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Photochemistry of 1,3,5-trithianes in solution
Steady-state and laser flash photolysis studies

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Abstract

In this work, we characterized the direct photochemistry of a set of five structurally-related 1,3,5-trithianes. The compounds were 1,3,5-trithiane, the α- and β-isomers of the 2,4,6-trimethyl derivatives, and the α- and β-isomers of the 2,4,6-triphenyl derivatives. Under steady-state, 254-nm irradiation of acetonitrile solutions of all five trithianes, dithioesters of the form $RC(=S)SCH(R)SCH_2R$ were identified and shown to be primary photoproducts ($R = H$, CH_3, or C_6H_5). Shorter dithioesters, $RC(=S)SCH_2R$, were also identified and shown to be secondary products. The presence of the dithioesters could be monitored by their strong absorption bands in the region of 310 nm. This same band was evident following the laser flash photolysis of the five trithianes. The laser-induced transient spectra showed another absorbing species (*I*) in all five trithianes. This species was not stable and showed a complementary decay that matched the growth of the stable photoproducts at 310 nm. This suggested that the intermediates (*I*) are the precursors of the corresponding dithioesters, $RC(=S)SCH(R)SCH_2R$. These correlated processes were related to monophotonic events. However, in the laser flash photolysis experiments in the triphenyl derivatives, there was an additional pathway for the formation of the dithioesters, and this was biphotonic. When the biphotonic formation of products was compensated for, $RC(=S)SCH(R)SCH_2R$ formation quantum yields from steady-state and laser flash photolysis matched within experimental error. The absorption band of (*I*) varied systematically with substituents, 320 nm in 1,3,5-trithiane, 340 nm in the 2,4,6-trimethyl derivatives, and 420 nm in the 2,4,6-triphenyl derivatives. The nature of these intermediates (*I*) were discussed as resulting from C—S bond cleavage, probably heterolytic.

Keywords: Photochemistry; Trithianes; C—S bond cleavage

1. Introduction

Carbon—sulfur bonds are relatively weak in general, and these bonds are known to be susceptible to photoinduced cleavage [1,2]. Such photochemistry is of commercial interest to pharmaceutical concerns in the synthesis of sulfur-containing drugs [3]. The photostability of these drugs can be disappointingly poor.

In recent years, there has been intense interest in whether photoinduced C—S bond cleavage arises from homolytic or heterolytic mechanisms [4–6]. These studies have mainly been on straight-chained compounds. In the current work, we look at excited-state processes in cyclic structures wherein the photo-fragments are constrained to remain in proximal contact allowing some control over the experimental parameters. The trithiane family of compounds in the current investigation has the advantage that they form symmetrical structures limiting the products formed.

Symmetrically substituted 1,3,5-trithianes (Chart 1) are formed by spontaneous trimerization of simple thiocarbonyl compounds [7]. Their special features are associated with the presence of three sulfur atoms in the ring and with their occurrence in two isomeric forms, *cis–trans* (α) and *cis–cis* (β).

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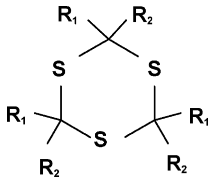


Plate 1.

Trisubstituted 1,3,5-trithianes (Chart 2) can easily undergo hydrogen and proton abstraction reactions [8,9] due to the presence of mobile hydrogen atoms (methine hydrogens from dithioacetal groups). The first step of the photo-induced hydrogen abstraction in aromatic ketone sensitized photoreactions, is electron transfer from the sulfur atom to a carbonyl compound to form a radical ion pair. The cation-radical formed can be stabilized by the three sulfur atoms of the trithiane ring [10,11]. Because there are two kinds of dithioacetal-type hydrogen atoms: axial and equatorial ones, their reactivity towards nucleophilic agents and radicals may differ, especially when the molecule contains bulky substituents [10,11]. The influence of the kind of substituent and the form (α or β) of the 1,3,5-trithiane derivative on its ability to reduce benzophenone (BP) under the influence of light was recently investigated, and the mechanism of the reaction was established [10]. It was also found that 1,3,5-trithianes can function as efficient co-initiators along with BP in two-component systems for photoinitiation of polymerizations. The activity of these co-initiator systems depends strongly both on the substituent type and also on the isomeric form of the trithiane [10,12]. It is noteworthy that simple aliphatic sulfides do not reduce BP in acetonitrile solution since the main process after the electron transfer is back electron transfer, not radical formation [13]. In the presence of 1,3,5-trithianes, being aliphatic sulfides, the quantum yield of radical formation is large which explains their activity in the initiation of the photopolymerizations when combined with BP [10].

