

Photochemical reactions of β -2,4,6-trimethyl-1,3,5-trithiane in solution

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Abstract

The mechanism for the photoreaction of β -2,4,6-trimethyl-1,3,5-trithiane (β -TMT) in acetonitrile was investigated using steady-state and laser flash photolysis. The main photoproducts were determined to be the thioester $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SCH}_2\text{CH}_3$ and the α -TMT isomer. These products were identified by analytical and spectroscopic methods. The quantum yield for β -TMT disappearance was measured as $\Phi_{\beta\text{-TMT}} = 0.43$, and quantum yields for the formation of products were $\Phi_{\text{thioester}} = 0.32$ and $\Phi_{\alpha\text{-TMT}} = 0.10$. A short-lived ($\tau = 13 \mu\text{s}$) intermediate was observed in the flash photolysis experiments that was seen to decay into the thioester (the stable photoproduct). A detailed mechanism of the primary and secondary processes was proposed and discussed that accounts for the experimental results. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, a series of 1,3,5-trithiane derivatives was found to be effective in coinitiating photopolymerizations [1–3]. The activity of these trithianes in accelerating photopolymerizations depends on their hydrogen-donating ability. In reactions with aromatic ketones which act as the sensitizer, the formation of initiating radicals normally occurs as the result of the excited ketone molecule abstracting a hydrogen from the coinitiator. The effective initiators of the polymerizations are radicals derived from the trithianes acting as hydrogen donors. The mechanism for the photoreduction of benzophenone by 2,4,6-trimethyl-1,3,5-trithiane (TMT) in acetonitrile was investigated in detail in references [4,5]. These studies led to an understanding of the mechanistic role of sulfides in benzophenone-induced photopolymerizations. 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 and diffusion apart of the radicals; (2) diffusion apart of the radical ions; and (3) back elec-

tron transfer. The first reaction leads to the formation of ketyl radicals and α -(alkylthio)alkyl radicals. The second reaction leads to the formation of separated ketyl radical anions and sulfur-centered radical cations. The third reaction leads back to the starting materials. The large quantum yields of ketyl-radical formation in the presence of TMT have direct implications for the polymerization processes. Specifically, these large quantum yields imply the existence of complementary radicals that are potentially capable of initiating polymerization reactions. Since β -TMT was shown [4] to be an effective coinitiator in photopolymerizations, knowledge of its photochemical properties is of great importance.

Photochemical reactions of some thiocarbonyl trimers were studied by Nishio, Yoshioka, Aoyama, and Sugijama [6,7]. However, the photoproducts in this work were determined only after long irradiation times. Such conditions could potentially account for the complex array of products which they found. In the current paper more controlled photolysis conditions were used in order to isolate primary and secondary photochemical reactions of β -TMT in acetonitrile. For instance, it was found that monochromatic (254 nm) irradiation of deoxygenated β -TMT in acetonitrile leads to the formation of a thioester $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SCH}_2\text{CH}_3$ (**A**), and the isomer α -TMT; whereas, under prolonged irradiation the thioester **A** was photolyzed to form the thioester $\text{CH}_3\text{C}(=\text{S})\text{SCH}_2\text{CH}_3$ (**B**).

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2. Experimental

2.1. Materials

β -2,4,6-trimethyl-1,3,5-trithiane (*cis-cis* form) and α -2,4,6-trimethyl-1,3,5-trithiane (*cis-trans* form) were generous gifts from Professor Ewa Andrzejewska. They were prepared by literature methods [8,9] and were purified by repeated recrystallizations. Ethyl dithioacetate was purchased from Aldrich and used as a reference compound. Acetonitrile (for spectroscopy, Merck) was refluxed over calcium hydride for at least one hour and then slowly distilled. Chloroform (Aldrich, >99%) was dried under calcium chloride and distilled. Hexane (OBRPR Plock, fraction pure) was distilled over sodium.

