The Photophysics, Physical Photochemistry, and Related Spectroscopy of Thiocarbonyls

Andrzej Maciejewski

Faculty of Chemistry, A. Mickiewicz University, 6 Grunwaldzka St., 60-780 Poznan, Poland

Ronald P. Steer*

Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0

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I. Introduction

Recent reviews[1-3] document that compounds containing the carbonyl group continue to play an important role in the development of our understanding of the photochemistry and photophysics of polyatomic molecules. However, in the last two decades, advances in the ability to synthesize and study thermodynamically less stable species have led to greatly enhanced interest in structurally similar compounds in which the carbonyl oxygen atom is replaced by sulfur (the thiocarbonyls), selenium, or tellurium and the carbonyl carbon atom is replaced by silicon or germanium. Prominent among the technical advances which have generated this interest are the development of (i) ever better laser methods for pumping and probing target molecules of increasing complexity and shorter lifetime, and (ii) supersonic expansion techniques for synthesizing and characterizing van der Waals molecules, clusters, and other unstable species in situ.

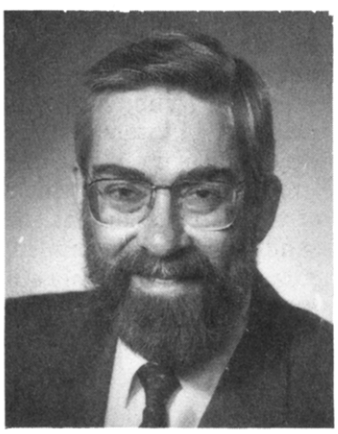
A detailed understanding of the photochemistry and photophysics of any system must be based on spectroscopic measurements and theoretical calculations of the structures of the ground and excited electronic states of the molecules of interest. A recent comprehensive review by Clouthier and Moule[4] describes the clear periodic group relationships which are emerging from studies of the spectroscopy of small carbonyls, thiocarbonyls, and selenocarbonyls such as 1 and 2 (cf. structures, Figure 1). Spectroscopic studies of larger thiocarbonyls such as **3**, **6a**, **7a**, and **8a** reveal similar trends; those related to the photophysics and photochemistry of these compounds will be discussed in this review.

The following general picture has emerged. The carbonyl and thiocarbonyl chromophores both possess a nuclear framework of either C_{2v} or C_s local symmetry in the ground state and exhibit bonding properties which are qualitatively similarly to one another. However, the C=S bond is weaker than the C=O bond (ca. 430 kJ mol^{-1} vs ca. 635 kJ mol^{-1}), and the excited electronic states are found at lower energies in the sulfur-containing species. Thus, the lowest excited states, S_1 and T_1 of (n,π^*) configuration, are accessible via absorption of single quanta in the visible or near infrared in the unconjugated aliphatic and simple aromatic thiocarbonyls, whereas the same transitions occur in the near UV in the corresponding carbonyls. Transitions to the lowest $^1(\pi,\pi^*)$ (S_2) and Rydberg (S_n, $n \geq 3$) excited states occur in the near UV-blue and in the quartz ultraviolet, respectively, in the thiocarbonyls, but are found at substantially higher energies in the parent carbonyls.

These differences in the energy and spacing of the electronic states lead to dramatic differences in the photochemistry and photophysics of the two classes of compounds. In particular, the (n,π^*) and (π,π^*) excited states of larger, unstrained thiocarbonyls are often photostable and tend to relax by photophysical rather than photochemical processes in unreactive media. In

* To whom correspondence should be addressed.

Andrzej Maciejewski was born in Poland in 1948. He obtained the Ph.D. and habilitation degrees at A. Mickiewicz University in Poznan where he is now a member of the Faculty of Chemistry. His research on thioketones began 10 years ago when he joined Ron Steer's group as a Postdoctoral Fellow. This happy collaboration has continued ever since. His research interests include studies of the dynamics of photophysical and photochemical processes in condensed media, solute–solvent interactions (with particular emphasis on perfluoroalkane solvents), and quenching processes. He carries out his research in a group of attentive co-workers and enjoys fruitful cooperation with Marek Szymanski and Wlodek Augustiniak. He is greatly indebted to his wife, Iwona, for her devotion and understanding.



Ron Steer, now almost a half-century old, was born and raised in the magnificent Canadian prairie region, obtaining both his B.Sc. and Ph.D. at the University of Saskatchewan. After postdoctoral research with Jim Pitts at the University of California, Riverside, he returned to his alma mater where he is now Professor of Chemistry and one of the Principal Investigators in the Canadian Centers of Excellence in Molecular and Interfacial Dynamics. His interest in thiocarbonyls arose from studies in his laboratory of the photochemistry of cyclic sulfides in which thioformaldehyde is a product and from the chance observation of fluorescence from the second excited singlet state of thiophosgene. This interest has been sustained over 20 years by the work in Saskatoon of a remarkable group of students, postdocs, and senior collaborators in whose accomplishments he takes considerable pride. Married (Sheilagh) with two grown children (David and Jennifer), he spends his spare time as a serious student of voice.

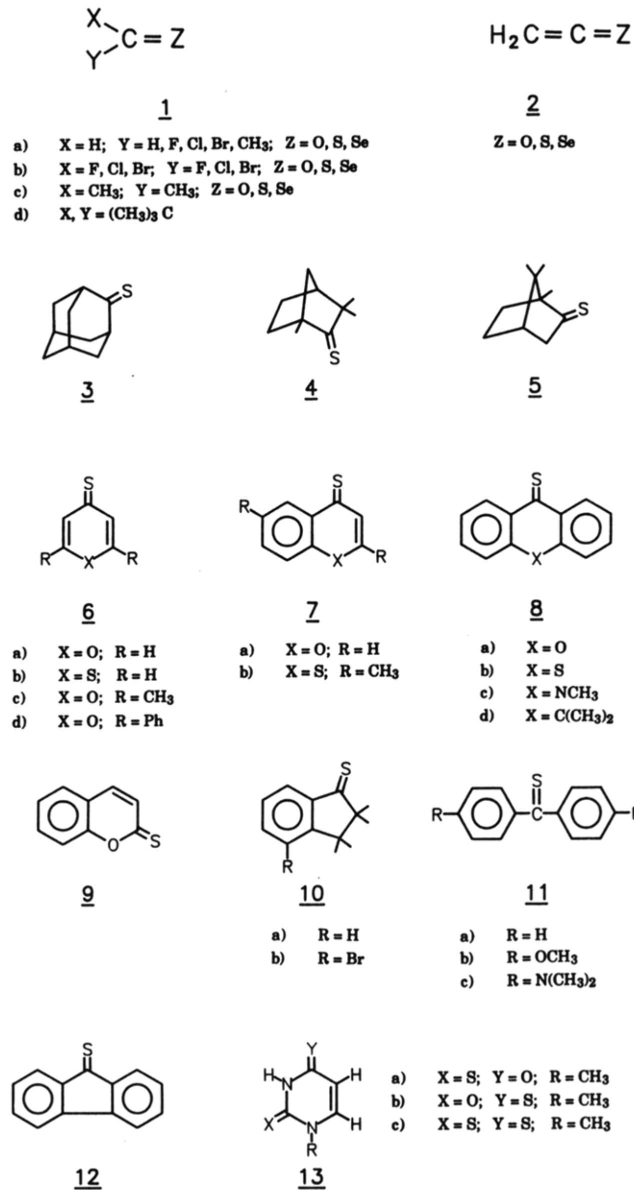


Figure 1. Structures of thiocarbonyls. I.

addition, the relatively large electronic energy gaps between the $^1(\pi,\pi^*)$ and the $^1(n,\pi^*)$ states in the thiocarbonyls lead to a strong Franck–Condon inhibition of the rates of radiationless decay of their upper states. The $^1(\pi,\pi^*)$ states can therefore be relatively long-lived, and this enables them both to fluoresce with large quantum yields (like azulene and its derivatives[5]) and to react chemically with solvent, ground state thiocarbonyl, and other species in violation of Kasha's rule.[6] Intense emission from both the $^1(\pi,\pi^*)$ and lower states thus may be used as a powerful diagnostic tool for elucidating the excited-state relaxation rates and mechanisms in these systems.

A. Scope of the Review

The brief introduction above suggests that thiocarbonyls can serve as useful models for examining the chemistry and physics of a given target molecule in a number of electronic states. Accessible states include those which, in other similar classes of compounds, would lie much higher in energy and would relax primarily by fragmentation or other very fast radiationless processes. This review will therefore focus on unique aspects of photochemistry and photophysics which are revealed in studies of the thiocarbonyls. It follows three previous reviews, two now more than a decade old, concerning wavelength-dependent photochemistry,[7] the structure and excited-state dynamics of small thiocarbonyls,[8] and intramolecular relaxation processes of thiones in solution.[9] Studies of both tetraatomic and larger molecules will be included, as will a discussion of the results of experiments in media ranging from cryogenic matrices to molecular beams.

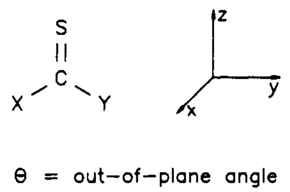


Figure 2. Axis convention employed in this review.

With one or two exceptions larger molecules possessing heteroatoms in positions α to the thiocarbonyl group will not be considered. Although this group includes several classes of biologically important compounds, such as the thiouracils, thiopurines, and thiopyrimidines, their photochemical and photophysical properties are quite different from those of the thioketones on which we shall focus. The organic photochemistry of the thiones has been reviewed comprehensively in the recent past[10-13] and will not be a major theme of the present work.

Throughout this review we shall use the notation for electronic states which is most familiar to photochemists; S_0 identifies the ground state, and S_1, S_2, ... and T_1, T_2, ... the excited states of increasing energy in the singlet and triplet manifolds, respectively. Herzberg's equivalent notation of $\tilde{X}$ for the ground state and $\tilde{A}$, $\tilde{B}$, ..., $\tilde{a}$, $\tilde{b}$, ... for the excited states is frequently used in the spectroscopic literature which we review. We shall also adopt the axis convention shown in Figure 2 when discussing symmetry-related matters.

II. Electronic Spectroscopy and Interstate Coupling

A minimum of five electronic states, S_0, S_1, S_2, T_1, and T_2, must be considered in describing the photochemistry and photophysics of thiocarbonyls excited in the near-UV and visible regions of the spectrum. The lowest Rydberg states are also accessible in the quartz ultraviolet in most thiocarbonyls, and there is now good evidence that doubly excited states of (n^0,π^{*2}) configuration also come into play in this region. Fortunately, the T_1, S_1, S_2, and low Rydberg states are often spectrally distinct, and when this is the case they may be populated selectively by suitable choice of excitation wavelength. Therefore, by starting from the bottom of the electronic manifold (i.e., S_0) and moving ever higher in energy, the behavior of a given thiocarbonyl can, in principle, be well-characterized. By doing the same for the series of structurally related species, a comprehensive picture of the whole class of compounds can be assembled and periodic group relationships established.

We therefore begin by examining the UV-visible spectroscopy of molecules containing the thiocarbonyl group. From this we shall learn about the energies and structures of the various electronic states and how they are coupled. This, in turn, provides the framework for interpreting the observed photochemistry and photophysics.

A. Tetraatomic Molecules

The electronic spectroscopy of molecules such H_2CS, D_2CS, the thiocarbonyl halides, thioacetaldehyde, thioacetone, and thioketene has been comprehensively reviewed recently by Clouthier and Moule.[4] Only material essential for the development of the present review and new results will be discussed here. Data describing the ground and best-characterized excited states of two representative small thiocarbonyls, H_2CS and Cl_2CS, are given in Table I.

The ground states of the symmetrically and asymmetrically substituted thiocarbonyls, X_2CS and XYCS of C_{2v} and C_s symmetry respectively, are planar about the four-atom framework of the chromophore. The tetraatomic thiocarbonyls possess six vibrational modes consisting of three a_1, one b_1, and two b_2 vibrations for C_{2v} molecules, or five a′ and one a″ vibrations for those belonging to the C_s point group. Analyses of the infrared, Raman, and microwave spectra of these compounds have provided well-established ground-state vibrational, rotational, and structural parameters.[4] The C=S bonds are ca. 1.60 Å in length and the X–C–X(Y) angles tend to be slightly less than 120° (cf. Table I).