The hydrogen abstraction reaction is the main reaction pathway when photochemical reactions occur in the presence of a light absorbing sensitizer, like BP. When the light absorbing compound is a trithiane itself (aliphatic trithianes absorb light at about 240 nm), the photochemical reaction may occur with the cleavage of the trithiane ring. Photochemical reactions of some 1,3,5-trithiane derivatives were studied by Nishio, Yoshioka, Aoyama, and Sugijama [14,15]. The photoproducts in these works were determined after long irradiation times (15–24 h), thus only secondary photolysis products could be identified. For instance, in the case of triphenyl derivatives, the main photolysis products were *cis*- and *trans*-stilbene and phenanthrene. The proposed mechanism [14,15] started with the formation of thioacetophenone, followed by further secondary reactions that were not discussed.

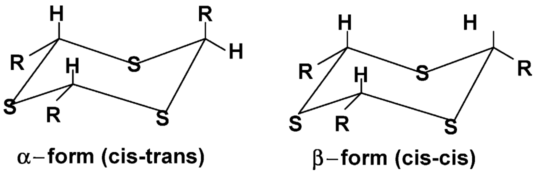


Plate 2.

In the current work, we characterize the direct photochemistry of 1,3,5-trithiane and its trimethyl and triphenyl derivatives. Preliminary results for the β-trimethyl derivative were published recently [16]; the current paper presents the full data for the α and β forms which enables us to discuss the general mechanism of the photolysis of 1,3,5-trithianes in solution including primary and secondary reaction steps.

2. Experimental section

2.1. Materials

1,3,5-Trithiane (TT), β-2,4,6-trimethyl-1,3,5-trithiane (*cis–cis* form) (β-TMT), α-2,4,6-trimethyl-1,3,5-trithiane (*cis–trans* form) (α-TMT), β-2,4,6-triphenyl-1,3,5-trithiane (*cis–cis* form) (β-TPT), and α-2,4,6-triphenyl-1,3,5-trithiane (*cis–trans* form) (α-TPT) were prepared by literature methods [17,18] and were purified by repeated recrystallizations. Acetonitrile (for spectroscopy, Merck) was refluxed over calcium hydride for at least one hour and then slowly distilled. All other chemicals were of the highest available purity and used as received.

2.2. Equipment and experimental conditions

UV–vis absorption spectra were measured on an M 40 Specord (Carl Zeis, Jena) and Photodiode Array Hewlett-Packard 8543A spectrometers. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 II instrument equipped with an FID detector. Analyses were done with a CP-Sil 5B capillary column (0.25 mm × 50 m) with a temperature program operating between 120 and 220 °C, a temperature increment rate of 10 °C/min, and a flow rate of 1.5 ml/min. The photolysis of the trithianes 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 × 150 mm, 5 μm particle size), eluent:water (40%)–methanol (60%), flow rate: 1 ml/min, with optical detection at 238 and 308 nm.

2.3. Preparative-scale irradiations

Preparative-scale irradiations were performed in a similar manner to that described previously [16]. 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. The solutions, after irradiation, were evaporated to concentrate the stable products of the photolysis, and the main product was isolated by column chromatography. The fractions containing the main photochemical product were combined, evaporated under reduced pressure, and analyzed by spectroscopic and chromatographic methods as described in [16].

2.4. *Optical bench irradiation system*

Steady-state photolysis experiments were carried out in a 1 cm × 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. All solutions were deoxygenized by bubbling solutions with O_2-free argon. Quantum yields were calculated based on the decrease in the concentration of the trithianes or the increase in appropriate products using analytical methods such as UV spectroscopy, GC, and HPLC. Uranyl oxylate actinometry was used to measure the light intensity. The quantum yield for this actinometry was taken to be 0.602 [19]. All quantum yields reported in this paper represent initial quantum yields obtained by extrapolation to zero irradiation time (see below).