2.2. Equipment and experimental conditions

A Varian–Gemini 300 MHz spectrometer was used to record ^1H and ^{13}C -NMR spectra to assist in the identification of the photoproducts. UV–VIS absorption spectra were taken on an M40 Specord (Carl Zeiss, Jena) and Photodiode Array Hewlett-Packard 8543A spectrometers, and IR spectra were measured on a FT-JR Bruker model JFS 113V infrared spectrophotometer. Low- and high-resolution electron impact (EI) mass spectra were determined on an AMD 402 mass spectrometer. Gas chromatographic analyzes were performed on a Hewlett-Packard 5890 II instrument equipped with an FID detector. Analyzes were done with a CP-Sil 5B capillary column (0.25 mm \times 50 m) with a temperature program operating between 120 and 220°C (heating rate, 10°C min $^{-1}$) and a flow rate of 1.5 ml min $^{-1}$. The photolysis of β -2,4,6-trimethyl-1,3,5-trithiane (β -TMT) was monitored by high-pressure liquid chromatography (HPLC) using a Waters Model 616 solvent pump system. The detection system consisted of a Photodiode Array UV–VIS detector Waters 996. Analytical HPLC was carried out on a Waters Symmetry C18 reverse phase column (3.9 mm \times 150 mm, 5 μm particle size), eluent: water (40%)–methanol (60%), flow rate: 1 ml min $^{-1}$, with optical detection at 238 and 308 nm. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 precoated (0.2 mm) plates using iod as the visualizing agent. Merck silica gel 60 H (5–40 μm) was used in column preparative chromatography.

2.2.1. Preparative-scale irradiations

Irradiations at $\lambda = 254$ nm were carried out in a cylindrical reactor consisting of an immersed, water-cooled, 15 W low pressure mercury lamp (Original Hanau TNN 15/30) with a cylindrical quartz filter. Solutions of β -TMT (250 mg) in acetonitrile (50 ml) were purged with high-purity argon and then irradiated. When the conversion of β -TMT was about 30% complete (about 15 min of irradiation) as monitored by HPLC analysis, the solutions were removed and analyzed. The solutions were then evaporated to concentrate the stable products of the photolysis, and the main product

(**A**) was isolated by column chromatography on silica gel (hexane:chloroform, 20:1 v/v). The fractions containing the main photochemical product **A** were combined and evaporated under reduced pressure. Compound **A** was obtained in pure form as a yellow oil.

2.2.2. Characterization of the main photochemical product **A**

TLC (hexane:chloroform, 2:1 v/v), $R_f = 0.68$.

HPLC (water:methanol, 40:60 v/v), retention time = 25.12 min.

GC retention time, 9.94 min.

^1H -NMR (CHCl_3) $\delta = 1.26$ (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{-CH}_2$), $\delta = 1.67$ (d, 3H, $J = 7.1$ Hz, $\text{CH}_3\text{-CH}$), $\delta = 2.56\text{--}2.79$ (m, 2H, $\text{CH}_2\text{-CH}_3$), $\delta = 2.80$ (s, 3H, $\text{CH}_3\text{-C=S}$), and $\delta = 4.96$ (q, 1H, $J = 7.0$ Hz, CH-CH_3).

^{13}C -NMR (CDCl_3) $\delta = 14.6$ ($\text{CH}_3\text{-CH}_2$), $\delta = 21.2$ ($\text{CH}_3\text{-CH}$), $\delta = 25.9$, ($\text{CH}_2\text{-CH}_3$), $\delta = 37.0$ ($\text{CH}_3\text{-C=S}$), $\delta = 51.0$ (CH-CH), and $\delta = 233.2$ (C=S).

IR (CHCl_3) 3686 cm $^{-1}$ (w), 2975 (m), 2928 (m), 2873 (w), 2239 (m), 1602 (w), 1448 (m), 1425 (w), 1373 (w), 1360 (w), 1269 (w), 1194 (s), 1096 (m), 1057 (m).

MS (EI) m/z (rel. int.) 180 (10, M^+), 91 (6), 89 (100), 61 (38), 59 (54), 45 (6), 32 (11), 28 (46).

High resolution mass spectrum (EI) m/z : 180.0114, calculated for $\text{C}_6\text{H}_{12}\text{S}_3$ 180.0101, error 0.7 ppm.

UV (acetonitrile) $\lambda_{\text{max}} = 308$ nm, $\epsilon_{\text{max}} = 10\,440$ M $^{-1}$ cm $^{-1}$.