The ground electronic configuration of H_2CS[14] is $KKL(5a_1)^2(6a_1)^2(2b_2)^2(7a_1)^2(2b_1)^2(3b_2)^2$ or $...(\pi)^2(n)^2$, whereas that for Cl_2CS[15] is $...(11a_1)^2(7b_2)^2(3b_1)^2(12a_1)^2(2a_2)^2(13a_1)^2(8b_2)^2(4b_1)^2(9b_2)^2$ in which $2a_2$, $13a_1$, and $8b_2$ are Cl lone pair orbitals lying below $(\pi)^2(n)^2$. The lowest unoccupied molecular orbital is one of the largely π^* (b_1) character, and the lowest excited electronic states are clearly of (n,π^*) electron configuration in both molecules. Accordingly, the electronic transitions of lowest energy, $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$, are of $^{1,3}A_2 \leftarrow {}^1A_1$ or $^{1,3}A'' \leftarrow {}^1A'$ symmetry for C_{2v} and C_s molecules, respectively. The $S_1 \leftarrow S_0$ transitions in the visible are electric dipole forbidden but appear weakly as a result of either magnetic dipole-induced interactions or vibronic mixing.[21] The $T_1 \leftarrow S_0$ transitions are formally electron spin forbidden and are weaker still, but are nevertheless much stronger than the corresponding transitions in the carbonyls because of larger spin–orbit coupling effects in the sulfur-containing species (vide infra). The S_1–T_1 energy gaps (cf. Table I) are small, owing to the rather small overlap of the n and π^* orbitals which, nominally, are singly occupied in these states. The $T_1 \leftarrow S_0$ transition therefore appears as a weak band system whose origin lies only slightly to the red of that of the corresponding $S_1 \leftarrow S_0$ system. Both band systems are extensively overlapped and perturbed, complicating their analysis.[21] Magnetic rotation techniques have been useful in distinguishing between the singlet and triplet systems in Cl_2CS,[22] and in characterizing singlet–triplet perturbations in H_2CS.[21]

Analyses of the visible spectra have led to unambiguous S_1 and T_1 excited state structure determinations for both H_2CS and Cl_2CS. Both the C–S stretching (a_1) and out-of-plane bending (b_1) modes are active in these spectra. Measurement of the inversion splittings in the latter permit the excited state equilibrium out-of-plane angles and inversion barrier heights to be obtained with the aid of model upper state potential functions.[23] The results are given in Table I. Whereas H_2CS is "floppy-planar" in the S_1 and T_1 states,[21] the tetraatomic thiocarbonyl halides are distinctly nonplanar, in accord with Walsh's postulate,[24] and exhibit decreasing inversion barriers and out-of-plane angles in the sequence F > Cl > Br. The C–S moiety sustains a nominal decrease in bond order from 2 to 1.5 on n → π^* excitation, and this coincides with an increase in both

Table I. Structural and Other Parameters for H_2CS and Cl_2CS in Several Electronic States

	H_2CS					Cl_2CS			
	S_0	T_1	S_1	S_2[a]	S_3[b]	S_0	T_1	S_1	S_2[a]
T_0, cm^{-1}	0	14 507.4	16 394.4	44 685	47 110.8	0	17 492	18 716	34 275
θ, deg	0	11.9	0	~0	0	0	32	32	30
barrier, cm^{-1}	0	4.1	0	<50	0	0	726	620	729
r(C=S), Å	1.613 8	1.683	1.682	~2.1	1.604 7	1.602	1.815[c]	1.70	~2.1
r(C—X), Å	1.096 2	1.082	1.077		1.111 9	1.728	1.796[c]	1.75	
∠(X-C-X), deg	116.26	119.3	120.7		122.68	111.2	112.7[c]	119	
μ, D	1.649	0.548	0.850		-2.2	0.28			
vert IP,[d] eV	9.38					9.84			
ref(s)	4, 30	4, 31	4, 31	4, 8, 25, 36	4, 25	4, 15	4, 16	4, 17	18–20

[a] S_2 is taken to be the $^1(\pi,\pi^*)$, $^1A_1$, state. See text. [b] S_3 is the $^1B_2$, ^{1}(n,4s) Rydberg state. [c] By ab initio calculation, ref 16. [d] Vertical ionization potential.

the equilibrium C–S bond length and the X–C–X bond angle.

The lowest energy electric dipole allowed transitions in the thiocarbonyls involve a one-electron promotion to upper states of nominal $^1(\pi,\pi^*)$ configuration ($^1A_1$ in C_{2v} molecules). However, in the tetraatomic thiocarbonyls and the larger unconjugated aliphatic thiones, both the lowest Rydberg states and doubly excited states of $^1(n^0,\pi^{*2})$ configuration are found at similar energies. The density of electronic states is even larger in the thiocarbonyl halides owing to the presence of states of nominal (n_x,π^*_{cs}) configuration (X = Cl, Br, I). Extensive state mixing is therefore expected, and this has recently been documented both by calculation and by experiment.

A recent MRD-CI study of H_2CS by Hachey et al.[14] has revealed that states having configurations of (π,π^*), (n^0,π^{*2}), $(n,4p_y)$R, (n,4d)R, and the (π^2,n^2) ground state, all contribute to shaping the observed $^1A_1$ potential surfaces to which one has access in the near UV. A vertical transition to an $(n,4p_{4y})$ Rydberg state of $^1A_1$ symmetry is predicted at 6.57 eV, and this corresponds closely to a sharp feature in the UV spectrum at 187 nm (6.60 eV), previously assigned to a Rydberg transition.[25] The other $^1A_1$–$^1A_1$ UV band system observed[26] in H_2CS is strong and broad, has an origin near 221 nm (5.60 ev) and a maximum near 200 nm (6.2 eV), and exhibits a long progression of bands assigned to single quantum increments in the excited-state C–S stretching mode. The upper state has been assigned as S_2, $^1(\pi,\pi^*)$. This is consistent with the electric dipole allowed, z-polarized nature of the transition and the expectation that the C–S stretching vibration should be Franck-Condon active, owing to the reduction of the C–S bond order from 2 to 1. The MRD-CI calculations[14] confirm this assignment in that they correctly predict the energy of the pure electronic transition and reveal that the upper surface is highly distorted with a broad minimum at greatly extended C–S distances (Δr(C–S) ≈ 0.4 Å). The calculations also show that the oscillator strength of this transition is carried primarily by the $\pi \rightarrow \pi^*$, one-electron promotion, but that the (π,π^*) configuration only dominates the description of the upper state at intermediate C–S distances. In fact the (π^2,n^2) *ground-state* and (π,π^*) excited-state configurations contribute nearly equally to the lowest excited $^1A_1$ state at its distorted equilibrium geometry as a result of an avoided crossing.

Two additional transitions to (n,4s) and $(n,4p_z)$ Rydberg states, both of $^1B_2$ symmetry, have also been observed[25,26] in the UV spectrum of H_2CS. The lower energy of these, $^1B_2$(n,4s) ← $^1A_1$, consists of a strong feature centered at 212 nm. Under high resolution this absorption is seen to consist of a single band with well-resolved rotational structure, the analysis of which reveals that the molecule is planar in the upper state and, surprisingly, suffers a contraction in C–S bond length of ca. 0.007 Å (cf. Table I).

One-photon transitions to doubly excited states are formally forbidden, and no direct spectroscopic evidence of the $^1A_1(n^0,\pi^{*2})$ state in H_2CS is yet available. However, a weak transition ($f \approx 5 \times 10^{-5}$) has recently been observed experimentally[27] in Cl_2CS at wavelengths immediately to the red of its strong $\pi \rightarrow \pi^*$ transition in the near UV. Excitation in this weak band populates an excited state which exhibits no measurable emission and which is very short-lived in condensed media. This dark excited state was tentatively assigned to a doubly excited $^1A_1$ (n_S^0,π_{CS}^{*2}) state, although a triplet of (n_{Cl},π^*_{CS}) configuration could not be ruled out.

Over the past two decades, repeated attempts have been made to analyze the $S_2 \leftarrow S_0$, $^1A_1 \leftarrow {}^1A_1$ UV absorption spectrum of Cl_2CS. Analysis has been difficult because, like H_2CS, the origin band carries only a small fraction of the oscillator strength and vibrational hot bands dominate the room-temperature spectrum in the origin region. Nevertheless, by means of a careful analysis of the chlorine isotope splittings in the photographic spectra Judge and Moule[18] were able to identify two upper-state vibrational progressions and assigned a weak band at 34 278 cm^{-1} as the origin. However Dixon and Western,[19] using an optical–optical double resonance technique ($S_2 \leftarrow S_1 \leftarrow S_0$), reassigned the origin of the $S_2 \leftarrow S_0$ system to 33 991 cm^{-1} and found four progressions in upper-state modes, none of which corresponded to those observed by Judge and Moule. Most recently Ludwiczak et al.[20] confirmed the analysis of Judge and Moule using laser-induced fluorescence excitation (LIFE) spectroscopy in supersonically expanded Cl_2CS and located an upper state predissociation threshold at 35 725 ± 50 cm^{-1}, some 1450 cm^{-1} above the zero-point level. The results of Dixon and Western remained unexplained. However, given the relatively large numbers of electronic states accessible at these energies, the possibility that sequential two-photon absorption does not populate the same final state as that reached on direct one photon excitation in the UV should be assessed.

Only the triplets of (n,π^*) configuration have been well characterized in the thiocarbonyls.[4] However, both ab initio calculations and fragmentary experimental

Table II. Electronic Energies of the Valence States, Ground-State Dipole Moments, and Vertical Ionization Potentials of Selected Thiocarbonyls

compound	μ, D	vert IP, eV	electronic energy,[a,b] cm^{-1} T$_1$	S$_1$	S$_2$	ref(s)
CH_2CS	1.02	8.89		~18 000 (g)		55, 30, 4, 34
CH_3CHS	2.33	8.98	16 294			56, 30, 4, 35, 36
$(CH_3)_2CS$	2.37	8.60	17 328 (g)	19 880(?) (g)		57, 30, 4, 37
1d	2.19	7.8				57, 58
3			17 280 (PF)	19 500 (PF)	~36 300 (g)	38, 39
4	2.59	8.1	17 920 (EPA)	19 400 (PF)	~36 300 (g)	57, 30, 38, 39, 40
5	2.89	8.17			~36 300 (g)	57, 58, 38, 39
6a	3.95		17 180 (PF)	17 790 (PF)	27 490 (PF)	59, 41, 49, 50
			17 305 (S)			42
6b	3.9					59
7a			16 090 (PF)	16 780 (PF)	25 540 (PF)	41, 49, 50
			16 090 (S)		25 841 (S)	42, 48
8a	5.4		15 130 (A)	15 970 (A)	23 650 (A)	60, 41, 49
			15 102 (S)	16 093 (S)	23 333 (S)	43, 44
			15 382 (C)	16 039 (C)	24 275 (SSJ)	45–48
					23 990 (PF)	50
8a-d_8			15 312 (S)		24 302 (SSJ)	42, 51
8b	5.4		13 843 (S)	~14 900 (PF)	21 980 (PF)	60, 42, 49, 50
8c	5.2		~14 900 (A)		20 650 (A)	60, 172
8d				14 700 (A)	~26 800 (PF)	50
10a			16 150 (PF)	17 540 (PF)	26 480 (PF)	41, 50
11a	3.4	8.0	14 600 (A)	15 975 (A)	~27 000 (S)	61, 30, 40
			13 880 (B)	15 830 (A)		52
11b				16 475 (EPA)		40
11c			15 625 (EPA)	17 180 (EPA)		40
12			13 300 (A, 77 K)	14 450 (A, 77 K)	26 660 (A, 77 K)	53, 54
			13 141 (S)			44

[a] Energies in cm^{-1} are taken from the origin bands of the absorption or excitation spectra. [b] Abbreviations: S, Shpolskii matrix; PF, perfluoroalkane solvent; A, alkane solvent; B, benzene; C, crystalline host; EPA, ether pentane alcohol glass; SSJ, supersonic jet expansion; g, gas phase.

evidence show that T_2, of $^3A_1$ symmetry, lies relatively close to S_1 and T_1 and may therefore play an important role in the photochemistry and photophysics. T_2 is the $^3(\pi,\pi^*)$ companion of the $^1A_1$, $^1(\pi,\pi^*)$ state, but unlike S_1–T_1, the S_2 and T_2 states are well separated in energy due to strong correlation effects of electrons in the spatially overlapping π and π^* orbitals. Among the small thiocarbonyls T_2 has been observed spectroscopically only in Cl_2CS. For this compound the electron-impact energy-loss spectrum[28] exhibits a broad feature with a maximum near 25 000 cm^{-1} (3.1 eV) and an onset near 20 000 cm^{-1} (2.5 eV). The assignment of the upper state to T_2 is consistent with ab initio calculations[29] which place this state only slightly higher than S_1 in the prototype, H_2CS.

B. Larger Molecules

Over the last 50 years substantial numbers of spectroscopic data have been accumulated for organic molecules containing the thiocarbonyl group. Table II summarizes the available electronic state energies, ground-state dipole moments, and vertical ionization energies for those compounds which have been the object of photochemical and photophysical study. In order to provide comparable data for the largest number of compounds, the energies of the various electronic states have been taken from the absorption or excitation spectra when possible. Because these are subject to medium-induced shifts, preferred values are given for a variety media, including Shpolskii matrices, crystalline hosts, liquid solvents, and, in a few cases, the gas phase. The most comprehensive source of data on ionization energies is the review by Gleiter and Spanget-Larsen.[30] Only scattered experimental measurements of the dipole moments of larger thiocarbonyls exist in the current literature. However, extensive tables of calculated ground-state dipole moments have been compiled by Jug and Iffert[32] using SINDO1 and by Dewar and McKee[33] using MNDO. Frequent reference will be made to the experimental data[34–61] in this review. Recent calculations[62–66] at various levels of approximation complement these measurements.