2.5. *Nanosecond laser flash photolysis*

The nanosecond laser flash photolysis setup has been described elsewhere [20,21]. The Quanta Ray DCR-1 YAG laser was operated at 266 nm, 2–12 mJ / pulse, 10 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 × 1 cm). All solutions were routinely degassed with argon. The monitoring light pathlength was 0.5 cm. In quantum yield determinations, an external relative actinometer was used. This actinometry employed the triplet state absorption of 4-carboxybenzophenone in water taking $\varepsilon_{535} = 6250\,M^{-1}\,cm^{-1}$ [22].

3. Results and discussion

3.1. *Steady-state photolysis*

Acetonitrile solutions of the individual trithianes were irradiated at 254 nm with a low-pressure mercury lamp. The photolytic runs were monitored by taking UV–vis spectra at regular time intervals. In all cases the formation of a new absorption band at ≈310 nm was observed, and the intensities of these bands increased with irradiation time. The experimental results for the unsubstituted TT and an aromatic-substituted trithiane are shown in Figs. 1 and 2, respectively. Prolonged irradiation, led to a decrease in the intensity of these bands as shown in the inset of Fig. 2.

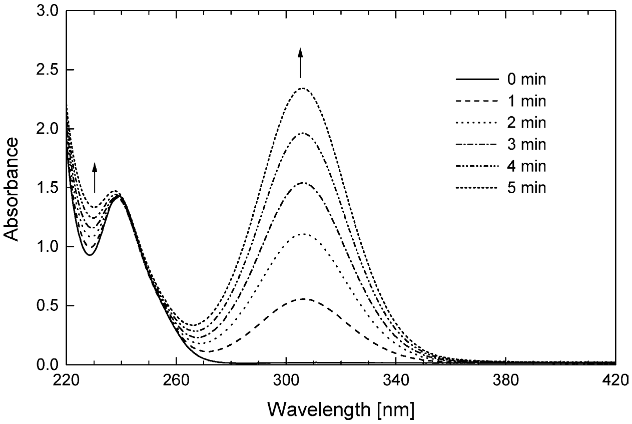


Fig. 1. Absorption spectra of TT in acetonitrile, undergoing steady-state photolysis at 254 nm.

Preparative scale irradiation of β-TMT was performed, and the main products were isolated by chromatographic methods and identified as the dithioesters, $CH_3C(=S)SCH(CH_3)SC_2H_5$, $CH_3C(=S)SCH_2CH_3$, and α-TMT [16]. As shown in the Experimental Section, analogous dithioesters, $RC(=S)SCH(R)SCH_2R$ and $RC(=S)SCH_2R$, where R represents H, CH_3, or C_6H_5, were identified in the other trithianes. In the case of α-TMT photolysis, the β-isomer was observed in addition to these dithioesters. All of these dithioesters have intense absorption bands around 310 nm, and their extinction coefficients are in the range of $10^4\,M^{-1}\,cm^{-1}$ [16,23].

In our previous work [16], it was shown that the shorter of the two dithioesters photoproducts from β-TMT arises in secondary photolysis, not as a double fragmentation of β-TMT itself, but directly from the C–S bond cleavage of the longer of the two dithioesters. Similar experiments were performed on the other trithianes. These experiments are illustrated using TT as an example. Fig. 3 shows the 254-nm irradiation of TT in acetonitrile. Both dithioesters are shown to increase with irradiation time. Fig. 4 shows the 313-nm irradiation of TT in acetonitrile. As with the analo-

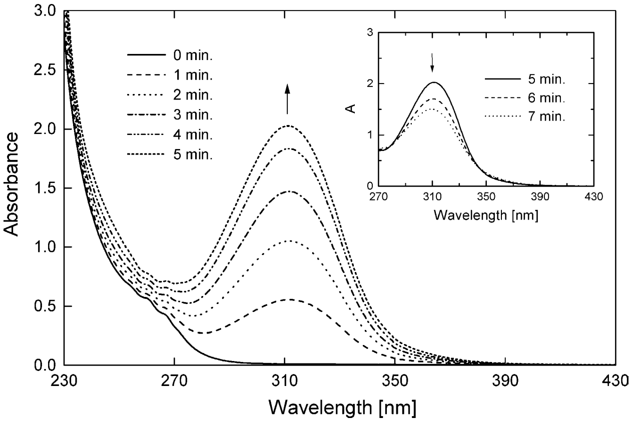


Fig. 2. Absorption spectra of α-TPT in acetonitrile, undergoing steady-state photolysis at 254 nm. Inset: results for longer irradiation times.