On the basis of these results the product **A** was identified as the thioester $\text{CH}_3\text{C(=S)SCH(CH}_3\text{)SCH}_2\text{CH}_3$.

2.2.3. Identification of additional stable photoproducts

During preparative-scale irradiation, two additional stable products were identified. These products were α -TMT and the thioester **B**, $\text{CH}_3\text{C(=S)SCH}_2\text{CH}_3$. The identification of α -TMT and thioester **B** was based on comparisons with authentic samples in GC, GCMS, and HPLC analyzes. Thioester **B** was observed to appear during prolonged irradiations. This thioester also has a large absorption band around 310 nm, and its extinction coefficient was determined to be $\epsilon_{306} = 12\,800$ M $^{-1}$ cm $^{-1}$ [10].

2.2.4. Optical bench irradiation system: quantum yield determinations

Steady-state photolysis experiments were carried out in 1 cm \times 1 cm rectangular UV cell on a standard optical bench system. A low-pressure mercury lamp (Original Hanau TNN 15/30) was used as the excitation source for 254 nm irradiation. A high-pressure mercury lamp (HBO 200) with the combination of a BC-4 glass filter and a 313 nm interference filter (Zeiss) was used for 313 nm irradiation. The quantum yields, Φ were computed from

$$\Phi = \frac{\Delta c}{(I_a t_{\text{exc}})}$$

where Δc is the decrease in concentration of β -TMT or the increase in concentration of photoproducts during the irradiation period, t_{exc} , and I_a the intensity of absorbed light from the actinometry. Uranyl oxalate actinometry was used to measure the light intensity. The quantum yield for uranyl oxalate actinometry at 254 nm was taken to be 0.602 [11], giving a light intensity, I_0 in the experiments of 1.54×10^{-4} einstein $\text{l}^{-1} \text{min}^{-1}$. The intensity of absorbed light was calculated by

$$I_a = I_0(1 - T_{254})$$

where T_{254} is the transmission of the absorbing sample at 254 nm.

2.2.5. Nanosecond laser flash photolysis

The nanosecond laser flash photolysis setup has been described, elsewhere [12]. The Quanta Ray DCR-1 YAG laser was operated at 266 nm, 2 mJ, 8 ns pulse width. The transients were monitored with a pulsed 1 kW xenon lamp, with the monitoring beam perpendicular to the laser beam. All experiments were repeated using a flow system with rectangular quartz cells (0.5 cm \times 1 cm). The monitoring light pathlength was 0.5 cm.

3. Results and discussion

3.1. Steady-state photolysis: product analysis

Solutions of β -TMT in acetonitrile, after deoxygenation with high-purity argon, were irradiated at 254 nm by a low-pressure mercury lamp. The photolytic runs were monitored by taking UV–VIS spectra at regular time intervals. One such experiment is shown in Fig. 1. Irradiation times were from 5 to 30 min. The resulting spectra (Fig. 1) show

the development of a new absorption peak at 308 nm, corresponding to at least one stable photoproduct.

In order to identify the products of the photochemistry of β -TMT, a preparative scale irradiation was performed and one of the main products was isolated by column chromatography. The isolated photoproduct **A** was identified as the thioester, $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$. Additional stable photoproducts identified were shown to be thioester $\text{CH}_3\text{C}(=\text{S})\text{SCH}_2\text{CH}_3$ (**B**) and α -TMT isomer (see Section 2).

It is of interest to know whether thioester **B** could arise directly from β -TMT by a double fragmentation. Since β -TMT does not absorb at 313 nm, but thioester **A**, $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$, does, a reaction mixture was exposed to 313 nm irradiation after being initially irradiated at 254 nm for 12 min. The results are presented in Fig. 2. This figure shows that β -TMT remains unchanged by 313 nm irradiation as expected. However, the concentration of $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$ decreases with 313 nm irradiation time while that of the thioester **B**, $\text{CH}_3\text{C}(=\text{S})\text{SCH}_2\text{CH}_3$, increases, at least initially. This behavior is indicative of the thioester **B** being formed by a photoinduced C–S bond cleavage of thioester **A**.