Maki and co-workers[42,44,67–71] and Burland[45,72] have employed both optical spectroscopy and optical detection of magnetic resonance (ODMR) techniques to characterize the lowest triplet states of a number of larger thiones in various cryogenic media. The T_1 states of the aromatic thiones **6a**, **6c**, **7a**, **8a**, **8a**-d_8, **8b**, and **12** are all of $^3(n,\pi^*)$ configuration in the n-pentane and n-hexane Shpolskii matrices and xanthone crystalline hosts used in these studies. The $S_2 \leftarrow S_0$, $S_1 \leftarrow S_0$, and $T_1 \leftarrow S_0$ absorption and $S_2 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emission spectra all consist of sharp lines in these ordered media at low temperatures, although they are complicated by phonon sidebands and multiple trap sites in some cases. The (n,π^*) triplets are characterized by unusually large values of the zero-field splitting parameter, D*, (cf. Figure 3), and this results in the observation of two clearly resolvable subspectra in the $T_1 \rightarrow S_0$ phosphorescence emission. The subspectra are assigned to transitions between T_{1z} and S_0 or between the closely spaced (T_{1x},T_{1y}) pair of substates and S_0. The relative intensities of these subspectra as a function of temperature are consistent with the establishment of a Boltzmann (thermal equilibrium) distribution of populations in the near degenerate (T_{1x},T_{1y}) and the higher

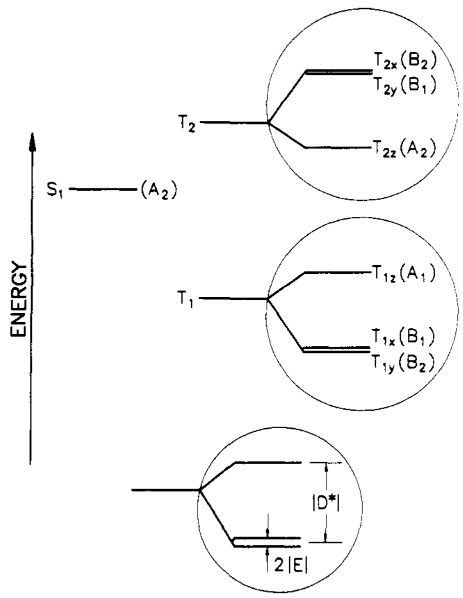


Figure 3. Schematic diagram showing the zero-field splittings and sublevel symmetries of the T_1 and T_2 states of C_{2v} thiocarbonyls. The ordering of the energies of T_{2z} and (T_{2x}, T_{2y}) is arbitrary in this diagram. $|D^*|$ and $2|E|$ are defined in the bottom panel.

T_{1z} sublevels even at temperatures as low as 1 K. This has enabled xanthione triplet (**8a**) to be used as a molecular sensor in a device for measuring temperatures in the $1\ K \le T \le 20$ K region.[67] The zero-field splitting parameters of the T_1 states of these thiones are summarized in Table III. Their energies are listed in Table II.

The (n,π^*) triplets of the aromatic thiones exhibit values of D^* ranging from −8.0 to −28 cm^{-1} and values of $|E|$ of ca. 0.05–0.07 cm^{-1}. (See Figure 3 for the definitions of these parameters.) The values of $|E|$ have been determined by microwave slow passage ODMR experiments, monitoring single vibronic band emission while sweeping through the $2|E|$ zero-field transition. The $2E$ splitting arises from spin–spin dipolar interactions in the triplet, but no discernible trend in $|E|$ is apparent in the series of thiones investigated to date. From a photophysics perspective, much more valuable information is obtainable from D^* which, in these thione triplets, is generally negative and unusually large.

Spin–orbit coupling is expected to be relatively important in these compounds owing to a modest "heavy atom" effect of the S atom (spin–orbit coupling constant of 397 cm^{-1} vs. 152 cm^{-1} for O). This, together with the close proximity of the T_2, $^3(\pi,\pi^*)$ state of $^3A_1$ electronic symmetry, was recognized in the first reports of Maki and co-workers[71] and of Burland[72] as the origin of both the sign and magnitude of D^*. As shown in Figure 3, the overall (spin ⊗ orbital) irreducible representations of T_{1x} and T_{1y} are the same as those of T_{2y} and T_{2x}, respectively, in C_{2v} symmetry. The spin–orbit interaction between the two pairs of states of the same symmetry raises T_{2x} and T_{2y} and lowers T_{1x},T_{1y}, whereas the T_{1z} level is affected primarily by spin–orbit coupling with S_2 ($^1A_1$). Because the T_2–T_1 separation is relatively small whereas the S_2–T_1 gap is large, (T_{1x},T_{1y}) are depressed and reside below T_{1z}, resulting in a large, negative D^*.

Measurements of D^* allow the location of T_2 to be deduced using a model in which the spin–orbit interaction is dominated by one-center terms on the S atom, viz.

$$\frac{D^*}{hc} = \frac{\alpha_{so}^2}{4}\left(\frac{1}{\Delta E(S_2 - T_1)} - \frac{1}{\Delta E(T_2 - T_1)}\right) \quad (1)$$

The spin–orbit coupling matrix element, α_{so}, may be estimated either from atomic parameters or from the observed radiative rate constant for T_1, leaving $E(T_2)$ as the only unknown in eq 1. The calculation suggests that T_2 should lie within 600–2400 cm^{-1} of T_1 for **8a** in a variety of host media,[44,45] which places it either slightly lower than or slightly higher than S_1. The dynamic studies of Molenkamp et al.[46] (vide infra) favor a T_2–T_1 gap at the high end of this range for **8a** in a crystalline xanthone host. Similar applications of eq 1 suggest that the structurally related series **6a**, **7a**, and **8a** could exhibit T_2–T_1 gaps which increase with increasing molecular size.

For comparison, Table III also presents values of $|D^*|$ and $|E|$ for several thiouracils,[70] **13**, in which the T_1 states are of $^3(\pi,\pi^*)$ configuration. Phosphorescence polarization measurements indicate that these triplets are nonplanar and that this enhances $^1(\pi,\pi^*)$–$^3(\pi,\pi^*)$ rather than $^1(n,\pi^*)$–$^3(\pi,\pi^*)$ mixing in these compounds. Note their relatively small values of $|D^*|$.

The T_1–S_0 phosphorescence and phosphorescence excitation spectra of a number of aromatic thiones have been measured under conditions which permit the resolution of their single vibronic features in some detail.[43–45,69,70] In each case in which T_1 is $^3(n,\pi^*)$, the origin is the strongest band in the spectrum, suggesting, on Franck–Condon grounds, that the molecule is not greatly distorted in the triplet state. In all such cases T_{1z}–S_0 carries the majority of the oscillator strength of the transition. This, in turn, suggests that spin–orbit coupling between T_{1z} and S_2 allows T_1–S_0 to "borrow" intensity from the strong, z-polarized S_2–S_0 transition. These ideas are completely consistent with the model used to explain the observed triplet zero-field splittings in the same aromatic thiones.

Although strong phosphorescence has been observed in almost all thiocarbonyls which have T_1 states of $^3(n,\pi^*)$ character, in condensed media at temperatures ≥77 K the emission generally consists only of several broad peaks separated by ca. 1100–1200 cm^{-1} (cf. Figure 4). Such spectra may be used to establish the energies of the T_1 states with modest accuracy, but are deceiving from a structural perspective. In the past[8,73] the 1100–1200-cm^{-1} spacing in $T_1 \rightarrow S_0$ was attributed to single quantum increments in the ground state C=S stretching mode. However, Mahaney and Huber[43] showed, in **8a**, that each peak in this apparent progression is in fact a composite of several strong bands, none of which is attributable to the C=S stretching mode. For this reason we shall discuss only those spectra which have been measured under conditions where sufficient vibrational resolution is available to permit a reasonable analysis.

Phosphorescence excitation spectroscopy in Shpolskii matrices has been used to establish the frequencies of a number of optically active fundamental vibrations in the T_1 states of **6a**,[42,69] **6c**,[42,69] **7a**,[42] **8a**,[42–44] **8a**-d_8,[43] **8b**,[44] and **12**.[44] $S_2 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emission spectroscopy in both low-temperature matrices[42–44,69] and, for **8a**, supersonic expansions[47] have also been employed to

Table III. Triplet Zero-Field Splitting Parameters for Several Thiocarbonyls in Cryogenic Matrices[a]

compd	host[b]	D^*, cm^{-1} [d]	$\lvert E\rvert$, cm^{-1}	ref(s)
6a	*n*-pentane (S)	−28,$^{(1)}$ −24$^{(2)}$	0.060 95,$^{(1)}$ 0.063 35$^{(2)}$	69
6c	*n*-hexane (S)	−24$^{(1)}$	0.067 84,$^{(1)}$ 0.068 13$^{(2)}$	69
7a	*n*-pentane, *n*-hexane (S)	−20.2	0.062 333	42
8a	*n*-pentane, *n*-hexane (S)	−15.9, (−15.5)	0.061 14	42, 44, 68, 71
	xanthone (C)	−20,$^{(1)}$ −11$^{(2)}$		45, 72
8a-d_8	*n*-pentane, *n*-hexane (S)	−15.9	0.061 44	42
8b	*n*-pentane, *n*-hexane (S)	−15.5	0.065 58	71
12	*n*-pentane, *n*-hexane (S)	−8.0,$^{(1)}$ −8.0$^{(2)}$	0.054 15,$^{(1)}$ 0.051 55$^{(1)}$	71
13a	1-methyluracil (C)	0.2895[c]	0.072 8	70
13b	1-methyluracil (C)	0.605[c]	0.050 0	70
13c	1-methyluracil (C)	0.870[c]	0.045 8	70

[a] See Figure 3 for definitions. [b] Abbreviation are as follows: S, Shpolskii matrix; C, crystalline host. [c] T_1 is $^3(\pi,\pi^*)$. Values of $\lvert D^*\rvert$ are given. [d] (1) and (2) are trap A and trap B, respectively.

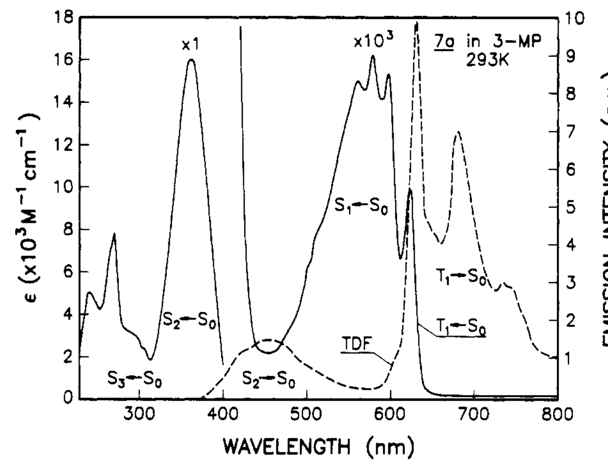


Figure 4. Absorption (—) and emission (- - -) spectra of **7a** in 3-methylpentane at 293 K. TDF refers to thermally activated delayed $S_1 \rightarrow S_0$ fluorescence.

determine the corresponding frequencies of the optically active modes in the ground state. Xanthione (**8a**) has been most thoroughly studies and is a useful model. This planar, C_{2v} molecule has 63 normal modes ($22a_1$, $9a_2$, $11b_1$, and $21b_2$), about one third of which can be identified as fundamentals in the emission, IR,[43] and Raman[45] spectra. The low-frequency modes are of particular interest because of their involvement in mode-selective vibrational predissociation of the van der Waals complexes.[47,48] In **8a** the observable fundamentals of lowest frequency are 239 (247), 320, and 380 (372) cm^{-1} in the ground state and 222 and 411 cm^{-1} in T_1. Progressions in the S_0 frequencies are attached to bands due to ring vibrations of 1031, 1243, and 1341 cm^{-1} frequency in the $T_1 \rightarrow S_0$ spectrum. The C=S stretching mode, which appears strongly in the spectra of the smaller thiocarbonyls, is observed only as a weak band at 1285 cm^{-1} in the $T_1 \rightarrow S_0$ spectrum of **8a**. In total, the spectra suggest that in the aromatic thiones T_1 is not greatly distorted compared with the ground state, that T_1 and T_2 are close in energy and significantly mixed, and that the shift in electron density associated with $T_1 \leftarrow S_0$ occurs mainly from S to the adjacent C. The latter is in agreement with CNDO/2-CI calculations.[73]

Measurement and partial vibrational analysis of the $T_1 \leftarrow S_0$ absorption and phosphorescence excitation spectra of thioacetaldehyde[35,36] in the gas phase at room temperature and of thioacetone[37] in a supersonic jet have also been reported. The room-temperature spectra are crowded, owing to the prominence of transitions involving the low-frequency internal rotational (torsional) modes of the methyl groups, and mild cooling in a supersonic expansion is of great help in simplifying the spectra and identifying the torsional progressions. In the planar ground state of CH_3CHS the eclipsed conformer is the preferred form, whereas in the pyramidal T_1 and S_1 states the antieclipsed conformer is preferred. In thioacetone the pattern of vibronic bands has been attributed to activity of both the methyl torsion and sulfur out-of-plane wagging modes. The planar ground state has an eclipsed–eclipsed conformation, but T_1 is pyramidal so that a complex potential surface governs the low-frequency motions.

The S_1–S_0 spectra of a limited number of larger thiocarbonyls have also been investigated by absorption and phosphorescence excitation spectroscopy in low-temperature matrices and in the gas phase. Fluorescence from S_1, $^1(n,\pi^*)$, is very weak in these compounds, however, owing to S_1's rapid radiationless relaxation to T_1 in all environments. The S_1–S_0 transitions are uniformly z-polarized in C_{2v} thiones, suggeting that they gain intensity by vibronic coupling between S_1 ($^1A_2$) and S_2 ($^1A_1$). (See ref 73, however, for an alternate interpretation.) The energies of a few S_1 vibrational levels have been reported only for **8a**,[43,46] thioacetaldehyde,[35,36] and thioacetone.[37] Nevertheless, the available data suggest that S_1 and T_1, both of (n,π^*) configuration, are structurally similar in all cases.

