a shorter distance between its radical cation and the paired radical anion. This favorably short distance in TMT is associated with steric considerations; the equatorial methyl substituents in TMT allow a relatively close approach of the radical ions in a pair which is in contrast to the steric hindrance caused by two rotating alkyl groups for diisopropyl sulfide. This ease of approach leads to a shorter distance between the oxygen atom of the radical anion and the acidic protons on the carbons  $\alpha$  to the sulfurs [35,36]. In contrast, the acidic protons on the carbons  $\alpha$  to the sulfur in radical cations of diisopropyl sulfide are less accessible to the oxygen atom of the paired radical anion.

In acetonitrile/water solutions, there were also much larger values of BPH' quantum yields for TMT than for DMS (and diisopropyl sulfide). However, the most striking feature of these solutions was that  $BP^{\cdot-}$  radical anions were detected for both TMT and dimethyl sulfide [16]. The ratio of  $k_{sep}/k_H$  was larger for TMT (1/4) than for DMS (1/7). The appearance of ketyl radical anions in acetonitrile/water solution (in contrast to the lack of  $BP^{\cdot-}$  in acetonitrile) can be

rationalized as follows. It can be understood in terms of an increase of the ion escape probability (dielectric constant dependence of the Onsager distance) in going from acetonitrile to acetonitrile/water [16] and by the solvation of the radical-ion pair in aqueous solutions [37]. The larger  $k_{sep}/k_H$  ratio for TMT than for DMS can be explained by an additional stability of sulfur-centered radical cations due to the formation of the intramolecular S...S-bonded species for TMT (Scheme 2). Recently [37], it was shown that the formation of CB radical anions in the CB-sensitized photooxidation of dimethyl sulfide in aqueous solution occurs via 'solvated ion pairs' in contrast to the formation of ketyl radicals that are formed via 'nonsolvated ion pairs'. Thus, the structure of the ion pairs, i.e., a distance between charged species in the 'solvated ion pairs' is different for TMT and DMS and may also be a reason for the difference in  $k_{sep}/k_H$  values for TMT and DMS.

The results presented in this work for the photoreduction of benzophenone by TMT in acetonitrile solution may help in understanding the role of sulfides in the mechanism of benzophenone-initiated photopolymerization. In particular, the large quantum yields of ketyl-radical formation (and the associated formation of  $\alpha$ -C radicals, Scheme 2) in the presence of TMT (in contrast to other non-cyclic sulfides) have direct implications for the polymerization processes. Specifically, these large quantum yields show that there are additional, efficient channels for the formation of radicals that might be able to participate in the initiation of polymerization reactions (Scheme 1).

This suggestion was confirmed by photopolymerization studies. Polymerizations were sensitized by BP alone and by BP in the presence of co-initiators: the two simple sulfides  $Pr_2S$  and TBE, in addition to TMT. BDM was used as the model monomer. The formation of initiating radicals can occur by the excited BP abstracting hydrogen from the additives and/or from the monomer itself. Under the conditions used (low initiating light intensity), polymerization occurred efficiently only in the presence of TMT (Fig. 3).

The polymerization curves of BDM in Fig. 3, registered by means of the DSC method, show a complex behavior, typical of multifunctional monomers [24]. In the presence of non-cyclic sulfides or in the absence of co-initiators, no BP-sensitized polymerization was observed (Fig. 3a). The observed dependencies of the polymerization rate ( $R_p$ ) on the polymerization time and the degree of double-bond conversion ( $p$ ) represent, in part, the net effect of the efficiency of the initiating process. However this observed behavior is also influenced by other processes occurring during the polymerization, such as chain-transfer reactions, etc. In spite of these difficulties in interpreting the kinetics of the polymerization process for multifunctional monomers and in estimating the contribution of the initiation process to the overall polymerization rate, the results clearly indicate that the efficiency of the polymerization initiated by BP depends on the structure of the organic sulfides used as co-initiators. This correlates well with the yield of the ketyl radical formation

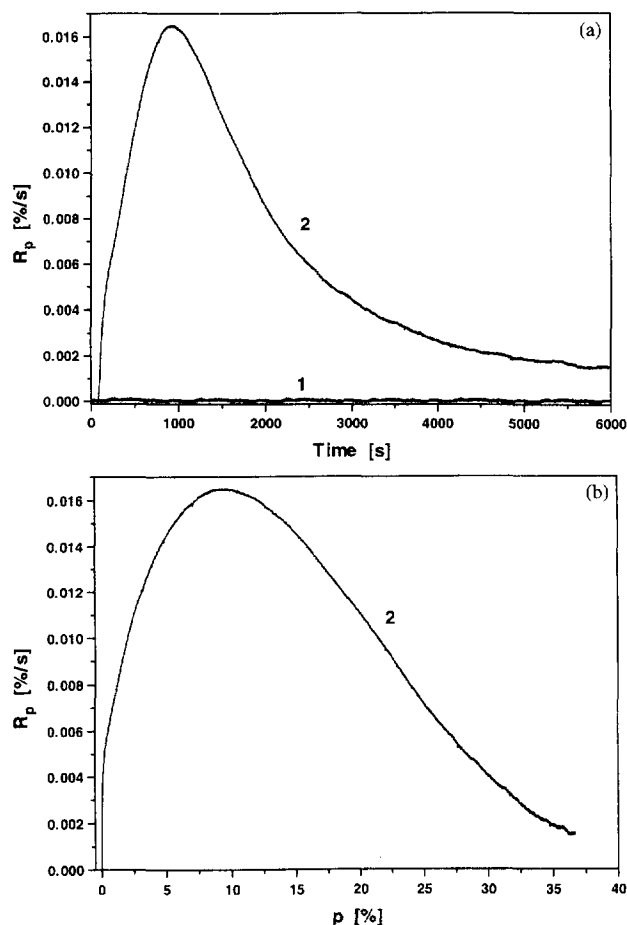


Fig. 3. Polymerization rate ( $R_p$ ) as a function of: (a) time and (b) double bond conversion ( $p$ ): 1, In the presence of 0.06 M BP or 0.06 M BP + 0.06 M  $Pr_2S$  or 0.06 M BP + 0.06 M TBE. 2, In the presence of 0.06 M BP + 0.06 M TMT.

in the photoreduction of BP by TMT and non-cyclic organic sulfides (Table 1).

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