3.2. Steady-state photolysis: quantum-yield determinations

Since authentic samples of the major products, α -TMT and $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$, were available, it was possible to use various chromatographic methods to determine the primary quantum yields of the photolysis of β -TMT (initial concentrations 5×10^{-4} to 1×10^{-3} M). The changes in the concentration of β -TMT and the various stable photoproducts, Δc were determined by both GC and HPLC measurements, with the authentic compounds as concentration standards (see Fig. 3). Because of complications caused by the photoproducts absorbing some of the photolytic light

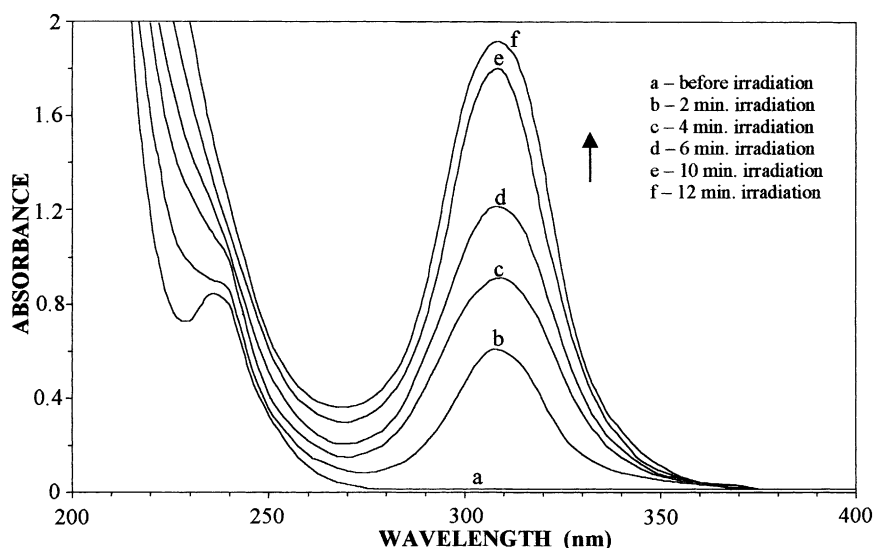


Fig. 1. UV–VIS absorption spectra of 0.7 mM β -TMT in acetonitrile undergoing steady-state photolysis at 254 nm.

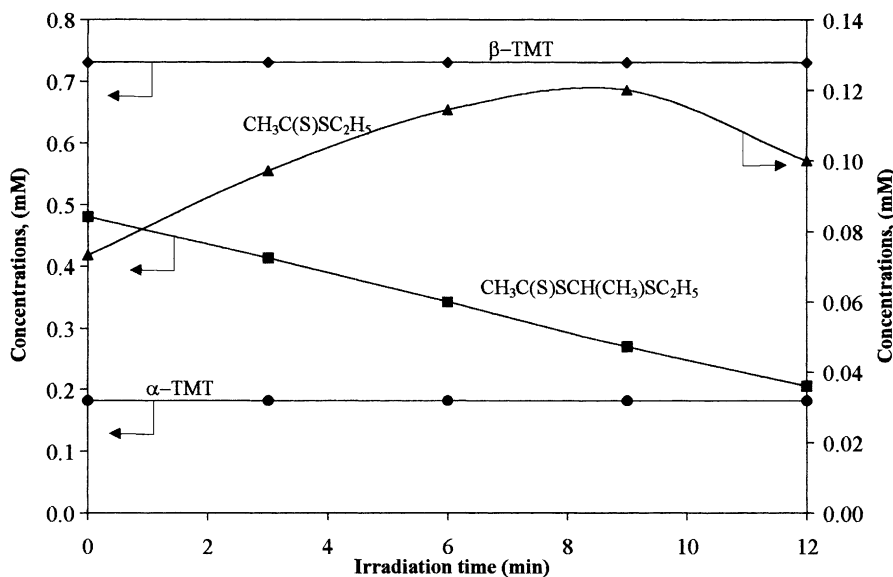


Fig. 2. Changes in the concentration of β -TMT and photoproducts during 313 nm irradiation of a reaction mixture that was preirradiated for 12 min at 254 nm of β -TMT acetonitrile solution (see Fig. 1).

and complications due to the secondary photolysis of product A, all quantum yields were extrapolated back to zero irradiation time. Quantum yields determined by this method are presented in Table 1. These quantum yields did not change significantly in the presence of oxygen, ethylene, 1,3-pentadiene, methyl viologen, or TEMPO.