The S_2 state is of $^1(\pi,\pi^*)$ configuration ($^1A_1$ in C_{2v} symmetry) in all the simple aliphatic thiocarbonyls and in most aromatic thiones examined to date. The S_2–S_0 absorption and emission spectra (cf. Figure 4) are much broader than those of lower energies, and the origin bands carry a smaller fraction of the oscillator strength. This suggests that, in general, the S_2 states are rather more distorted than S_1 and T_1. This is particularly true in the bi- and tricyclic thiones[39] **3–5**, and in thioacetaldehyde,[4,36] thioacetone,[37] and related thioketones,[74] which exhibit structureless $S_2 \leftarrow S_0$ spectra at low resolution.

Thiofluorenone (**12**) is apparently exceptional[53,54] and exhibits a weak S_2 ($^1B_2$) $\leftarrow$ S_0 ($^1A_1$) transition at ca. 18 710 cm^{-1} (3-methylpentane glass at 77 K). The strong $\pi \rightarrow \pi^*$ transition is then S_3–S_0 with an origin at 26 600 cm^{-1}.

Vibrationally resolved S_2–S_0 fluorescence, fluorescence excitation, and phosphorescence excitation spectra have been measured[43,47] only for **8a**, although an S_2–S_0 fluorescence excitation spectrum of supersonically expanded **7a** has also been reported recently. The

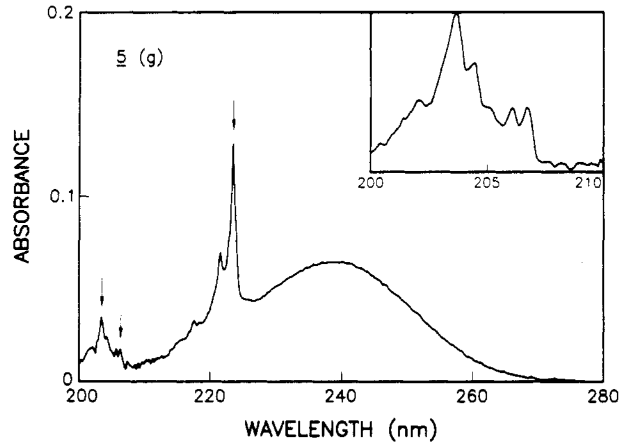


Figure 5. Absorption spectrum of gaseous **5** in the UV region. Arrows mark the origins of Rydberg transitions. The inset shows the 200–210-nm region in greater detail.

excitation spectra of **8a** in both Shpolskii matrices and in a supersonic expansion are rich in vibrational information, but a detailed analysis from which an S_2 structure might be obtained has not yet been attempted. Low-frequency excited-state modes of 147, 186, 230, 335, 340, 405, 623, and 651 cm^{-1} can be identified from the spectrum. Of these the 335 and 623 cm^{-1} vibrations are particularly active in the spectra and also act as promoting modes in the nonradiative decay of the upper state (vide infra). Both the spectra and CNDO/2-CI calculations[73] suggest that the $S_2 \leftarrow S_0$ transition in **8a** is well characterized by a one-electron $\pi_{CS} \rightarrow \pi^*_{CS}$ promotion involving the transfer of considerable electron density from S to the thiocarbonyl C atom, but relatively little to the ring C atoms. This is in sharp contrast to **8a**'s carbonyl analogue, xanthone, in which the lowest $\pi \rightarrow \pi^*$ transition is localized mainly in the aromatic rings.[73]

The lowest Rydberg transitions in the larger thiocarbonyls are readily identified as sharp features superimposed upon the broad, structureless $S_2 \leftarrow S_0$ system in their gas-phase UV absorption spectra (cf. Figure 5). Vibrational structure is associated with these transitions in some cases. Three such absorptions are generally observable in the quartz ultraviolet, the upper states of which are of $^1B_2(n,4s)$, $^1B_2(n,4p_z)$, and $^1A_1(n,4p_y)$ character for the C_{2v} molecules. The corresponding transition to the $^1A_2(n,4p_x)$ state is electric dipole forbidden and has not been observed. Substantial mixing of the $^1A_1$, $^1(n,4p_y)$ Rydberg, and $^1(\pi,\pi^*)$ valence state conjugates[75] is expected. In the larger thioaldehydes the (n,4s) Rydberg state is of $^1A'$ symmetry and is expected to mix substantially with the underlying $^1A'$, $^1(\pi,\pi^*)$ valence state. In thioacetaldehyde[4,36] this results in the appearance of a progression of five bands separated by single quantum increments of 1150 cm^{-1} in the Rydberg state's C=S stretching mode. The energies of the lowest Rydberg states of thioacetaldehyde, thioacetone, and related thiones, and the bi- and tricyclic thiones, **3–5**, are collected in Table IV. The assignments are supported by high-level, ab initio multireference CI calculations on H_2CS[29] and $(CH_3)_2CS$.[76]

With the gas-phase spectra in hand it is possible to assign weak features in the UV spectra of **3–5** in transparent *condensed* media to the same Rydberg transitions.[39] In such cases these bands are featureless and are asymmetrically broadened to higher energies, but are unambiguously assignable. There are no published reports of the observation of Rydberg transitions in the aromatic thiones.

Table IV. Energies of the Lowest Rydberg States of Thioacetaldehyde and Several Thioketones[a]

compd	$^1B_2(n,4s)^b$	$^1B_2(n,4p_z)^{b,c}$	$^1A_1(n,4p_y)^{b,c}$	ref
CH_3CHS	5.61	6.39	6.54	36
$(CH_3)_2CS$	5.49	6.40	6.52	37
$(CH_3)_3CCSCH_3$	5.54	6.21	6.42	74
$(CH_3)_2CHCSCH_3$	5.59	6.27	~6.4	74
3	5.43	6.01	6.15	39
4	5.55	5.94	6.08	39
5	5.54	6.00	6.09	39

[a] Energies in eV (1 eV = 8066 cm^{-1}). [b] Symmetries are given for the C_{2v} point group. [c] The ordering of the $(n,4p_z)$ and $(n,4p_y)$ states is based exclusively on the order predicted by calculation, refs 29 and 76, and could be reversed in some cases.

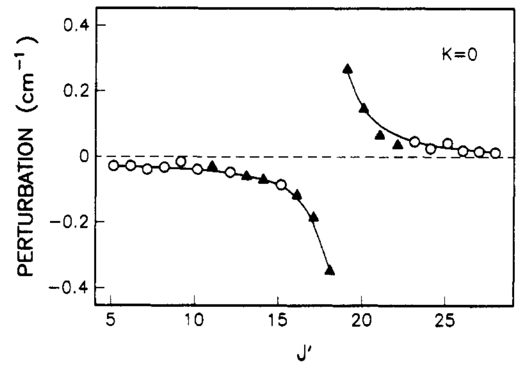


Figure 6. Perturbations in the $v' = 0$, $K = 0$ level of the S_1 ($^1A_2$) excited state of H_2CS. The open circles indicate levels observed only in absorption; the triangles indicate levels observed in both absorption and magnetic rotation. The full lines show the fit using calculations based on the vibronic spin–orbit mechanism (from ref 21).

C. Interstate Coupling

Full comprehension of the photochemistry and photophysics of any molecular system must include an understanding of the nature and extent of the mixing of its zeroth-order electronic states. In principle both singlet–singlet and singlet–triplet perturbations will be manifest in the electronic spectra of all molecules with closed-shell ground states. In practice, however, the details of such perturbations can only be observed in the gas-phase spectra of relatively small species with open rotational structures. Fortunately, thioformaldehyde is one such molecule, and it has been the subject of intense study in the past decade. Perturbations in the rovibronic spectra of H_2CS were first noted by Judge and King[77,78] and have since been the subject of a series of papers by Clouthier, Ramsay, and co-workers[79–87] and recent, elegant work by Dunlop and Clouthier.[88]

The rotationally resolved S_1–S_0 absorption and LIF spectra of H_2CS clearly exhibit perturbations of S_1 by both T_1 and S_0. For example, the large triplet perturbation of the $K_a' = 0$ subband of the magnetic dipole allowed S_1–S_0 origin is shown in Figure 6. The general selection rules for perturbations between rovibronic states require that only levels of the same overall symmetry species may interact, and that $\Delta J = 0$. The application of these rules to the S_1 ($^1A_2$) and T_1 ($^3A_2$)

states of H_2CS have been discussed.[21] Although direct spin–orbit coupling between states of the same orbital symmetry is not allowed, second-order vibronic-spin–orbit coupling[89] can quantitatively account[80] for the observed $^1A_2$–$^3A_2$ perturbations in H_2CS.

Coupling of S_1 to high vibrational levels of the ground state of H_2CS has also been observed by Ramsay and co-workers using microwave–optical double resonance,[81–84] sub-Doppler intermodulated fluorescence,[85,86] and Zeeman effect techniques.[87] The perturbations are small but are clearly associated with coupling to the ground state because magnetic rotation effects are absent. Measurements of the rotational g factors of the combining levels show that K_a is not a good quantum number in the high vibrational levels of S_0.[86,87]

The wealth of detail available from the study of H_2CS is of considerable value in interpreting the electronic spectra and excited state dynamic behavior of the larger thiocarbonyls. In particular, the observation of both singlet–singlet and singlet–triplet perturbations in the S_1 state of H_2CS demonstrates that both internal conversion and intersystem crossing must be considered in elucidating S_1's excited state dynamics. The following provides an overview of our current understanding of the nature of the nonradiative processes which are associated with interstate coupling interactions in these systems.

In the thiones the radiative T_1–S_0 transitions are z-polarized, in keeping with a direct T_{1z}–S_2 spin–orbit coupling mechanism. The $T_1 \leftarrow S_0$ absorption thus initially populates the T_{1z} sublevel almost exclusively, and subsequent spin–lattice relaxation (spin depolarization) is therefore required to populate T_{1x} and T_{1y}. T_{1z} undergoes direct spin–orbit coupling with S_0, and this provides the preferred mechanism of $T_1 \rightsquigarrow S_0^v$ intersystem crossing. However, the T_1–S_0 electronic energy gap is relatively large, and unfavorable Franck–Condon factors limit the rate of the process.

S_1 ($^1A_2$) is vibronically coupled with S_0 ($^1A_1$) via any of the non-totally symmetric vibrations of the molecule. Nevertheless $S_2 \rightsquigarrow S_0^v$ can also be relatively slow, again because of the small Franck–Condon factors associated with the transition.

S_1 does not exhibit direct spin–orbit coupling with T_1, but does interact directly with T_{2z} which is also of A_2 molecular symmetry. T_{1x} and T_{1y} interact directly with T_{2y} and T_{2x} respectively, as previously described, but T_{1z} does not exhibit first-order spin–orbit coupling with any of the T_2 sublevels or with S_1. Spin–lattice relaxation would be required (i) before T_{1z}^v produced by direct $T_{1z}^v \leftarrow S_0$ absorption could cross to T_2, and (ii) before T_{2z} produced by intersystem crossing from S_1^v could relax to T_1 by direct spin–orbit coupling mechanisms. The fact that the quantum yields of $S_1 \rightsquigarrow T_1$ intersystem crossing approach 1 and the lifetimes of S_1 are very short[46] both in condensed media at low temperature and in the gas phase therefore indicate that second-order vibronic-spin–orbit coupling between S_1 and T_1 is very effective in the larger thiones. This conclusion is in complete accord with the direct spectroscopic observations on H_2CS. However, studies of the dynamic behavior of S_1 at 1 K indicate that direct spin–orbit coupling of S_1^v to T_2 is even more effective[46] (vide infra). The close proximity of T_1, S_1, and T_2 suggests that each state will contain sizeable admixtures of the other two.

S_2 ($^1A_1$) will be vibronically coupled with S_1 ($^1A_2$) via the non-totally symmetric vibrational modes of the molecule. Nevertheless, the $S_2 \rightsquigarrow S_1^v$ internal conversion rate can still be relatively slow in rigid thiones like **7a** and **8a**, owing to the presence of a relatively large S_2–S_1 electronic energy gap. Within the framework of the theory of radiationless transitions,[90] high-frequency a_1 and b_2 in-plane symmetric and antisymmetric C–H stretching vibrations are expected to be the preferred accepting modes for $S_2 \rightsquigarrow S_1^v$ internal conversion. Direct spin–orbit coupling between S_2 and T_{1z} provides a possible mechanism for $S_2 \rightarrow T_1^v$ intersystem crossing, but the S_2–T_1 energy gap is large and no evidence of such a process has yet been found in the thiocarbonyls (vide infra).

The S_2 and S_0 states are of the same orbital symmetry, so strong coupling between them is expected in regions of close approach of the zeroth-order states. Such interactions lead to avoided crossings which severely distort the zeroth-order surfaces and alter the electronic character of the resulting upper state at different geometries. The upper-state surface can therefore be very complex, as demonstrated by calculations on H_2CS.[14]

D. van der Waals Complexes and Microsolvation

The solvent plays several important roles in the photochemistry and the photophysics of larger thiones in condensed fluid media. First, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions of the thiones undergo hypsochromic and bathochromic shifts, respectively, with increasing solvent polarizability, in a manner similar to that of many other systems. However, because T_1 and T_2 are in close proximity and are of different configuration in the thiones, they can invert in energy in more strongly interacting solvents such as benzene and acetonitrile.[91] Second, and of even greater importance, excited solute–solvent interactions dominate the photophysics of the S_2 states of the aromatic thiones in most common solvents, and as well, often dominate the S_2 and T_1 photochemistry of both the aliphatic and aromatic thiones. These matters will be reviewed in detail in subsequent sections. Recently, however, important information about solute–solvent interactions in the aromatic thiones has been obtained from studies of the spectra of van der Waals complexes of **7a** and **8a** in supersonic expansions, and this will be reviewed separately in the following section.

