

## SHORT-LIVED TRIPLETS OF ALIPHATIC THIOKETENES

K. BHATTACHARYYA, V. RAMAMURTHY† and P. K. DAS

*Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (U.S.A.)*

S. SHARAT

*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012 (India)*

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### Summary

The photophysical behavior of the triplets of three aliphatic thioketenes, namely di-*tert*-butylthioketene (1), 2,6-di-*tert*-butylcyclohexylthioketene (2) and 2,2,6,6-tetramethylcyclohexylthioketene, has been studied in fluid solutions at room temperature by nanosecond laser flash photolysis. Upon 532 nm laser excitation into the  $S_1$  state, the thioketenes in concentrated benzene solutions produce very short-lived transient absorptions ( $\tau < 5$  ns;  $\lambda_{\max} \approx 450$  nm) attributable to their triplets. The photogeneration of the latter under  $S_1$  excitation has also been established by energy transfer to *all-trans*-1,6-diphenyl-1,3,5-hexatriene. The factors which render the triplet lifetimes short are shown to be intrinsic in origin (rather than self-quenching). Unlike thiocarbonyl compounds in general, the thioketenes possess low intersystem crossing yields (less than 0.1 in benzene). From the kinetics of the quenching of a series of sensitizer triplets by 1 and 2, the thioketene triplet energies are estimated to be 43 - 44 kcal mol<sup>-1</sup>.

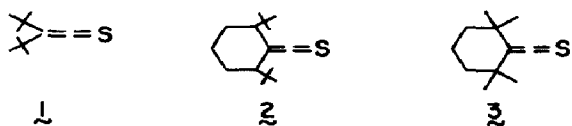
### 1. Introduction

Thioketones have been the subject of many photophysical and photochemical studies [1 - 4] in recent years. By comparison, interest in the excited state properties of thioketenes has been limited. Photolysis ( $\lambda_{\text{ex}} = 215 - 260$  nm) of the parent thioketene,  $\text{CH}_2=\text{C}=\text{S}$ , in argon and nitrogen matrices at low temperatures (about 8 K) results in photodecomposition and conversion to ethynyl mercaptan [5]. The suggested mechanism for this reaction involves the intermediacy of thiirenyledene carbene and thiirene [6]. Surprisingly, the thioketene is stable to irradiation by light of wavelengths longer than 280 nm. Recent photochemical studies [7, 8] with

†Permanent address: Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India.

di-*tert*-butylthioketene (1) and 2,2,6,6-tetramethylcyclohexylthioketene (3) in fluid solutions at room temperature have led to the isolation of a variety of photoproducts, namely alkoxythiiranes, thioacid esters, diketones and arylalkylthiones. The photoreactivity is observed only upon excitation into the second singlet excited state ( $S_2$ ). Also, thioketenes are known to undergo photo-oxidation via reaction with singlet oxygen [9, 10].

To the best of our knowledge, no photophysical study has been undertaken regarding the excited state properties of thioketenes. In the present paper, we examine several aspects of the behavior of aliphatic thioketene triplets based on a nanosecond laser flash photolysis study of three representative systems, namely 1, 2,6-di-*tert*-butylcyclohexylthioketene (2) and 3.



Unlike thiocarbonyl compounds in general, these thioketenes are found to have very low intersystem crossing yields (less than 0.1 in benzene). Their triplets are characterized by very short lifetimes (of the order of nanoseconds) attributable primarily to intrinsic factors rather than self-quenching. From the kinetics of the quenching of a series of sensitizer triplets by 1 and 2, their triplet energies are estimated to be in the vicinity of 43 - 44 kcal mol<sup>-1</sup>. This information, obtained by laser flash photolysis and transient absorption measurements, is most valuable, particularly when one considers that the thioketenes under examination do not exhibit significant fluorescence or phosphorescence at room temperature or at 77 K, and hence are not amenable to photophysical studies based on luminescence measurements.

## 2. Experimental details

The thioketenes 2 and 3 were obtained as generous gifts from Professor E. Schaumann's group at the University of Hamburg. 1 was prepared by a reported procedure [11]. The thioketene samples were purified by passage through a silica gel column and elution with benzene. Benzene (Aldrich, spectral grade) was used as received. The sources and methods of purification of various reagents have been given in previous publications [12 - 14] from the Radiation Laboratory.