3.3. Nanosecond laser flash photolysis

Solutions of 0.7 mM β -TMT in acetonitrile were irradiated at 266 nm by fourth harmonic, 8 ns pulses from a YAG laser operated at 10 Hz. Transient absorptions were seen in

the region of 305–450 nm, see Fig. 4. The transient spectrum shown in Fig. 4 is taken from a time window of 300–350 ns after the laser flash. The kinetic traces from which this spectrum was generated showed an almost constant absorbance in this time range. However, as seen in the kinetic traces in the two insets to Fig. 4, there are significant variations in the time profiles as the monitoring wavelength changes. Inset 4a shows a 360 nm kinetic trace on an expanded time scale. This kinetic trace decays with a rate constant of $7.5 \times 10^4 \text{ s}^{-1}$ or a lifetime of 13 μs . On the same time scale, the kinetic trace at 310 nm shows an immediate rise and then a secondary growth with a time constant of $7.8 \times 10^4 \text{ s}^{-1}$.

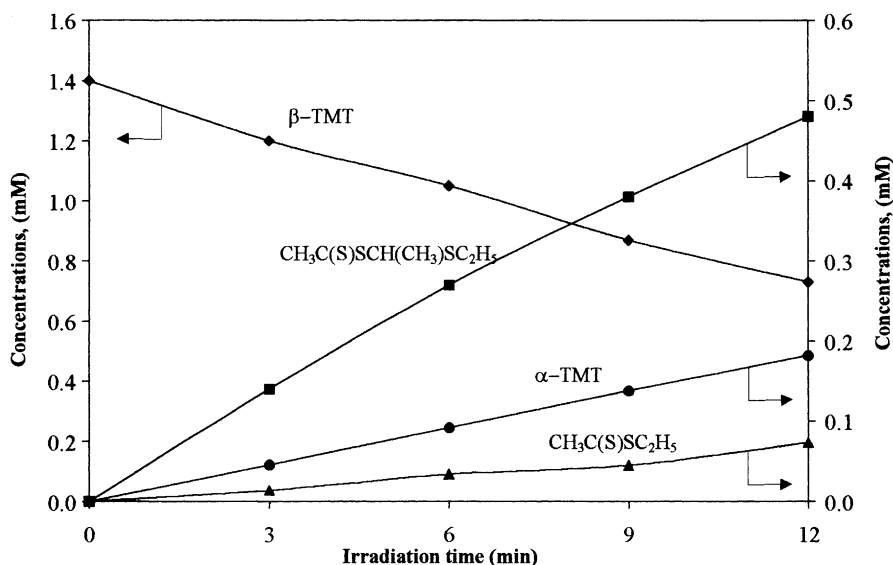


Fig. 3. Changes in the concentrations of substrate and photoproducts during 254 nm photolysis of β -TMT ($c = 1.7 \text{ mM}$) in acetonitrile solution.

Table 1

Quantum yields of β -TMT disappearance ($\Phi_{\beta\text{-TMT}}$) and primary products formation (Φ_{A} , $\Phi_{\alpha\text{-TMT}}$) in steady-state photolysis at $\lambda = 254$ nm in acetonitrile^a

	Φ			Φ_{av}
	UV	GC	HPLC	
$\Phi_{\beta\text{-TMT}}$	–	0.44	0.42	0.43
Φ_{A}	0.29	0.33	0.34	0.32
$\Phi_{\alpha\text{-TMT}}$	–	0.10	0.10	0.10

^a $[\beta\text{-TMT}] = 5 \times 10^{-4}$ to 1×10^{-3} M, $I_0 = 1.54 \times 10^{-4}$ einstein $\text{l}^{-1} \text{min}^{-1}$.