Topp and co-workers[47,92] were the first to synthesize several van der Waals complexes of an aromatic thione, **8a**, in a supersonic expansion and to examine them spectroscopically using both S_2–S_0 fluorescence and ground-state depletion (hole-burning) techniques. The S_2–S_0 LIFE, LIF, and hole-burning spectra of the bare thione are rich in vibrational structure and are in many ways typical of the rovibrationally cold, isolated species produced in supersonic expansions. Additional, red-shifted features appear in the low excitation energy region of these spectra when the fluorophore is coexpanded with a smaller complexing partner. These groups of lines are assigned to van der Waals complexes consisting of the substrate and one or more addends. Topp and co-workers[47,92] examined **8a** with a number of C_5–C_{10} alkanes, perfluoro-n-hexane and benzene. Later Steer and co-workers measured the S_2–S_0 LIFE

Table V. Microscopic Solvent Shifts Observed in the S_2–S_0 LIFE Spectra of 1:1 van der Waals Complexes of Benzopyranthione (7a) and Xanthione (8a)

partner	shift: $-\Delta\bar{\nu}$, cm^{-1} [a] 7a	8a [b]	ref
He	3.5(?)	7.5 (6.4)	48
Ne	17.5	18.5 (15.4)	48
Ar	57.0	55.5 (53.4)	48
Kr	76.0	76.0 (82.2)	48
Xe	103.0	108.8 (108.5)	48
CH_4		103.5	93
n-pentane		215	47
n-hexane		235	47
n-heptane		252	47
n-octane		264	47
n-decane		277	47
isooctane		130	92
cyclohexane		234	92
CF_4		78	93
n-C_6F_{14}		107, 144[c]	92

[a] Shifts are for the origin band. [b] Numbers in parentheses are calculated for $\mu(S_2) = \pm2.0$ D. [c] Possibly two isomers (cf. ref 92).

spectra of **7a** and **8a** complexed with the rare gases[48] and a wide variety of other species.[93]

The spectra due to the van der Waals complexes have a number of characteristics in common. First, the features due to the 1:1 complex are uniformly red-shifted by almost identical amounts compared with the same bands in the bare substrate molecule. This is taken as strong evidence that coupling between the vibrational modes of the aromatic substrate and either the low-frequency "van der Waals" modes of the complex or the vibrational modes of the complexing partner itself is weak. Small perturbations are seen, however, and these are significant.[92] Second, the microscopic solvation shifts are always to lower energies, consistent with the observed (S_2–S_0) transitions in condensed media (Table II). This shows unequivocally that the 1:1 complexes are more strongly bound in the S_2 state than in S_0. Third, as shown in Table V the magnitude of the shift depends upon the structure of the complexing partner, increasing with its increasing size within a homologous series and with increasing polarizability down a group, and is generally larger for the alkanes than for the corresponding perfluoroalkanes. Fourth, the features due to the van der Waals complexes disappear from the spectra when exciting to higher levels in the vibrational manifold due to vibrational predissociation. Finally Topp et al.[47,92] have used both hole-burning and emission techniques to show elegantly that several upper-state vibrations ($\bar{\nu}$ = 335, 623 cm^{-1}) act as promoting modes for the $S_2 \rightarrow (S_1/T_1)$ radiationless transition in the bare molecule. The effect is amplified in the van der Waals complexes with some larger molecules through perturbations by and conformational changes of the addend. The implications of these and related observations will be reviewed in section IV.

The spectra of the complexes of **7a** and **8a** with polyatomic addends are crowded and have not yet admitted a detailed vibrational analysis. On the other hand, the spectra of the complexes with the rare gases are relatively simple; those of **7a** are more revealing than those of the larger thione, **8a**.[48] Figure 7 shows a small portion of the S_2–S_0 LIFE spectra of **7a** with Ne. The spectra of both **7a** and **8a** expanded with He,

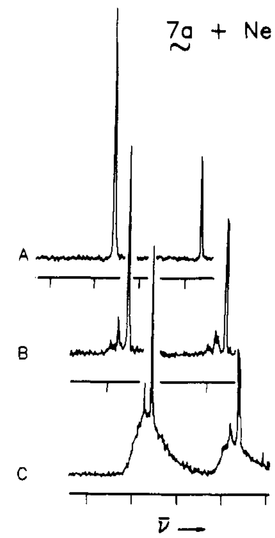


Figure 7. A portion of the S_2–S_0 fluorescence excitation spectrum of supersonically expanded **7a** in the region of the origin. A is the bare molecule. B is with ca. 1 atm of Ne. C is with ca. 3 atm of Ne. The total pressure is 4 atm, with the balance composed of He.

Ne, Ar, Kr, and Xe all exhibit two line like features shifted by equal increments to the red of each corresponding band in the bare molecule. These bands have been assigned to the 1:1 and 2:1 complexes. The rare gas atoms reside over the pyranthione ring, and the 2:1 complex therefore has a sandwich structure which, in **8a**, preserves C_{2v} symmetry. The spectra also show broad, underlying features which grow with increasing pressure of the complexing partner. These features are attributed to cluster formation and resemble similar features seen in the spectra taken in Shpolskii matrices.[43]

The rare gas atoms are bound to the thione by dipole-induced dipole and by dispersive forces. The theory of microscopic solvation[94,95] permits one to calculate the shifts in the vibronic bands on complexation using the ground-state polarizabilities and ionization energies of the substrate and its complexing partners, the ground- and excited-state dipole moments of the substrate, the energy and moment of the transition, and the distances between the centers of mass of the substrate and rare gas atom. For the rare gas complexes of **8a**, all of the required information except the excited-state dipole moment is either available (cf. Table II) or can be calculated.[48] The magnitude of the excited-state dipole moments of **8a** can therefore be deduced by finding the value which results in the best agreement between the calculated and observed shifts. For **8a**, $\mu(S_2) = \pm2.0$D results in an excellent fit (cf. Table V). Since $\mu(S_0)$ = 5.4 D (Table II), a substantial *decrease* in dipole moment must occur on excitation of **8a**, in agreement with the qualitative results of CNDO/2-CI calculations.[73] Because $\mu(S_2)$ of **8a** is small, its excited-state van der Waals complexes with nonpolar molecules will be stabilized almost exclusively by dispersive interactions.[48] This conclusion has important implications in the interpretation of the photochemistry and photophysics of the second excited singlet states of the aromatic thiones.

III. Photophysics and Photochemistry of Tetraatomic Thiocarbonyls

With a few exceptions,[96] excited-state emission measurements have proved to be the most useful—and often the only—tools for examining the photophysical behavior of the small thiocarbonyls. When emission can be observed both quantum yields and excited-state lifetimes can, in principle, be measured as a function of a number of experimental variables. This, in turn, allows both intramolecular and intermolecular excited-state relaxation processes to be explored at levels of detail limited only by one's ability to resolve and understand the spectroscopic features of the target molecule.

H_2CS is photostable in S_1 and T_1 and its electronic spectroscopy is relatively well understood, whereas Cl_2CS is known to undergo molecular and/or free radical dissociation when excited to S_2 or high vibrational levels of S_1. These two molecules have therefore been adopted as models in studies of the photophysical and photofragmentation dynamics of the tetraatomic thiocarbonyls. With the exception of some early work on ClFCS,[8,97] no photochemical or photophysical studies of the other known tetraatomic thiocarbonyls have been reported.

A. H_2CS

The H_2 + CS dissociation limit in H_2CS lies about 2000 cm^{-1} below S_1.[98] However, calculations[99-101] predict that the barrier to molecular dissociation on the ground-state surface is very high in the isolated molecule, and lies at about the same energy as those for fragmentation to H + HCS and isomerization to thiohydroxymethylene (HSCH). Thioformaldehyde is therefore expected to be photostable in S_1 and T_1, and unlike H_2CO,[102] the presence of the H_2 + CS dissociative continuum should not affect the dynamic behavior of the molecule. Although there have been some suggestions[103,104] that photochemistry plays an active role in the intramolecular dynamics of H_2CS in S_1 or T_1, recent experiments[88] have shown this not to be the case.

S_1–S_0 fluorescence from H_2CS was first observed by Clouthier and co-workers,[105] and the initial photophysical measurements on the molecule were made by Bruno and Steer[106] and by Kawasaki et al.[103,104] using relatively broad band laser excitation sources. However, recent work[88] has shown that the S_1 fluorescence lifetimes reported in these earlier studies were not measured under collision-free conditions and are too short.

In a tour de force of H_2CS photophysics Dunlop and Clouthier[88] recently measured the fluorescence lifetimes and relative fluorescence quantum yields of a large number of single rotational levels in the S_1 (4^1) state under collision-free conditions (pressures as low as 5×10^{-7} Torr). The absence of quantum interference effects and the single exponential nature of the fluorescence decay in all cases led them to the conclusion that the whole set of molecular eigenstates associated with a given rovibronic transition and lying within the Doppler width of the absorption line was excited within the 0.04 cm^{-1} line width of their pulsed laser excitation source. Four groups of excited-state levels were distinguishable and were classified using the theoretical framework of Tramer and Voltz,[107] Jortner et al.,[108,109] and others.[90] Unperturbed levels exhibited fluorescence quantum yields near unity and produced a very narrow range of lifetimes centered at 174 μs. The latter was taken to be the pure radiative lifetime of H_2CS (S_1) in the 4^1 level. Single rovibrational levels coupled to T_1 (as shown by triplet perturbations in the spectra) exhibited moderately longer lifetimes and quantum yields which were not significantly smaller than 1. The couplings are weak and rely on accidental near-coincidences of levels in S_1 and T_1. Levels of S_1 coupled to S_0 fell into two categories: those which exhibited behavior similar to those coupled to T_1, and a small number, characteristic of intermediate case photophysics, which exhibited substantially reduced fluorescence quantum yields and the longest lifetimes. Dunlop and Clouthier proposed a sequential coupling model similar to that developed for pyrazine[110] to account for the observed dynamics of molecules excited to these levels.

Phosphorescence from the T_1 state of H_2CS was first observed by Clouthier and Kerr[111,112] who employed laser-induced phosphorescence excitation spectroscopy to extend the vibrational analysis of the T_1–S_0 spectrum,[111] to measure the upper-state dipole moment,[112] and to determine the rudiments of T_1's collisional behavior,[111] The phosphorescence intensity of H_2CS was reported to increase with increasing pressure, and it was concluded that the bimolecular interactions of T_1 are dominated by collisional rovibrational relaxation. This behavior is in sharp contrast to that of the S_1 state which exhibits very efficient electronic quenching[105,106] and little or no rovibrational relaxation.[111]

No photophysical or photochemical studies of H_2CS excited to higher electronic states have been reported, although the potential for important work is clear. First, H_2CS excited to the S_2 ($^1A_1$) state may undergo photofragmentation: molecular or free radical dissociation and photoisomerization are all thermodynamically possible.[99-101] In the molecular dissociation channel CS is an obvious candidate for state-to-state dynamics studies because of its ready detection by either LIF or photoionization methods.[113] In addition, the sharp rotational structure seen in the S_3 ($^1B_2$) $\leftarrow$ S_0 spectrum of the molecule[26] suggests that the upper Rydberg state may be sufficiently long-lived to produce measurable fluorescence. If observable, such fluorescence would provide a useful experimental handle for examining this state's dynamics.

B. Cl_2CS

Thiophosgene, Cl_2CS, has been the subject of numerous photochemical and photophysical studies since the observation of its $S_1 \rightarrow S_0$[114] and $S_2 \rightarrow S_0$[115] fluorescence nearly two decades ago. Early work on this molecule has been reviewed.[8] Later work has focused on elucidating the dynamic behavior of both the ground and several excited states. Most of this research has been conducted on gas-phase systems, but several reports of the photochemistry and photophysics of the molecule in fluid condensed media have also appeared recently. The electronic energy level diagram of Cl_2CS (Figure 8) will aid in the following discussion.