The laser flash photolysis experiments were carried out in a computer-controlled set-up described in detail elsewhere [12 - 15]. The laser pulses were provided by a Molectron UV-400 nitrogen or a Quanta-Ray DCR-1 Nd-YAG system. Rectangular quartz cells of path length 2 - 3 mm were used at a front-face geometry between the directions of the excitation pulses and the analyzing light. Some experiments were also done at a right-angle

geometry to minimize the scattered light entering the analyzing monochromator. The deoxygenation of the solutions was effected by saturation with high purity argon.

### 3. Results and discussion

As is usually the case with thiocarbonyl compounds, each of the three thioketenes under examination is characterized by a weak broad absorption band system in the visible ( $\lambda_{\text{max}}$  in benzene, 565 nm, 591 nm and 572 nm for 1, 2 and 3 respectively;  $\epsilon_{\text{max}} = 8 - 11 \text{ M}^{-1} \text{ cm}^{-1}$ ). This is assigned [2] to the lowest lying singlet  $\pi^* \leftarrow n$  transition. The higher lying transition ( $S_2$ ) displays onsets at 400 - 450 nm. Unlike many of the thiocarbonyl compounds, no phosphorescence or  $S_2$  fluorescence is observed from the thioketenes in fluid solution at room temperature or in glassy matrices (3-methylpentane) at 77 K.

Upon excitation with an intense laser pulse (532 nm; 20 - 40 mJ) into the lowest energy band system ( $S_1$ ), relatively concentrated solutions of 1 - 3 (0.1 - 0.4 M in benzene) produce short-lived transients the decay of which nearly follows the laser pulse (duration, about 6 ns). The transient absorption spectra and representative kinetic traces are shown in Fig. 1. Evidently, the spectra from the three thioketenes are very similar to one another and display absorption maxima at 450 nm. Under the conditions of direct observation, the transients are too short lived to be subjected to quenching studies using typical triplet quenchers (e.g. oxygen, di-*tert*-butylnitroxy radicals or ferrocene).

Attempts were made to observe the fast decaying transients upon laser excitation into  $S_2$ . However, only weak long-lived transient absorptions were observed at 350 - 500 nm as a result of flash photolysis of 30 - 40 mM solutions of 1 - 3 in benzene by 337.1 nm laser pulses (3 mJ; about 8 ns). The transient absorption spectra and kinetic traces are presented in Fig. 2. The 266 nm laser excitation of 1 in cyclohexane led to transient phenomena similar to those seen upon 337.1 nm excitation of 1 in benzene (Fig. 2(A)). The decay of the long-lived species ( $\tau_{1/2} > 100 \mu\text{s}$ ) occurs slowly over the microsecond time scale and does not follow clean first- or second-order (equal concentration) kinetics; it remains practically unaffected upon going from deoxygenated to air-saturated solutions ( $k_{\text{q}, \text{O}_2} < 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ). Furthermore, the species are not quenched by di-*tert*-butylnitroxy radical (at a concentration of 0.06 M or below) or ferrocene (5 mM or below). This behavior strongly rules out the assignment of these species in terms of thioketene triplets. Addition of methanol (up to 12 M) showed practically no effect on the decay kinetics of the long-lived transient species photogenerated from 1 and 2 ( $\lambda_{\text{ex}} = 337.1 \text{ nm}$ ) in benzene. Note that the long-lived species are not observed upon 532 nm laser flash photolysis and appear to be related to photochemistry from  $S_2$ . Also, the nanosecond transients seen in the course of 532 nm laser flash photolysis (*vide supra*) are not observed