That the two traces show complementary decay and growth suggest that there are at least two species absorbing and that they are related through these kinetics. As mentioned above, thioester **A**, $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$, absorbs strongly at 310 nm, and it seems likely that this is the species that is responsible for the secondary growth at 310 nm. If so, then the decay at 360 nm is likely its precursor (360 nm was chosen to avoid absorption by thioester **A**). This could be a biradical from the C–S bond cleavage or the triplet state of β -TMT. Saturation of the solution with air did not affect the lifetime of this kinetic trace, so it is likely not a triplet state. We take the decaying transient to be a biradical (see Scheme 1). The initial fast growth of the kinetic trace at 310 nm (inset Fig. 4b) would then be the absorbance of the biradical at this wavelength. The lack of quenching by air is consistent with the steady-state results, where the yields of photoproducts were also not affected by oxygen.

The assignments of what species are responsible for the observed kinetic traces can be checked by comparing quantum yields determined from the transient absorptions with those in Table 1 from the steady-state photolysis. If it is assumed that the biradical has decayed near the end of the displayed trace in Fig. 4a, then the absorbance of this thioester at the end of the kinetic trace in Fig. 4b is equal to

$$\Delta A_{310} = \Delta A_{310}(t = 70 \mu\text{s}) - \Delta A_{310}(t = 0) \left\{ \left(1 - \frac{\text{offset at } 70 \mu\text{s}}{\Delta A_{360}(t = 0)} \right) \right\}$$

where the expression in the curved brackets is a correction factor compensating for the residual 360 nm absorption at 70 μs . The actinometer used was the triplet state of 4-carboxybenzophenone (CB) in water using $\epsilon_{540} = 6250 \text{ M}^{-1} \text{ cm}^{-1}$ [13]. The laser output was set to only 2 mJ, and the actinometry gave $[\text{CB}^*] = 4.8 \mu\text{M}$. The quantum yield of $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$ from these considerations is then $\Delta A_{310}/(10400 \text{ M}^{-1} \text{ cm}^{-1} \times 0.5 \text{ cm})/4.8 \mu\text{M} = 0.44$. This is in the range of the quantum yield obtained in the steady-state experiments (Table 1).

3.4. Mechanism

Given the approximations made, the reasonable agreement between the quantum yields from the steady-state and the time-resolved measurements is taken as an indication that both sets of data support the reaction mechanism, shown in Scheme 1. The scheme indicates that the biradical is