Brenner and co-workers[116-121] have used IR–optical double resonance techniques to examine the photophysical behavior of Cl_2CS in both S_0 and S_1. In the

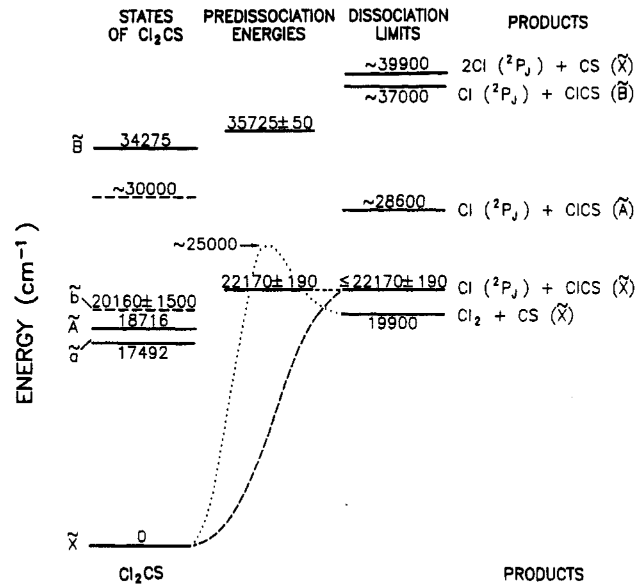


Figure 8. Energy level diagram for Cl_2CS and its dissociation products. The state at ca. 30 000 cm^{-1} is a dark, doubly excited state (cf. ref 27).

studies of S_0, S_1–S_0 laser-induced fluorescence was used as a probe to monitor the populations of ground-state rovibrational levels in the presence of CO_2 laser fields under both collisionless and collision-perturbed conditions.[116–118] Of particular photophysical interest, very-long-range interactions were found to *reduce* the probability of infrared multiphoton absorption (IRMPA) in Cl_2CS, likely as a result of collisional dephasing. The relative efficiency of this collisional perturbation was shown to be related to the Lennard-Jones well depth for the perturber, thiophosgene itself having the largest effect.[118]

Fluorescence from the S_1 state of Cl_2CS was first observed by McDonald and Brus[114] who reported single exponential decay ($\tau \sim 35$ μs in the collisionless limit) at all $E_{vib} \leq 3450$ cm^{-1}, followed by an abrupt break off of emission ($\tau < 150$ ns) at higher levels. This was confirmed by Brenner[119] who also examined the photophysics of S_1 by populating selected vibrational states by one-photon optical excitation and observing the extinguishing of their fluorescence by subsequent IRMPA and dissociation of the molecule using a CO_2 laser.[119–121] Evidence of intramolecular relaxation of the molecule at $E_{vib} \leq 2500$ cm^{-1} was found. Later, Kawasaki and co-workers[104] reported that the emission from Cl_2CS (S_1) under effusive flow conditions at low pressure consisted of two components: a short one of lifetime similar to that observed by McDonald and Brus,[114] and a much longer one which was not T_1 phosphorescence. These observations were interpreted in terms of an intermediate case coupling model in which S_1 and T_1 exhibit mutual perturbations at all energies within the S_1 vibrational manifold.

Although the intramolecular dynamics of the bound levels of the S_1 state of Cl_2CS are complex and remain uncertain, there can be little doubt that the abrupt break off of fluorescence at $E_{vib} \gtrsim 3450$ cm^{-1} is due to dissociation. Using a chemical scavenging technique Okabe[122] observed the production of Cl atoms at photolysis wavelengths of 435.8 and 366.0 nm within $S_1 \leftarrow S_0$. He therefore deduced that the lowest dissociation limit for Cl_2CS [i.e. that for fragmentation to $Cl(^2P_{3/2})$ + $ClCS(^2A')$] corresponded to the energy at which McDonald and Brus[114] observed fluorescence weakening (by predissociation) in S_1. Okabe[122] reported quantum yields of Cl production, ϕ_{Cl}, of 0.38 ± 0.19 at λ = 435.8 nm (E_{vib} = 4089 cm^{-1}) and 0.90 ± 0.17 at λ = 366.0 nm (E_{vib} = 8606 cm^{-1}), by extrapolation of data obtained at rather high-pressure to a low-pressure limit of 1 Torr. Brenner and Peters[120] took the report of $\phi_{Cl} < 1$ at $E_{vib} > 3450$ cm^{-1} as evidence that another bound state (T_2) was involved in the dynamics. However, this interpretation should be viewed with caution in light of the difficulties in obtaining reliable values of ϕ_{Cl} by Stern–Volmer extrapolation of data taken at pressures very far from the collision-free limit. Moreover, details of the curve crossing leading to predissociation are not known, and it is therefore prudent to consider that the onset of fluorescence weakening in S_1 provides only an upper limit of the ground-state dissociation energy.[99,123]

Excitation of low pressures of Cl_2CS to low vibrational levels of S_2 results in strong fluorescence, the lifetime of which ($\tau \approx$ 20–40 ns) is comparable to the radiative lifetime of the upper state obtained from the oscillator strength.[8] At modest vibrational energies ($E_{vib} \gtrsim 1450$ cm^{-1}) fluorescence weakening is observed, and this has been attributed by Ludwiczak et al.[20] to predissociation by a state of undetermined identity. At still higher vibrational energies in S_2, Okabe[122] found $\phi_{Cl} \approx 1$, whereas Ondrey and Bersohn[124] observed photofragmentation of Cl_2CS by two parallel processes:

$$Cl_2CS(S_2^v) \rightarrow Cl + ClCS \qquad (2)$$

$$Cl_2CS(S_2^v) \rightarrow Cl_2(^1\Sigma_g^+) + CS(^1\Sigma) \qquad (3)$$

with $\phi(2) = 0.8$ and $\phi(3) = 0.2$. In both experiments Cl_2CS was excited to energies well above both the molecular and free-radical dissociation barriers on the ground-state surface.[99] By measuring the time-of-flight distribution of the fragments Ondrey and Bersohn[124] determined the average translational energy content of the radical products and showed that this was consistent with an impulsive spectator model for the photofragmentation (eq 2). However, both Ondrey and Bersohn[124] and Brenner and Peters[120] assumed that only ground-state, bent $ClCS(^2A')$ radicals could be produced in eq 2, whereas subsequent calculations by Chan and Goddard[125] and by Hachey et al.[123] show that a very-low-lying excited singlet state ($^2A'' \equiv {}^1\Pi$ (linear)) is also thermodynamically accessible (cf. Figure 8). Hachey et al.[123] reevaluated the energy disposal in the UV photofragmentation of Cl_2CS to account for this possibility.

The observation of strong fluorescence from both S_1 and S_2 offers the possibility of doing various two-photon experiments with Cl_2CS. Clouthier et al.[126] showed that S_2 could be excited by one-color, resonant two-photon absorption via T_1. Dixon and Western[19] used S_2–S_1–S_0 two-color, optical–optical double resonance to attempt to sort out the difficult spectroscopy of S_2, but the results are at odds with those obtained by direct, one-photon S_2–S_0 excitation[18,20] and remain unexplained (vide supra).

$S_2 \rightarrow S_0$ emission resulting from singlet–singlet annihilation has also been observed in Cl_2CS.[126] When Cl_2CS(g) is excited to S_1 in the mid-visible, weak emission from S_2 in the blue can be observed in addition to the red-near infrared emission from S_1. This blue emission is clearly excited by the absorption of two photons, but cannot be due to prompt $S_2 \leftarrow S_1 \leftarrow S_0$ because such a sequence populates vibrational levels of S_2 which lie above its dissociation threshold and are therefore nonfluorescent. The blue emission is characterized, however, by pressure-dependent growth and decay and is therefore clearly attributable to a unique singlet–singlet electronic energy pooling process:

$$2Cl_2CS(S_1) \rightarrow Cl_2CS(S_2) + Cl_2CS(S_0^v) \qquad (4)$$

Triplet–triplet and triplet–singlet annihilation processes are both well known in fluid media, but singlet–singlet annihilation is exceedingly rare in polyatomic molecules. The subject has been reviewed recently.[127]

Several reports of the photophysics and photochemistry of Cl_2CS in condensed media have also appeared recently.[128–130] At high concentrations, thiophosgene undergoes aggregation in solution to form van der Waals dimers and higher oligomers. However, the monomers can be investigated without interference from aggregates in solutions which are sufficiently dilute.[130] Emission from three states, S_2, S_1, and T_1, has been observed.

The near-infrared $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emissions[130] are weak and the spectra are severely overlapped. However, this emission exhibits a clear, biexponential temporal decay profile, consisting of a short-lived (τ = 40 ps), concentration-independent, relatively blue-shifted component assigned to $S_1 \rightarrow S_0$ fluorescence, and a longer-lived, concentration-dependent, relatively red-shifted component assigned to $T_1 \rightarrow S_0$ phosphorescence. Phosphorescence from Cl_2CS has not been observed in the gas phase, despite several attempts to find it.[104,131]

Measurements of the fluorescence and phosphorescence quantum yields and lifetimes as a function of Cl_2CS concentration permitted values of the rate constants for radiative and nonradiative decay of S_1 and T_1 at infinite dilution, and the rate constant for bimolecular self-quenching of T_1 to be determined.[130] T_1 self-quenching occurs at diffusion-limited rates. At infinite dilution in inert solvents, both S_1 and T_1 decay primarily by relaxation directly to the ground state, and unlike the larger thiones (vide infra), thermal equilibrium between S_1 and T_1 is not established in solution at room temperature. In liquid solution Cl_2CS therefore behaves like a statistical limit molecule with respect to the coupling of S_1 and T_1 to S_0, in immediate contrast with its small or intermediate case behavior in the gas phase.

Cl_2CS is also observed to emit relatively strongly from S_2 and to exhibit nanosecond lifetimes when embedded in sufficiently inert solvents, such as the perfluoroalkanes.[128,129] Two processes dominate the decay of S_2 in inert media at infinite dilution; fluorescence to S_0 and a single fast radiationless decay process. The latter is characterized by an activation energy which is nearly identical to the zero point-to-predissociation thereshold energy difference observed in the S_2–S_0 LIFE spectrum[20] and is therefore ascribed to dissociation over a low barrier. The nature of the photolysis products have not been reported.

In more concentrated perfluoroalkane solutions self-quenching of S_2 is observed to occur at diffusion-limited rates. In solvents other than inert perfluoroalkanes the quantum yields of fluorescence and the S_2 lifetimes are drastically reduced.[128] An additional radiationless decay channel, solvent-induced excited-state relaxation—a photophysical rather than a photochemical process—appears to be responsible.[129]

IV. Photophysics of Larger Thiocarbonyls

As is the case for the tetraatomics, the observation of strong emission from several excited states has proved to be the most useful tool for elucidating the dynamic behavior of larger photoexcited thiocarbonyls.[8] Unlike the smaller molecules, however, most of the work on the larger thiones has been carried out in condensed media where prompt emission is generally seen only from S_2 and/or T_1, not S_1. On the other hand, thermally activated delayed fluorescence from S_1 can be observed under favorable circumstances from some of the larger thiones in condensed media,[41] and extensive use has been made of triplet–triplet absorption methods to characterize the lowest triplet states.[40,52,132–138] In addition, intermolecular interactions can be investigated by using well-established energy transfer and quenching techniques. A variety of tools is therefore available for studies of the photophysics of the larger thiocarbonyls in condensed media.

The solvent plays a critical role in these studies. First, the excited state radiative decay rates generally depend upon the square of the refractive index of the medium.[139] Second, the "solvating power" of the medium influences the effective electronic energy spacings of the dissolved solute. This, in turn, alters the rate of intramolecular radiationless decay of a given excited state since (in the weak coupling limit for large molecules) the nonradiative rate constant decreases approximately exponentially as the energy gap between the two coupled states increases.[90] Third, the T_1 ($^3A_2$) and T_2 ($^3A_1$) states of the thiocarbonyls can invert in strongly interacting solvents.[91] Finally, interaction with the solvent can provide additional, fast nonradiative decay channels for excited-state relaxation.[140] Electronic energy transfer to or net photochemical reaction with the solvent are possible for some solvent-excited thione combinations. However of greater importance in sorting out the behavior of the second excited singlet states of the thiones in liquid solution is the observation that many common solvents (alkanes, CCl_4, benzene) induce the rapid, radiationless decay of S_2 by a mechanism which involves neither electronic energy transfer nor net photochemical reaction.[140] This solvent-induced photophysical decay process is not seen in azulene[5] and other nonalternant hydrocarbons which have long-lived S_2 states and has been the object of considerable speculation and some experimental study. It will be dealt with separately under the heading of quenching in this review. We introduce the matter early in this section, however, because the nature and impact of solvent-excited solute interactions have not always been appreciated in earlier photochemical and photophysical studies. For this reason, readers of the literature must be very careful when interpreting the results of experiments in which the dynamics of the T_1 and S_2 states of the thiones have been investigated in common solvents at ambient temperature.

Of the various solvents employed to date, only the perfluoroalkanes have proved to be sufficiently inert to permit the "intramolecular" photochemical and photophysical behavior of the larger thiocarbonyls to be unmasked in solution. The perfluoroalkanes generally cause the smallest shifts in the energies of the T_1, S_1, and S_2 states of the thiones relative to those of the bare molecule (cf. Table I). They are almost completely photochemically inert (vide infra). The unquenched lifetimes of T_1, and particularly S_2, are longer in the perfluoroalkanes than in any other liquid solvent investigated to date, and the $S_2 \rightarrow S_0$ and $T_2 \rightarrow S_0$ emission quantum yields are the largest. In 1:1 van der Waals complexes with the S_2 states of **7a** and **8a**, the perfluoroalkanes exhibit only small microsolvation spectral shifts (Table V) and modest S_2 lifetime reductions compared with the bare molecules.[92] The overall conclusion is therefore that the perfluoroalkanes act very nearly as classical heat baths[141] in photochemical and photophysical studies of the thiones. That is, the perfluoroalkanes act as effective vibrational thermalizing media, but have a minimal effect on the intramolecular electronic relaxation processes of the chromophoric solute molecules. Other common solvents interact much more strongly with the excited thiones (particularly with S_2) and may mask the intramolecular dynamics of the vibrationally relaxed electronic excited state. The use of perfluoroalkane solvents in studies of the photochemistry and photophysics of polyatomic molecules in solution has recently been reviewed thoroughly by Maciejewski.[142]

A. T_1

The lowest triplet states of the larger thiones may be populated selectively by direct one-photon absorption in the spectrally resolved, long wavelength part of the $T_1 \leftarrow S_0$ absorption band, by intersystem crossing, following excitation to S_1 or S_2, or by energy transfer from triplet sensitizers. The dynamics of the T_1 state have been explored using phosphorescence lifetime and quantum yield measurements, triplet–triplet absorption, and intermolecular triplet quenching and energy transfer techniques. Thermally activated, delayed emission has been observed from S_1 in the aromatic thiones[41] and from T_2 in the alicyclic thiones,[38] and this has provided crucial information about the decay dynamics of the thione triplets in solution at room temperature.