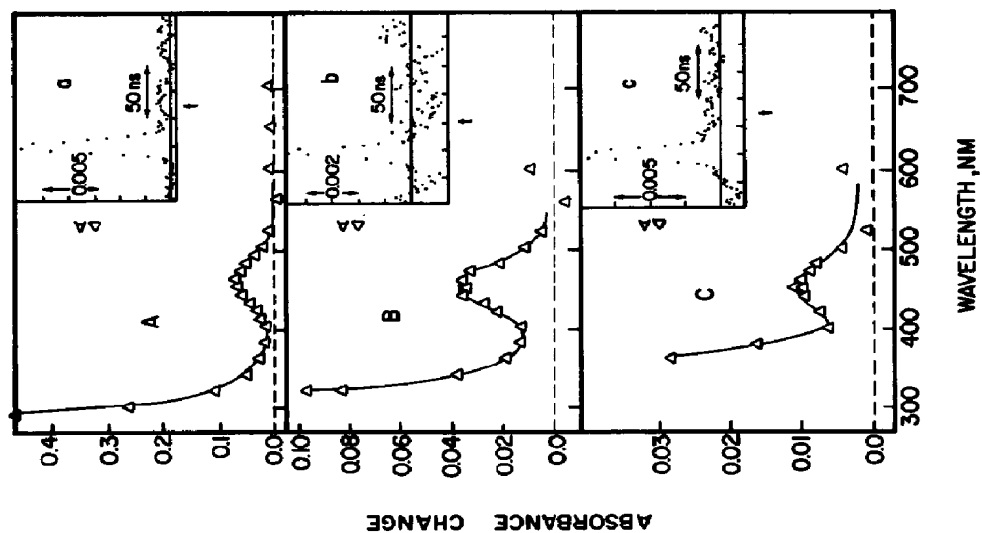
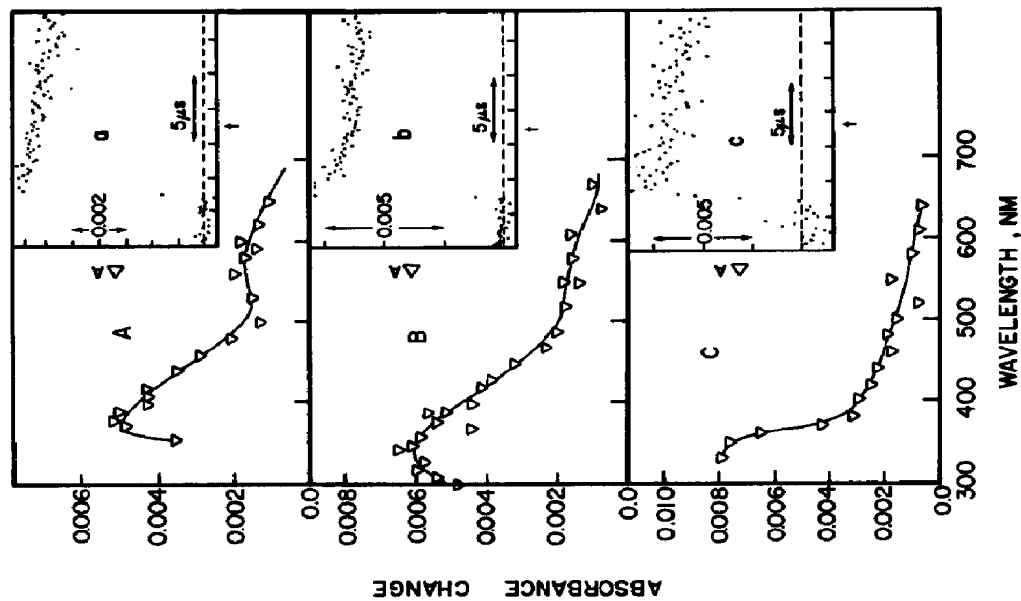


Fig. 1. Transient absorption spectra (end-of-pulse) observed upon 532 nm laser flash photolysis of approximately 0.2 M thioketenes in benzene: (A) 1; (B) 2; (C) 3. The insets show kinetic traces at 450 nm for (a) 1, (b) 2 and (c) 3 in benzene.

Fig. 2. Transient absorption spectra (end-of-pulse) observed at 7  $\mu$ s following 337.1 nm laser flash photolysis of (A) 1 (0.03 M), (B) 2 (0.03 M) and (C) 3 (0.04 M) in benzene. Insets: kinetic traces for (a) 1 at 385 nm, (b) 2 at 385 nm and (c) 3 at 330 nm.

under 337.1 or 266 nm laser excitation (the observations in the latter case are not considered to be definitive because of the lower laser intensity and distortions from spurious emissions and noise).