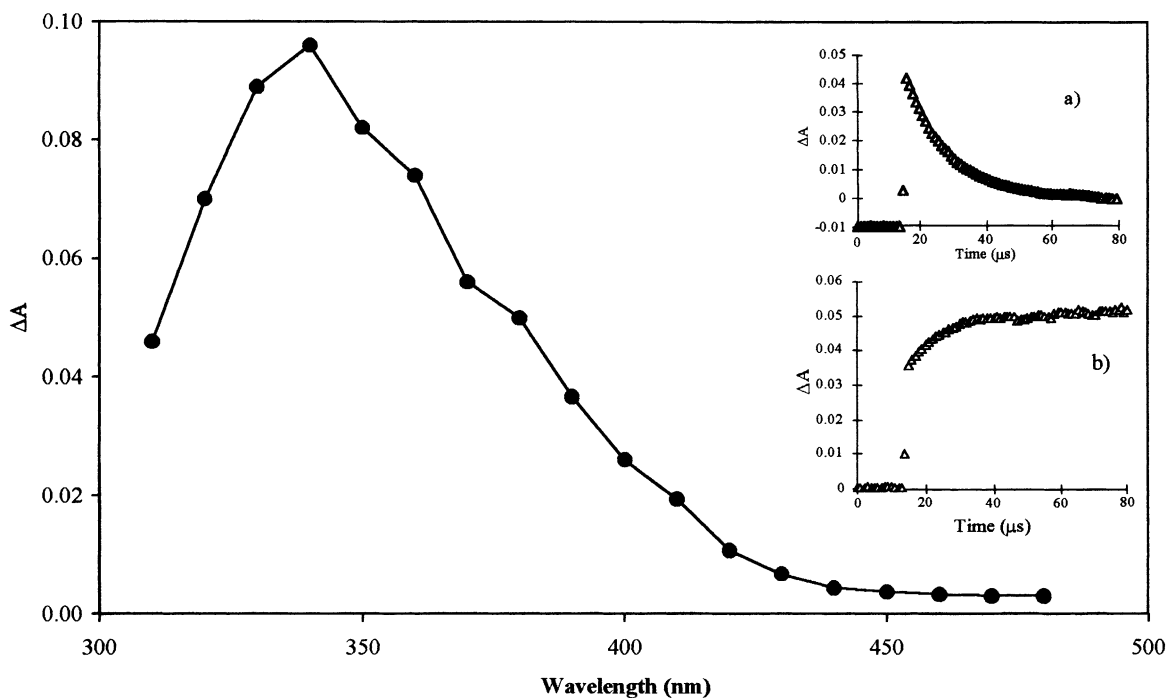
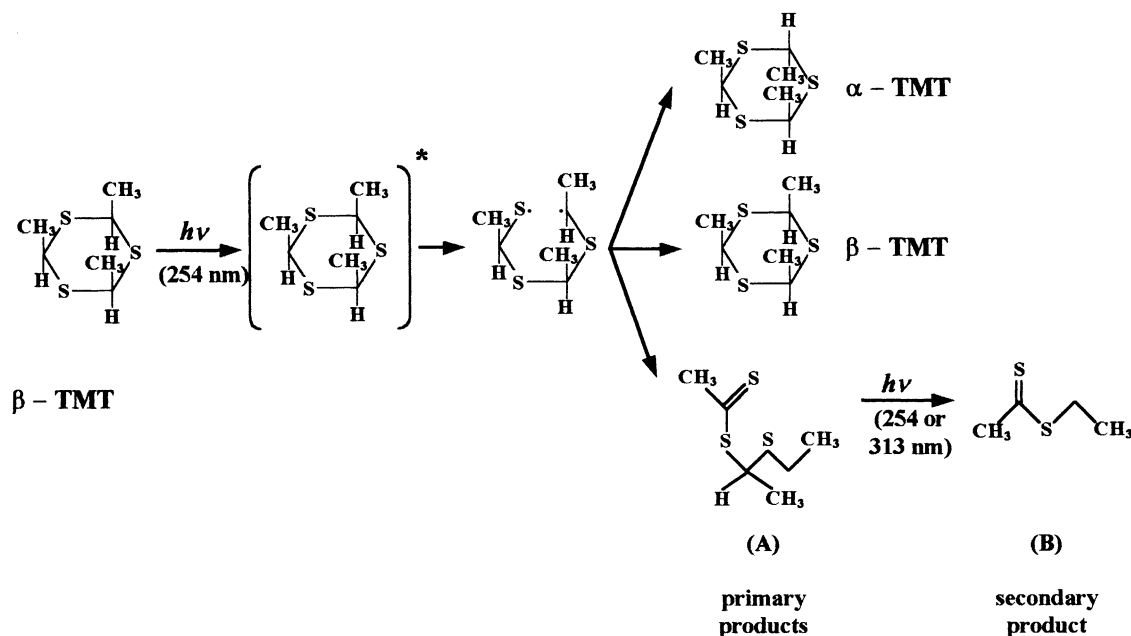


Fig. 4. Transient spectrum following 266 nm laser flash photolysis of 0.7 mM β -TMT in acetonitrile (time delay, 320 ns). Inset (a) shows a kinetic trace at 360 nm, and inset (b) is the corresponding kinetic trace at 310 nm.



Scheme 1.

generated from the singlet excited state of β -TMT. This is tentative, but the lack of any oxygen effects indicates that there was no triplet involvement or that the triplet state was very short-lived. Such a short-lived triplet is conceivable if the biradical is formed from it very quickly. The α -TMT product is almost certainly formed from the biradical because isomerization from the ground state of β -TMT is not likely due to the large activation energy. In order to form thioester **A**, $\text{CH}_3\text{C}(=\text{S})\text{SCH}(\text{CH}_3)\text{SC}_2\text{H}_5$, from the biradical, hydrogen migration is necessary. As indicated by the evidence from the 313 nm irradiation of photoreaction mixtures, it is likely that thioester **B** comes from a C–S bond fragmentation of thioester **A**. The sum of all the stable products of the steady-state photolysis is equal to the disappearance quantum yield of β -TMT itself. At this time it is not clear what process or processes are responsible for deactivating the excited singlet states in an unreactive manner. Either radiationless decay to the ground state or formation of the biradical with it reclosing back to β -TMT are likely possibilities.

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