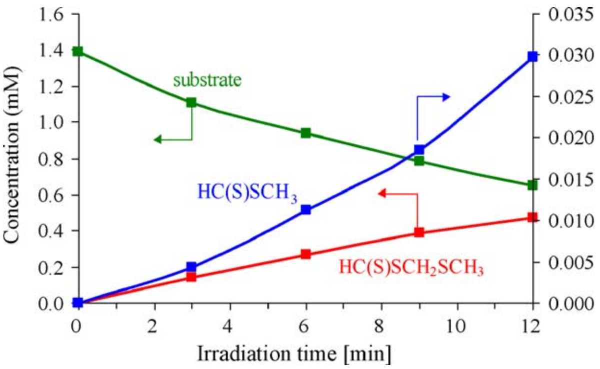


Fig. 3. Changes in concentrations of substrate and products during 254 nm photolysis of TT in acetonitrile solution.

gous experiment with β-TMT, TT does not absorb 313 nm, but the long dithioester, HC(= S)SCH_2SCH_3, does. It can be seen that there is no corresponding variation in the concentration of TT, in the preirradiated (by 254 nm) mixture, as the concentration of the shorter of the two dithioesters varies with the 313-nm irradiation. However, there is an inverse relationship between the concentrations of the two dithioesters in the early part of the 313-nm irradiation. With even longer irradiation times (> 8 min), the concentration of the shorter dithioester, HC(= S)SCH_3, also decreases, indicating that it also is photolyzed by 313-nm irradiation.

Because of the secondary photochemistry occurring in these systems, as it was shown above, reliable measurements of primary quantum yields requires extrapolation procedures to zero time of irradiation. Since authentic samples of the major products were available, it was possible to use various chromatographic methods to determine the primary photolytic quantum yields of the trithianes' disappearance, dithioester formation, and, in the case of α-TMT and β-TMT, isomer formation. These extrapolated quantum yields for all the trithianes are presented in Table 1 (see first three rows). It can be seen that the material balance for all the trithianes was satisfied, except for α-TMT. The lack of agreement between the quantum yield for α-TMT disappearance and the sum of the quantum yields of the observed products indicates that not all the products were identified and analyzed with the methods used in this work. Isomerization reactions were only observed for the trimethyl derivatives.

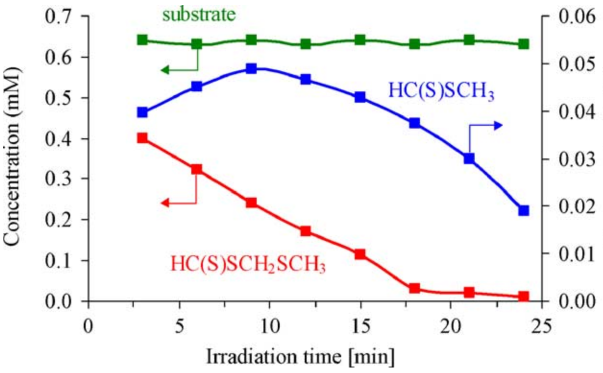


Fig. 4. Changes in concentrations of TT and photoproducts during 313 nm irradiation of a reaction mixture that was preirradiated for 12 min at 254 nm of TT in acetonitrile solution (see Fig. 3).

Table 1

Quantum yields (Φ) of trithiane disappearance and primary products formation in steady-state photolysis at 254 nm and in laser flash photolysis at 266 nm in acetonitrile

	Quantum yields (Φ)				
	TT	α-TMT	β-TMT	α-TPT	β-TPT
Trithiane disappearance	0.54	0.38	0.43	0.19	0.48
Dithioester formation	0.49	0.22	0.32	0.14	0.44
Isomer formation	–	0.01	0.10	< 0.01	< 0.01
Dithioester formation from laser flash photolysis	0.52	0.25	0.32	0.17	0.52

It was observed that these quantum yields, obtained in steady-state photolysis of the trithianes, were not affected by the presence of oxygen, ethylene, or 1,3-pentadiene. This indicates that these quenchers do not influence the reaction patterns (meaning that they do not affect excited states or other chemical intermediates involved in the reaction mechanism). This finding agrees well with results presented for β-TMT [16].