The triplet energies  $E_T$  of thioketenes 1 and 2 were estimated from kinetic data for the quenching of a series of sensitizer triplets ( $E_T = 42 - 69$  kcal mol<sup>-1</sup>) in benzene. The sensitizer triplets were generated by direct excitation at 337.1 nm and were monitored at or near their absorption maxima. The experiments with pyrene and *all-trans*-1,4-diphenyl-1,3-butadiene were performed in the presence of 0.06 M ethyl iodide. For the butadiene, intrinsic intersystem crossing is negligible, but the external heavy-atom effect from ethyl iodide leads to efficient triplet formation [12]. In the case of pyrene, the purpose of adding ethyl iodide was to render the singlet lifetime short so that the triplet decay kinetics could be sorted out without the complications that would arise if the singlets were to be formed slowly. For all of the sensitizers (Table 1), the rate constant  $k_{obs}^T$  for triplet decay was monitored as a function of the concentration of 1 or 2.

TABLE 1

Bimolecular rate constants for sensitizer triplet quenching by thioketenes 1 and 2 in benzene

Sensitizer	$E_T^a$ (kcal mol <sup>-1</sup> )	$\lambda_{mon}$ (nm)	$k_q^T b$ ( $\times 10^9$ M <sup>-1</sup> s <sup>-1</sup> )	
			1	2
Benzophenone	68.6	532	4.8	5.1
Fluorenone	53.0	440	6.2	6.5
1,2,3,4-Dibenzanthracene	50.8	450	6.0	4.3
Pyrene <sup>c</sup>	48.2	420	5.1	4.3
Benz( $\alpha$ )anthracene	47.2	490	6.0	4.6
Pyrene-1-aldehyde	$\approx 45.0$	440	2.4	3.5
Anthracene	42.7	428	0.37	0.69
<i>all-trans</i> -1,4-Diphenyl-1,3-butadiene <sup>c</sup>	42.3	410	0.023	0.23
1-Chloroanthracene	42.1	435	0.27	0.58
Benz( $\alpha$ )pyrene	41.9	475	0.20	0.53

<sup>a</sup>Taken from refs. 16 - 18.

<sup>b</sup> $\pm 15\%$ .

<sup>c</sup>In benzene containing 0.06 M ethyl iodide (see text).

The bimolecular rate constants  $k_q^T$  for quenching were obtained from linear plots based on the equation

$$k_{obs}^T = \tau_T^{-1} + k_q^T [TK]$$

where  $\tau_T$  is the triplet lifetime in the absence of a quencher and [TK] is the thioketene concentration.

Figure 3 shows the Sandros plots [19] for triplet quenching by 1 and 2. The bending regions of the plots give estimates for the  $E_T$  of 1 and 2 as

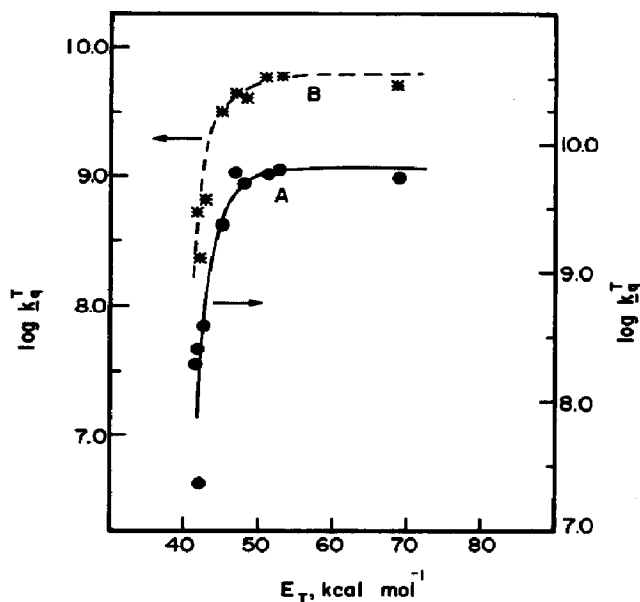


Fig. 3. Sandros plots for the quenching of sensitizer triplets by (A) 1 and (B) 2 in benzene.