Owing to the large values of D^*, individual triplet sublevels of the aromatic thiones may be selectively populated either by direct absorption ($T_{1z} \leftarrow S_0$) or by intersystem crossing from S_1 ($S_1 \rightsquigarrow T_{1x}$, T_{1y} is likely) at low temperatures in ordered media. However, because spin–lattice relaxation is very fast ($<10^{-7}$ s),[68] a Boltzmann distribution of triplet sublevel populations is observed in both steady-state and submicrosecond-pulsed experiments at all temperatures down to ca. 1 K.[67] The population relaxation time of the upper T_{1z} level at very low temperatures is therefore determined by its rate of spin–lattice relaxation to T_{1x} and T_{1y}. Fortunately, microwave fast passage experiments may be used to distinguish between those $T_1 \rightarrow S_0$ vibronic transitions originating in T_{1x} and those originating in T_{1y} and to measure directly the lifetimes of the individual T_{1x} and T_{1y} sublevels.[42] The lifetime of T_{1z} may then be obtained indirectly by measuring the

Table VI. Triplet Sublevel Lifetimes of Several Aromatic Thiones in Cryogenic Media[a]

compd	host[b]	τ_x, ms	τ_y, ms	τ_z, μs	τ_{av},[c] μs	ref
6a	*n*-pentane (S)	2.3	3.7	21	85	69
6c	*n*-hexane (S)	4.7	2.9	26	104	69
7a	*n*-hexane (S)	1.1	1.8	16	61	42
8a	*n*-hexane (S)	0.76	1.4	10	35	42
8a-d_8	*n*-hexane (S)	1.4	2.6	18	64	42

[a] Rate constants for the decay are the inverse of the lifetimes. [b] S signifies a Shpolskii matrix at 1.2 K. [c] τ_{av} is measured at 77 K and is used to derive τ_z.

average lifetime of the thermally equilibrated triplet, τ_{av}, at a higher temperature (e.g. 77 K) and employing the relationship

$$\tau_{av}^{-1} = (\sum_i p_i \tau_i^{-1})/(\sum_i p_i) \quad (4)$$

where τ_i and p_i are the lifetimes and populations of the individual sublevels at the temperature in question. Since thermal equilibrium is maintained at all temperatures, the p_i may be obtained from the Boltzmann equation, leaving τ_z as the only unknown in eq 4. Using these techniques Maki and co-workers[42,69] have determined the triplet sublevel decay constants of a number of aromatic thiones, and these are summarized in Table VI.

The fact that spin–lattice relaxation among the T_1 sublevels is faster than 10^{-7} s at 1 K is very unusual and caused some initial confusion[44,45,71] concerning the S_1 to T_1 intersystem crossing mechanism in **8a**. However, despite the fact that $T_{1z} \rightsquigarrow T_{1x}, T_{1y}$ spin–lattice relaxation requires the spontaneous creation of a 15.5-cm^{-1} lattice phonon at an unprecedented rate at 1 K, Maki and co-workers[42,68] have shown that the preferred mode of population of T_1 from the singlet manifold is $S_1 \rightsquigarrow T_{1z} \rightleftarrows T_{1x}, T_{1y}$. The $S_1 \rightsquigarrow T_{1z}$ process must occur by a second-order vibronic-spin–orbit coupling mechanism.

In rigid cryogenic media there is little doubt that S_1 decays irreversibly to T_1 and that T_1 then decays directly to S_0 by either radiative or nonradiative means. Table VI shows that T_1 lifetimes generally increase with deuteration or with decreasing molecular size in the series **8a**, **7a**, **6a**. The quantum yield of $T_1 \rightarrow S_0$ phosphorescence of **6a** is very large (0.47) in perfluoroalkane solution even at room temperature (vide infra).[143] Therefore the fact that the average lifetime of **6a** is a factor of ca. 2 larger at 77 K than at infinite dilution at room temperature suggests that **6a** decays almost exclusively by radiative means at cryogenic temperatures. Similar arguments indicate that the fraction of T_1 which decays nonradiatively increases in the order **6a** < **7a** < **8a**. Since $\Delta E(T_1\text{–}S_0)$ decreases in the same sequence (Table II), these results are all in qualitative accord with the energy-gap law of radiationless transition theory.[90]

At room temperature, the quantum yields of triplet formation, triplet lifetimes, $T_n \leftarrow T_1$ absorption spectra, and $T_1 \rightarrow S_0$ emission spectra and quantum yields have been measured for a substantial number of thiones in a variety of fluid media. Table VII summarizes the results of phosphorescence lifetime and quantum yield experiments, and Table VIII presents the intrinsic triplet lifetimes, quantum yields of triplet formation, ϕ_T, and quantum efficiencies of $^1O_2$ formation on triplet quenching, ϕ_T^Δ, obtained from time-resolved triplet–

Table VII. Photophysical Decay Parameters for Triplet Thiones in Fluid Solvents at Room Temperature

thione	solvent[a]	$10^2\phi_p^0(S_2)$[b]	$10^2\phi_p^0(S_1)$[b]	$10^2\phi_p^0(T_1)$[b]	τ_T^0, μs	$10^{-3}k_{RT_1}$, s^{-1}	$10^{-4}\Sigma k_{NRT_1}$ s^{-1}	ref(s)
3	PFDMCH	2.3	2.0		43.3	0.47	2.3	38, 144
	PFH	2.5	2.2		38.8	0.57	2.5	
	c-hexane	1.1	1.2		17.6	0.68	5.6	
4	PFDMCH	5.6	7.2		154	0.53	0.6	38, 144
5	PFDMCH	2.4	2.9		46.3	0.63	2.1	38, 144
6a	PFDMCH	33	33	47	43	11	1.2	143
	3-MP	3.4	5.1	5.6	6.5	8.6	1.4	
7a	PFDMCH	7.6	9.2	13	16	8.1	5.4	145, 146
	3-MP	3.2	3.6	5.4	7.3	7.4	13	
7b	PFDMCH	4.8		8	8.5	9.4	11	145, 146
	3-MP	4.2		7.0	5.8	12	16	
8a	PFDMCH	3.8		(6.2)[c]	8.2	7.6	11	145, 146
	PFH	3.6		(5.9)[c]	8.1	7.3	12	
	3-MP	3.5	4.3	5.4	7.1	7.6	13	
8a-d_8	PFDMCH	7.6		(12)[c]	21	5.7	4.2	145, 146
	3-MP	8.6	9.6	15	14.5	10	5.9	
8b	PFDMCH	0.54		0.9	1.01	8.9	100	145, 146
	3-MP	0.48		0.8	0.99	8.1	100	
10a	PFDMCH	6.8	8.3	12	38	3.1	2.3	145, 146
	3-MP	6.9	8.2	13	30	4.3	2.9	
10b	PFDMCH	8.3	12	13	21.7	6.0	4.0	145, 146
	3-MP	5.0		12	17.9	6.7	4.9	
11b	PFDMCH	0.087		0.15	3.04	0.49	33	145, 146
	3-MP	0.079		0.14	3.0	0.46	33	
11c	3-MP	1.3		2.2	0.72	30	140	145, 146

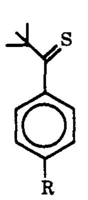
[a] Abbreviations are as follows: PFMCH, perfluoro-1,3-dimethylcyclohexane; PFH, perfluoro-*n*-hexane; 3-MP, 3-methylpentane. [b] Upper state of the initial absorption given in parentheses. [c] Estimated. See ref 145.

Table VIII. Triplet Energies, Lifetimes, and Yields from the Flash Photolysis of Thiones at Several Wavelengths

				ϕ_T[a]		ϕ_T^Δ[d]		
thione	solvent	E_T, kJ mol^{-1}	τ_T^0, μs	$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$	ref(s)
1d	benzene	190	0.56[c]	0.95		0.85		133
3	EPA, 77 K	208	120					40
4	EPA, 77 K	214	455					40
	benzene		0.17[c]	1.1				133
5	benzene		0.28[c]	1.0				133
8a	benzene	181	1.8	1.0	0.8 (0.5)[b]			52
8b	benzene	166	0.83		0.8 (0.6)[b]			52
8c	c-hexane	180	2.6	0.95	0.79	1.1		132
	benzene		2.5	0.88	0.85	0.92		
	CH_3OH		2.3	0.90	0.75	1.0		
	CH_3CN		1.6	0.87	0.76	0.85		
9	benzene	212	≥2.5	~1	≥0.9	1.0	0.8	136
11a	benzene	166	1.7	1.0	0.6	~1		52
	EPA, 77 K	170	44					40
11b	benzene	172	1.4	1.0	0.5			52
	EPA, 77 K	176	123					40
11c	benzene	176	1.3	1.0	0.4 (0.6)[b]			52
	EE, 77 K	182	170					40
14a	benzene	~190	0.33	1.0	0.7	1.0		135
14b	benzene	~190	1.1	1.0	0.9	0.87		135
14c	benzene	~190	0.61	1.0	0.7	0.98		135
14d	benzene	~190	0.30	1.0	0.8	1.1		135
15	c-hexane	163	0.13	0.7				138
	benzene		0.86	0.7		~1		
	CH_3OH		0.78	0.4				
16b	benzene	187	0.06	1.0	≥0.8	1.0	0.7	136
16c	benzene	187	0.08	1.0	≥0.3	1.0	0.8	136
17	benzene	195	≥5	1.0	≥0.4	0.9	0.6	136
18a	c-hexane		0.60	1.0				133, 134
18b	c-hexane		0.50	1.0				134
18c	c-hexane		0.20	1.2				134
18d	c-hexane		0.50	1.1				134
18e	c-hexane		0.50	1.0				134

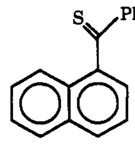
[a] ϕ is normally accurate to ±10 or ±20%. [b] Numbers in parentheses are for λ_{ex} = 425 nm, in the region of overlap of $S_2 \leftarrow S_0$ with $S_1 \leftarrow S_0$. See text. [c] At 1 × 10^{-3} M thione. Highly self-quenched. [d] See text for definition.

triplet absorption studies. Figure 9 shows the structures of the thiones examined, and Figure 10 shows a typical triplet–triplet transient absorption spectrum. The general picture is that thione triplets are formed in high yield by intersystem crossing from the singlet manifold, have unquenched lifetimes ranging from ca.



a) R = H
b) R = OCH_3
c) R = F
d) R = Cl

14



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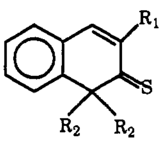
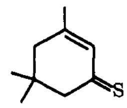
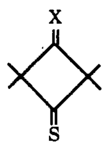


a) $R_1 = CH_3$, R_2 = H
b) R_1 = H, $R_2 = CH_3$
c) $R_1,R_2 = CH_3$

16

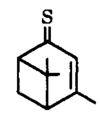


17



a) X = S
b) X = O
c) X = $C(CN)_2$
d) X = $C(CN)(COOC_2H_5)$
e) X = N - Ph

18



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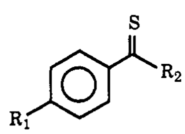


a) R_1 = H, $R_2 = C(CH_3)_2CH_2CH_2CH_2CH_3$
b) R_1 = H, $R_2 = C(CH_3)_2CH_2CH(CH_3)CH_2CH_3$
c) R_1 = H, $R_2 = C(CH_3)_2CH_2CH_3$
d) $R_1 = CH_3O$, $R_2 = C(CH_3)_2CH_2CH_2CH_2CH_3$
e) $R_1 = (CH_3)_2N$, $R_2 = C(CH_3)_2CH_2CH_2CH_2CH_3$

20

Figure 9. Structures of thiocarbonyls. II.

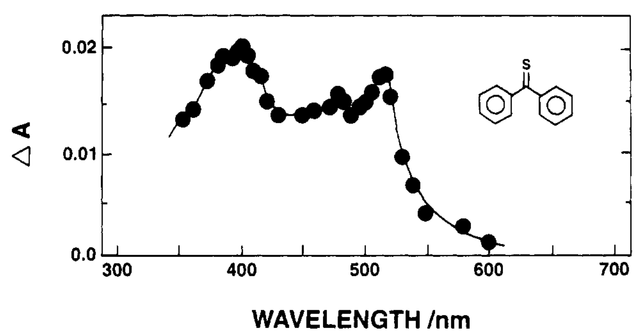


Figure 10. Triplet–triplet transient absorption spectrum of **11a** in benzene at room temperature (from ref 52).

100 ns to 100 μs, are self-quenched (or are quenched by O_2 and many other addends) at diffusion limited rates in the absence of steric crowding, tend to phosphoresce strongly in fluid media, and are often quite photostable (vide infra).

The precise interpretation of the triplet dynamics in fluid solution at room temperature is, however, not so straightforward as it is in rigid cryogenic media. First, self-quenching of sterically unhindered triplet thiones generally occurs at diffusion-limited rates (vide infra). The intrinsic lifetimes of the T_1 states can therefore only be approached when the measurements are made in very dilute (e.g. $<10^{-7}$ M) solutions in common solvents at room temperature. Many triplet lifetimes reported in the literature have been measured in much more concentrated solutions in which the lifetime is determined primarily by the rate of self-quenching. Second, the influence of the solvent on the photophysics is not always readily apparent. For example, Das and co-workers[52,132-137] have measured the triplet–triplet absorption spectra and triplet decay kinetics of a large number of thiones in liquid solution using nanosecond laser flash photophysics methods. However, many of these measurements have been made in benzene in which T_1 and T_2 are energetically very similar; the lowest triplet is of $^3A_1$, $^3(\pi,\pi^*)$ character in some cases.[91] The assignment of the identity of the transient and the interpretation of the photophysics are not always straightforward in these experiments.