3.2. *Nanosecond laser flash photolysis*

The individual trithianes (0.3–1 mM) in acetonitrile solutions were irradiated at 266 nm by the fourth harmonic, 10 ns pulses from a YAG laser operated at 10 Hz. Transient absorptions were measured in the region of 280 to 700 nm. Typical transient absorption spectra for the unsubstituted TT and an aromatic derivative, β-TPT, are shown in Figs. 5 and 6, respectively.

The time-resolved behavior of the photolysis of TT, shown in Fig. 5, is similar to the behavior already described for β-TMT [16]. In particular, immediately after the laser flash, a broad transient absorption appears around 320 nm. This transient-absorption band does not evolve as a single component. At 360 nm (Fig. 5, upper inset), the kinetic trace decays

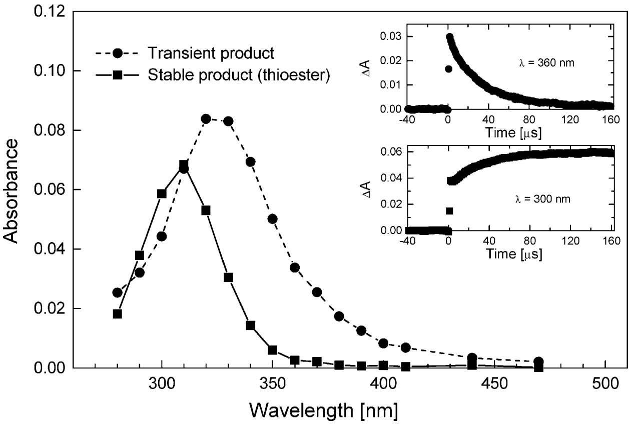


Fig. 5. Transient spectra following 266 nm laser flash photolysis of TT in acetonitrile (time delays 300 ns and 120 μs).

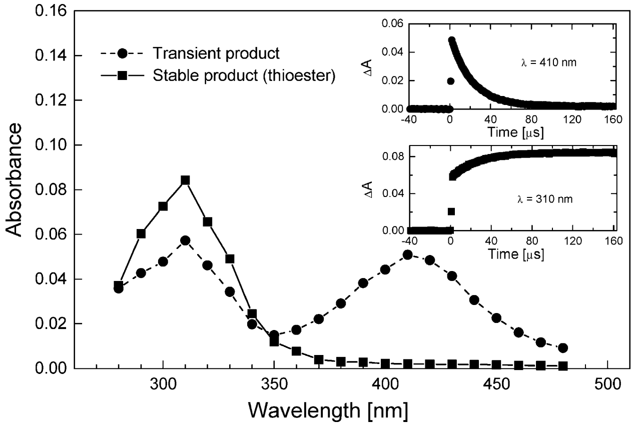


Fig. 6. Transient spectra following 266 nm laser flash photolysis of β-TPT in acetonitrile (time delays 300 ns and 80 μs).

monoexponentially with a rate constant $3.6 \times 10^4\ \mathrm{s}^{-1}$. On the other hand, the kinetic trace at 300 nm (Fig. 5, lower inset), shows two growth patterns, one immediate on the time scale of Fig. 5, lower inset, and another longer one with a growth rate constant of $3.2 \times 10^4\ \mathrm{s}^{-1}$.

The difference in the kinetic traces at different wavelengths indicates that there are at least two different absorbing species present. In addition, the similarity of the decay rate constant of the 360-nm kinetic trace and growth rate constant of the 300-nm kinetic trace indicates that one of the absorbing species is likely the precursor of the other absorbing species. By 60 μs the 360-nm kinetic trace has substantially decayed, leaving a product that is stable on the 200-μs time scale, see Fig. 5, lower inset. This remaining spectrum is reminiscent of the stable product seen in steady-state photolysis, Fig. 1. The other species contributing to the observed absorptions must then be the transient precursor to the observed stable dithioester.

The laser-intensity dependence of ΔA at 310, 340, and 360 nm (measured for α-TMT) were all linear. These measurements were preformed for two delay times, after the flash (200–400 ns) and after the stable product reached a plateau (30–40 μs). The conclusion is that the processes are all monophotonic. Similar conclusions can be drawn for TT and β-TMT based on analogous experiments.