43 - 44 kcal mol<sup>-1</sup>. From the onsets of the lowest energy  $n, \pi^*$  band systems, the lowest singlet states ( $S_1$ ) in 1 and 2 are located in the vicinity of 46 kcal mol<sup>-1</sup>. Thus, small  $S_1-T_1$  energy separations (2 - 3 kcal mol<sup>-1</sup>) are suggested; this is characteristic of the transitions of  $n, \pi^*$  origin [20], especially in the case of thiocarbonyls.

The near total quenching of benzophenone and acetophenone triplets ( $\lambda_{ex} = 355$  nm) by 1 at 15 - 20 mM in benzene does not lead to any long-lived residual absorption following the rapid decay of the ketone triplets. The latter are very short lived under the conditions of the experiment ( $\tau \leq 12$  ns). Since the mechanism of the quenching is most probably triplet energy transfer (exothermic) leading to the formation of the thioketene triplet, the lack of observation of the latter suggests that it is too short lived and/or very weakly absorbing.

From the location of their triplet energies (43 - 44 kcal mol<sup>-1</sup>), thioketene triplets are expected to behave as efficient sensitizers for *all-trans*-1,6-diphenyl-1,3,5-hexatriene (DPH) triplet ( $E_T \approx 34$  kcal mol<sup>-1</sup>) [21, 22]. The ground state of DPH does not absorb at 532 nm and its triplet is characterized [12, 21] by very high extinction coefficients ( $\epsilon_{max}^T \approx 1 \times 10^5$  M<sup>-1</sup> cm<sup>-1</sup> at 426 nm in benzene). Thus, DPH is suitable for monitoring any triplet formation under 532 nm laser excitation of the thioketenes. Experiments were done using optically matched solutions of 4,4'-dimethoxythiobenzophenone (reference,  $\phi_T = 1$  [23]) and the thioketenes in benzene (absorbance, 0.01 in a 1 cm cell at 532 nm). The end-of-pulse absorbance changes due to <sup>3</sup>DPH\* were measured at 426 nm in the presence of varying

concentrations of DPH (5 - 20 mM). The following various photophysical processes occurred in the experiment:



Based on reactions (2) - (5), the absorbance changes  $\Delta A_{\text{DPH}}^T$  due to  ${}^3\text{DPH}^*$  are related to  $[\text{DPH}]$  by the equation

$$\Delta A_{\text{DPH}}^T = \text{const} \times \phi_T \frac{k_q^T \tau_T [\text{DPH}]}{1 + k_q^T \tau_T [\text{DPH}]}$$

( $\phi_T$ , intersystem crossing yield of a thioketene). As expected from this equation, the plots of  $1/\Delta A_{\text{DPH}}^T$  against  $1/[\text{DPH}]$ , shown in Fig. 4, are reasonably linear. The intercept-to-slope ratios of these plots give  $k_q^T \tau_T$  while a comparison of the intercept for a thioketene with that for 4,4'-dimethoxythiobenzophenone ( $\phi_T = 1$ ) allowed us to determine the triplet yield  $\phi_T$  of the