α-TMT shows similar spectral and kinetic behavior to that shown by TT in Fig. 5 and to the kinetic results on β-TMT [16]. In addition, similar to results on β-TMT [16], the transients from TT and α-TMT were not quenched by oxygen or 1,3-pentadiene. This indicates that these transients could not be assigned to triplet excited states of the trithianes. Based on the analogy to β-TMT, we assign the transient species to a biradical-like intermediate, *I*, (see below), formed after C—S bond cleavage in these trithianes. Therefore, for all three trithianes (TT, α-TMT, β-TMT), not possessing aromatic substituents, we propose the reaction mechanism shown in Scheme 1.

$$\text{Trithiane} \xrightarrow{h\nu} \boldsymbol{I} \longrightarrow \text{Dithioester (+ isomer for } \alpha\text{- and } \beta\text{-TMT)}$$

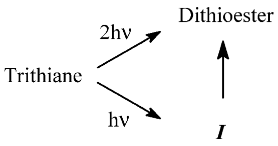
Scheme 1. For TT, α- and β-TMT.

The behavior of trithianes possessing aromatic substituents (α-TPT and β-TPT) show distinctly different characteristics in their laser-induced transient spectra, as well as, in their response to laser intensity. The spectral and kinetic results for β-TPT are presented in Fig. 6. Similar results were obtained for α-TPT.

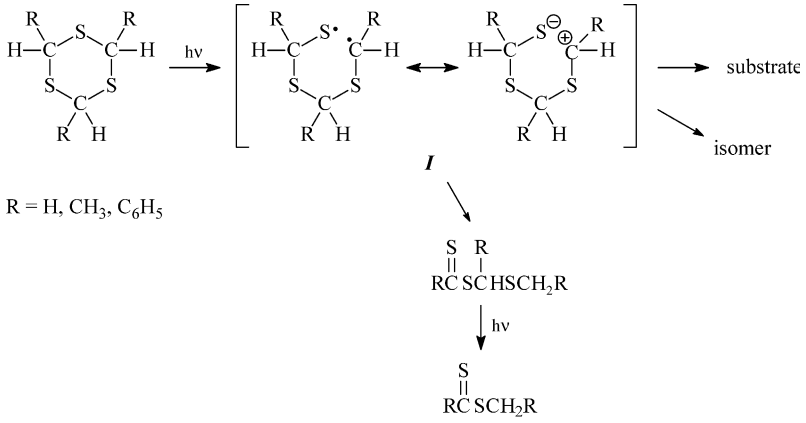
In contrast to the results shown in Fig. 5 for TT, there are multiple bands in the prompt (300 ns delay) transient spectra of β-TPT following laser excitation. In particular, there is a prominent longer wavelength band at 420 nm, in addition to a band at 310 nm which was also seen in TT on the microsecond time scale. However, it can be seen from the insets to Fig. 6 that the kinetic traces behave in an analogous manner to the kinetic traces in TT. The transient-absorption band at 410 nm decays (Fig. 6, upper inset) with a rate constant of $3.4 \times 10^4\ \mathrm{s}^{-1}$, and there is a complementary growth (Fig. 6, lower inset) of the 310 nm band with rate constant $3.3 \times 10^4\ \mathrm{s}^{-1}$. This again indicates that the 420-nm transient is the precursor of the 310-nm species. Furthermore the 310 nm kinetic trace in Fig. 6, lower inset, is stable on the 200 μs time scale, and the spectrum shown at 80 μs is similar to the dithioester, $C_6H_5C(=S)SCH(C_6H_5)SCH_2C_6H_5$, from α-TPT seen in Fig. 2.

With regard to the optical transients' dependence on the laser intensity, there was a distinct difference between the trithianes having aromatic substituents and those having none. The intensity-dependence of the yield of 410-nm transient was found to be linear, and, therefore, the production of this transient is monophotonic. In contrast, the initial yield of the dithioester formation, measured at 310 nm, showed a nonlinear dependence on the laser intensity. These data points (yield versus intensity) fit well to a quadratic function. This indicates that the dithioester in α-TPT can be formed directly by a biphotonic process. An identical conclusion can be drawn from the laser-intensity experiment for β-TPT.

A picture of the reaction scheme emerges from the complementary growth (310 nm)/decay (420 nm) in combination with the laser-intensity dependence experiment. We can now return to the analysis of the 310-nm kinetic trace in Fig. 6, lower inset. The initial yield of the 310-nm absorption is due to the dithioester in the biphotonic process. However, there is an additional channel for the formation of the dithioester seen as the slower, resolved growth curve in the 310-nm kinetic trace. These alternate formation pathways are illustrated in Scheme 2.



Scheme 2. For α- and β-TPT.



Scheme 3.

For the sake of using the information on the transients seen in flash photolysis to understand the overall mechanism, it is of interest to compare yields from the steady-state and the time-resolved measurements. Since the extinction coefficients of the main transient (*I*) are not known, it was not possible to determine quantum yields of those transients. However, the extinction coefficients of the dithioesters are well known, and this allowed us to determine the appropriate quantum yields in the laser flash photolysis experiments. In order to put the two experiments (steady-state versus flash photolysis) on the same footing, it is necessary to discount the initial absorbances due to the biphotonic formation of dithioesters for the trithianes with aromatic substituents. With this modification, the rest of the procedure is exactly the same as previously described for β-TMT [16]. The resulting quantum yields for the monophotonic formation of the dithioesters in the time-resolved experiments are given in the last row of Table 1. It can be seen that these quantum yields are within experimental error of the values determined from steady-state irradiation (second row of Table 1).

3.3. Mechanism

Comparison of the spectral characteristics of the main transients (*I*) give us a clue to the nature of the transient and, hence, to the nature of the overall photochemical mechanism. There is a progressive red-shift in the spectral maxima of the main transient (*I*) in going from unsubstituted (320 nm) to 2,4,6-trimethyl-substituted (340 nm) to 2,4,6-triphenyl-substituted (420 nm) trithianes. More importantly, the transients (*I*) from the α- and β-isomers (for given substituents) show almost identical spectral shapes as well as identical maxima, within experimental error. This indicates that, for a given substituent, the same transient is formed regardless of the initial isomer photolyzed.

The simplest way that the main transients from the corresponding α- and β-isomers can form identical transients is for the ring to break through a C–S bond cleavage. The resulting straight-chained species would not show evidence of its isomeric parentage. The question still remains as to the nature of the C–S bond cleavage.

There certainly is enough energy in the 266-nm photons (or 254 nm) to homolytically cleave a normal C–S bond (61.9 kcal/mol) [24]. The resulting biradical is one possibility for the observed transient. The dithioesters would follow from a 1,3-hydrogen-atom shift from the carbon adjacent to the sulfur atom, see Scheme 3. The lack of quenching found in experiments with quenchers oxygen, 1,3-pentadiene and methylviologen makes this assignment problematical [25].

Another promising possibility for the nature of the transients is a zwitterion formed from heterolytic cleavage of one of the C–S bonds in the trithiane rings. On the basis that sulfur atoms are normally good donors in electron-transfer reactions, we could consider that the bond would fragment, leaving a hole on the sulfur atom and an extra electron formally on the carbon atom [6]. In order to form the observed dithioesters from such a zwitterion, the likely step would be a 1,3-proton transfer from the carbon adjacent to the sulfur atom to the negatively charged carbon center. Evidence from pulse radiolysis [26] shows that sulfur radical cations are very susceptible to such deprotonations.

However, preliminary experiments with methanol, as the solvent, have indicated that methoxy derivatives are formed at the carbon-end of the cleaved bond. This indicates that the transients observed in the laser flash photolysis experiments were derived from heterolytic cleavage with the pair of electrons from the broken bond remaining on the sulfur, leaving a carbocationic site as the carbon end of the broken bond. Other preliminary experiments, in methanol and in acetonitrile/methanol mixtures, indicate that methanol dramatically decreases the yield of dithioesters and also reduces the lifetime of the observed transient (*I*) [27]. A strong interaction of the intermediates (*I*) with methanol is easier to understand if the intermediates were of the zwitterionic form as opposed to that of a biradical.

Another possibility is for the C–S cleavage to be homolytic, followed by an electron transfer between the end fragments from the broken bond [4]. However, in this case the fragments are tied together by the molecular unit, so it would be more appropriate to consider the transient (*I*) as the resonance structure shown in Scheme 3. Further experimental and theoretical results on the radical versus ionic behavior will be reported elsewhere [27].

It is not clear why oxygen has no effect on the transient (*I*). Nonpolar biradicals with carbon ends are quenched by oxygen [25] which is a reason against assigning the transient as one. On the other hand, in a bipolar biradical, its radical cationic end would be expected to react with electrophiles [28] like oxygen, and its radical anionic end would only react if its redox potential were sufficient to reduce oxygen to superoxide.

Acknowledgements

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