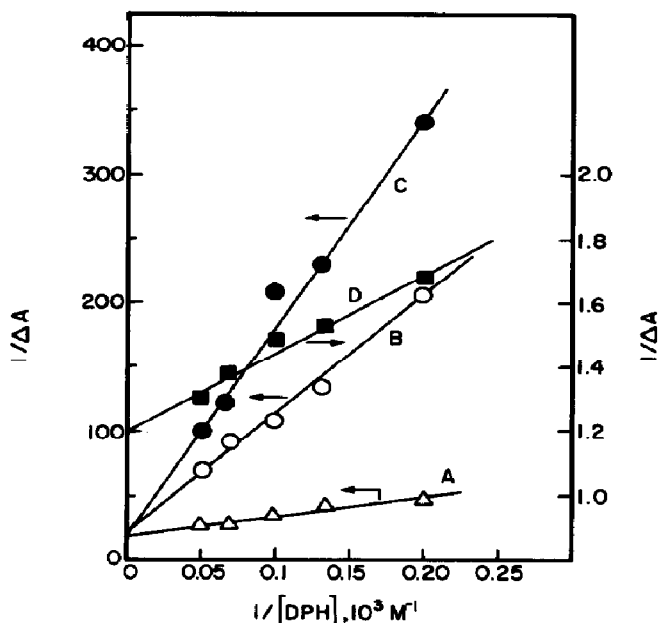


Fig. 4. Double reciprocal plots of absorbance change at 426 nm due to DPH triplet vs. DPH concentration in benzene: (A) 1; (B) 2; (C) 3; (D) 4,4'-dimethoxythiobenzophenone. The solutions were optically matched at the laser excitation wavelength of 532 nm (absorbance, 0.01 in a 1 cm cell).

former. It should be noted that blank experiments were done using the highest [DPH] in the absence of the thioketene substrates to ensure that the absorbance changes due to  $^3\text{DPH}^*$  were not spurious. Singlet-singlet energy transfer from thioketenes to DPH followed by intersystem crossing in the latter is ruled out on the basis of the following. First, the process would be endothermic by more than 20 kcal mol $^{-1}$ , based on the locations of  $S_1$  in thioketenes (seen in absorption) and DPH (estimated from fluorescence). Second, no DPH fluorescence is observed in the course of the quenching. Third, short thioketene singlet ( $S_1$ ) lifetimes (in analogy to thioketones [2, 24 - 26]) and negligible quantum yields of intersystem crossing in DPH ( $\phi_T = 0.03$  in benzene [12]) render the singlet-singlet energy transfer pathway inefficient.

The data concerning  $\phi_T$  and  $k_q^T \tau_T$  are given in Table 2. Based on a reasonable value of  $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the rate constant  $k_q^T$  for diffusion-controlled triplet energy transfer, the  $\tau_T$  are estimated to be in the range 2.4 - 26 ns. These short triplet lifetimes are probably in part due to self-quenching



this being well known for thioketone triplets [2, 4, 13, 23, 27 - 33]. However, using the highest value (about  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) of  $k_{\text{SQ}}$  measured [31] for thioketone triplets in benzene, one can see that less than 50% of the magnitudes of the high rate constants ( $\tau_T^{-1}$ ) observed for triplet decay at millimolar thioketone concentrations are accounted for by the self-quenching. Also, static quenching from extensive ground state self-association is unlikely for these sterically crowded molecules at millimolar concentrations in fluid solution. In particular, for 2 and 3 the very short  $\tau_T$  (shorter than 5 ns) are possible if and only if the thioketene triplets are intrinsically short lived. In view of the facts that the lowest triplet state ( $T_1$ ) of 1 is not photoreactive [7] and that no phosphorescence is observed for 1 - 3 at room temperature (or at 77 K), it is concluded that the  $T_1 \rightsquigarrow S_0$  process is unusually fast for the thioketenes.

Thioketones, both aromatic and aliphatic, are usually characterized by triplet yields close to unity [2, 13, 23, 29, 31, 33]. In contrast, the thio-

TABLE 2

Triplet photophysical data of thioketenes in benzene at 295 K

Thioketene	Concentration used (mM)	$\phi_T$	$k_q^T \tau_T$ ( $\text{M}^{-1}$ )	$\tau_T^a$ (ns)
1	1.6	0.06	130	26
2	1.7	0.05	24	4.8
3	1.3	0.06	12	2.4

<sup>a</sup>Based on  $k_q^T = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .



ketenes under examination apparently possess very low intersystem crossing efficiencies (less than 0.1 in benzene). Again, thioketene 1 has been found [7] to be photostable in various solvents upon excitation to its  $n,\pi^*$  singlet state ( $S_1$ ). This, combined with the fact that there is no detectable fluorescence from 1 - 3, suggests that the  $S_1$  photophysics of the thioketenes is dominated by internal conversion to the ground state.

In view of the small  $S_1$ - $T_1$  gap (2 - 3 kcal mol<sup>-1</sup>), it is possible that the lowest excited singlet and triplet states of thioketenes are substantially mixed. Even if unmixed, it is possible for  $S_1$  and  $T_1$  to be in thermal equilibrium. Based on an energy difference of 2 kcal mol<sup>-1</sup>, the population of  $S_1$  equilibrated with  $T_1$  at room temperature would be about 3% of that of the latter. Thus, the intrinsic rapidity of triplet decay may arise from the contribution of  $S_1$ , mixed into and/or in equilibrium with  $T_1$ . However, if this is the case, it is not obvious why the triplet yields measured from energy transfer to DPH are very small (less than 0.1). The spin-orbit coupling mechanism by which  $S_1$  and  $T_1$  would be mixed should also render intersystem crossing ( $S_1 \rightleftharpoons T_1$ ) facile. In terms of fast equilibration between  $S_1$  and  $T_1$  with an equilibrium constant  $K = [T_1]/[S_1]$ , and on the assumption that the quenching of  $T_1$  by DPH would result in triplet energy transfer with unit efficiency while that of  $S_1$  would not give any  $^3\text{DPH}^*$ , it can be shown that the limiting triplet yield at  $[\text{DPH}]_{\rightarrow\infty}$  is given by  $K/(r + K)$ , where  $r$  is the ratio of thioketene singlet and triplet quenching rate constants (by DPH). It is unlikely that  $r > 6$ . Thus, based on a value of 30 for  $K$ , the observed  $\phi_T$  should be greater than 0.8. Note that an energy transfer mechanism for  $S_1$  quenching by DPH is improbable because it is endothermic by more than 20 kcal mol<sup>-1</sup> (*vide supra*).

Owing to a number of theoretical calculations having been reported on thioketenes and related systems [34 - 37], some information on their ground and excited state potential energy surfaces is available. Based on *ab initio* self-consistent field (SCF) and self-consistent field-configuration interaction (SCF-CI) calculations, ketenes have been predicted to have a geometry with a planar  $C_s$  symmetry on the excited singlet and triplet surfaces [34, 35]. Furthermore, the molecule is bent ( $C-\hat{C}-O$ , 130°) in the molecular plane. Interestingly, a bent geometry appears to be preferred in the excited singlet of allenes also [36]. Recent theoretical studies (SCF gradient and CI methods) on thioketene also suggest that the optimized geometry of its lowest triplet state is bent ( $C-\hat{C}-S$ , 137.1°) [37]. It is noteworthy that this calculation estimates the triplet energy of thioketene to be 42.6 kcal mol<sup>-1</sup>, which is in close agreement with the value measured by us for thioketenes 1 and 2. Based on the information available on the excited singlet state geometries of allenes and ketenes [34 - 37], it is likely that thioketenes also possess a bent geometry, similar to the triplet, in their lowest excited singlet state.

The unusual geometry adopted by the thioketenes on the excited singlet and triplet surfaces may be responsible for the low quantum yields of intersystem crossing from  $S_1$  to  $T_1$  and for the short lifetime of the triplet

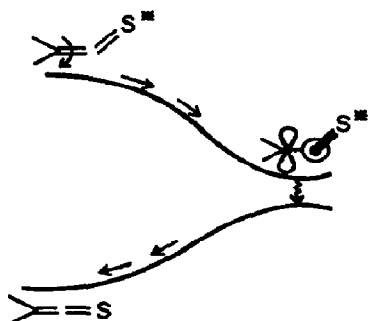


Fig. 5. The pseudoisomerization process responsible for fast internal conversion from  $S_1$  and  $T_1$ .

state. We believe that the radiationless process which competes with the intersystem crossing in the singlet state and with the usual radiative and non-radiative processes in the triplet state is most probably a pseudogeometrical isomerization process (illustrated in Fig. 5). This process does not lead to isolable products and does not operate in the absence of a bent geometry. The analogous geometrical isomerization of olefins in the excited singlet and triplet states is a classical reaction. At this stage, no further evidence can be presented for the presence of this process or any other fast process accounting for the short lifetimes of excited singlets and triplets of thioketenes.

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