The data in Tables VII and VIII refer to the intrinsic triplet lifetimes, τ_T^0, i.e., those which would be measured at infinite dilution in the solvent in question. Both τ_T^0 and the corresponding phosphorescence quantum yields, ϕ_p^0, have been obtained by linear extrapolations of measurements at finite concentration of thione ([S]) using the Stern–Volmer formalism, i.e.

$$\frac{1}{\tau_T} = \frac{1}{\tau_T^0} + k_{SQ}[S] \tag{5a}$$

$$\frac{1}{\phi_p} = \frac{1}{\phi_p^0} + \frac{k_{SQ}}{k_{RT_1}}[S] \tag{5b}$$

The τ_T^0 and ϕ_p^0 data in Table VII were obtained in solvents in which it is certain that T_1 is of $^3(n,\pi^*)$ configuration in all cases. From these data one may obtain k_{RT_1}, the rate constant for the radiative (phosphorescence) decay of T_1, and $\sum k_{NRT_1}$, the sum of the rate constants for all parallel first-order or pseudo-first-order radiationless processes by which T_1 relaxes, using

$$k_{RT_1} = \phi_p^0/\tau_T^0 \tag{6}$$

$$\sum k_{NRT_1} = (1 - \phi_p^0)/\tau_T^0 \tag{7}$$

Although these parameters apply to infinitely dilute solutions in which the identity of T_1 is clear, thermal activation effects complicate their interpretation when the measurements are made at room temperature because $\Delta E(S_1-T_1)$ and $\Delta E(T_2-T_1)$ are small.

B. S_1 and S_1–T_1 Equilibria

Close examination of the red and near-infrared emission spectra of many aromatic and alicyclic thiones reveals the presence of a weak, but distinct shoulder on the blue edge of the $T_1 \rightarrow S_0$ spectrum (cf. Figure 4). The intensity of this feature grows with increasing temperature and has been identified unequivocally as E-type, thermally activated, delayed $S_1 \rightarrow S_0$ fluorescence in the aromatic thiones **6a**, **7a**, **8a**, and **10a**.[41] The lifetime of this thermally activated emission is the same as that of phosphorescence from T_1, and the ratio of its intensity to that of phosphorescence (i.e. I_{TDF}/I_p) is proportional to $\exp\{-\Delta E(S_1-T_1)/RT\}$. Thus for these aromatic thiones S_1 and T_1 are in thermal equilibrium in liquid solution at room temperature. The average instantaneous thermal vibrational energy content of a thione such as **8a** is about the same as the S_1–T_1 energy gap.[147] S_1 levels will therefore be populated significantly at room temperature in condensed media whenever T_1 is produced.[147,148]

The existence of an $S_1 \rightleftarrows T_1$ equilibrium has important implications for studies of both the photochemistry and photophysics of the thiones. First, all photochemical reactions involving the n,π* states of the thiones could conceivably proceed on either the lowest triplet or the lowest singlet surfaces in fluid media at room temperature. This may be of importance in evaluating a number of apparently anomalous reports in which an excited-state photochemical reaction of a large thione appears to proceed by a singlet mechanism despite the fact that the yield of triplet is high and the lifetime of the singlet very short. The pericyclization of 1-(thiobenzoyl)naphthalene (15) and similar polycyclic aromatic thiones, first reported by de Mayo and co-workers[149] and recently reinvestigated by Minto et al.,[138] is a case in point.

Back-intersystem crossing from $T_1^v \rightsquigarrow S_1$ followed by $S_1 \rightsquigarrow S_0$ internal conversion may also act as an important intramolecular radiationless decay channel for thiones in their lower excited states at room temperature. The observation of a large deuterium isotope effect on T_1's nonradiative decay rate and the existence of a good linear relationship between log $(\sum k_{NRT_1})$ and $\Delta E(T_1-S_0)$ has been taken as evidence that the main radiationless decay path of the thione triplets is $T_1 \rightsquigarrow S_0$ intersystem crossing.[49] However because $\Delta E(S_1-T_1)$ is small compared to $\Delta E(S_1-S_0)$ or $\Delta E(T_1-S_0)$, a good correlation is also found if one plots log $(\sum k_{NRT_1})$ vs $\Delta E(S_1-S_0)$. The most complete kinetic data are available for xanthione (8a). For this compound Szymanski et al.[148] recently showed that ca. 40% of the molecules in the coupled $S_1 \rightleftarrows T_1$ system could decay by the $T_1 \rightsquigarrow S_1 \rightsquigarrow S_0$ route at room temperature.

Thermally activated emission is also observed in the alicyclic thiones 3, 4, and 5.[38] In these cases, however, the temperature dependence of the intensity of the emission, while Arrhenius-like in nature, was found not to be related to the S_1-T_1 energy gap. The thermally activated emission was therefore assigned to $T_2 \rightarrow S_0$ phosphorescence in these compounds.

The lowest excited singlets have been the most difficult states to obtain dynamic information about in the larger thiocarbonyls. These states are very short-lived, exhibit no measurable prompt emission when excited in condensed media at low temperatures, and have never been observed in transient absorption experiments. The only report of the direct observation of the dynamics of the S_1 state of a larger thiocarbonyl is that of Molenkamp et al.[46] who used photon-echo and optical detection methods to examine 8a in a crystalline xanthione host at low temperatures. Accumulated photon-echo decays revealed a temperature-dependent dephasing (attributed to activation of a local phonon mode) and a low-temperature, single-exponential S_1 population decay time of 19.6 ps for E_{vib} = 0 at 1.7 K. The latter was shown to be due to $S_1 \rightsquigarrow T_1$ intersystem crossing. The S_1 lifetime at 1.7 K was also found to be a function of E_{vib} in S_1, as a result of vibrational relaxation preceeding $S_1 \rightsquigarrow T_1$ at low E_{vib}. At E_{vib} = 1256 cm^{-1} the S_1 lifetime was 1.0 ps, decreasing to ≤0.4 ps at $E_{vib} \geq$ 1678 cm^{-1}. This drastic reduction in S_1's lifetime at these higher vibrational energies was attributed[46] to intersystem crossing to T_2 by a direct, spin-orbit coupling mechanism. (S_1 and T_{2z} are both of A_2 spin $\otimes$ orbital symmetry.) If this interpretation is correct, T_2 would be located approximately 2000 cm^{-1} above T_1, in almost perfect agreement with Burland's

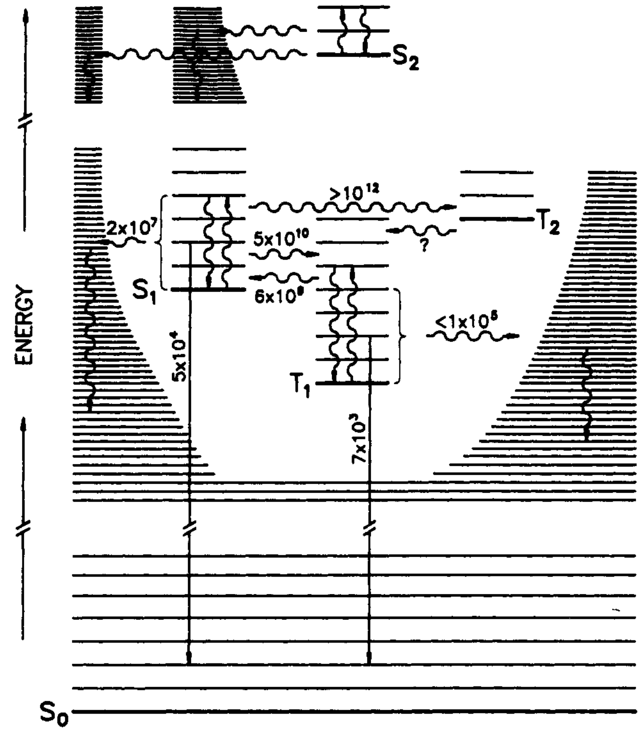


Figure 11. Schematic energy-level diagram of a typical aromatic thione in a perfluoroalkane solvent. The numbers are the values of the rate constants in units of s^{-1} of the processes shown for 8a.

estimate[45] for 8a in the same medium based upon its T_1 zero-field splitting. Note also that $S_1 \rightsquigarrow T_1$ is very fast at E_{vib} = 0 in S_1 despite the fact that a second-order vibronic-spin-orbit coupling mechanism must be involved.

The data of Molenkamp et al.[46] on the lifetime of the S_1 state of 8a have been employed together with measurements of the relative intensity of thermally activated delayed fluorescence to that of phosphorescence[41] to establish an approximate value of its rate constant for back-intersystem crossing ($T_1 \rightsquigarrow S_1$, $k_{T_1S_1}$) in fluid media at room temperature. The value is large ($k_{T_1S_1} \approx 6 \times 10^9$ s^{-1}) and shows that $S_1 \rightleftarrows T_1$ equilibrium is established rapidly. These data, in turn, have permitted the remaining rate constants for the radiationless and radiative decay of S_1 to be evaluated for 8a.[148] The data are shown schematically in Figure 11. Xanthione (8a) is the only thiocarbonyl for which a complete set of such data is available.

Laser flash photolysis/transient absorption studies have been carried out for a relatively large number of aromatic, arylalkyl, and aliphatic thiones in solution (cf. Table VIII). Since the experiments often involve excitation at several wavelengths in the singlet absorption bands ($S_3/S_2/S_1 \leftarrow S_0$) the quantum yields of the triplet transients give quantitative information about the fate of the initially populated singlet states. The same information is available from measurements of the quantum yields of $T_1 \rightarrow S_0$ phosphorescence resulting from excitation within the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ absorption systems, compared with direct excitation to T_1 within the resolved $T_1 \leftarrow S_0$ absorption band (cf. Table VII). The two sets of experiments give similar, but not quantitatively identical, results for the same thione. Triplet-triplet absorption studies show that the yield of triplet is high—often 1 (within an error of ±10-20%)—on excitation to S_1. Relative phospho-

Table IX. Photophysical Decay Parameters for the S_2 States of Thiones in Perfluoroalkane Solution at Room Temperature

thione	solvent	$\phi_f(S_2)$	$\tau(S_2)$, ps	k_{RS_2}, s^{-1}	Σk_{NRS_2}, s^{-1}	ref(s)
3	PFDMCH	1.7×10^{-4}	0.3[a]	6×10^8 [a]	3×10^{12} [a]	144
4	PFDMCH	3.4×10^{-5}	0.05[a]	7×10^8 [a]	2×10^{13} [a]	144
5	PFDMCH	6.5×10^{-5}	0.1[a]	6×10^8 [a]	1×10^{13} [a]	144
6a	PFMCH/PFH	1×10^{-4}	<20	$>0.5 \times 10^7$	$>5 \times 10^{10}$	50
7a	PFMCH/PFH	2.3×10^{-2}	210	1.1×10^8	4.8×10^9	50
7b	PFMCH/PFH	3.8×10^{-3}	101	3.8×10^8	9.9×10^9	50
8a	PFMCH/PFH	1.4×10^{-2}	175 (162)	8.0×10^7	4.8×10^9	50 (156)
8a-d_8	PFDMCH	3.8×10^{-2}	626	6.1×10^7	1.5×10^9	158
8a-d_6		4.2×10^{-2}	602	7.0×10^7	1.6×10^9	158
8a-d_4		3.8×10^{-2}	571	6.1×10^7	1.7×10^9	158
8b	PFMCH/PFH	2.3×10^{-3}	64	3.6×10^7	1.6×10^{10}	50
8d	PFMCH/PFH	1.7×10^{-2}	410	4.1×10^7	2.4×10^9	50
10a	PFMCH/PFH	0.14	880	1.6×10^8	9.7×10^8	50
11b	PFMCH/PFH	5.6×10^{-4}	35	1.6×10^8	2.9×10^{10}	50
16b	PFMCH/PFH	2.6×10^{-2}	153	1.7×10^8	6.4×10^9	160
16c	PFMCH/PFH	3.3×10^{-3}	19	1.7×10^8	5.9×10^{10}	160
17	PFMCH/PFH	1.8×10^{-3}	11	1.6×10^8	9.1×10^{10}	160
19	PFMCH/PFH	4.1×10^{-2}	250	1.6×10^8	3.9×10^9	160

[a] Based on a calculation of k_{RS_2}. See ref 144.

rescence quantum yield data show that the apparent quantum yield of triplet formation often approaches 1, but is in fact slightly less than unity at all excitation wavelengths within $S_1 \leftarrow S_0$ in many systems. Direct $S_1 \rightsquigarrow S_0$ internal conversion is most likely responsible for the small difference, and the possible nonequilibrium mechanisms whereby this may occure have been discussed recently.[147,148]

C. S_2 and Higher States

The second excited singlet states of the thiones are of interest because, like azulene and other nonalternant hydrocarbons, many of them are photostable in inert media and are relatively long-lived, owing to the intrinsic slowness of their nonradiative decay rates (large $\Delta E(S_2-S_1)$). Because the $S_2 \rightarrow S_0$ transitions of the thiocarbonyls are electric dipole allowed, the rigid photostable thiones therefore fluoresce with large and readily measurable quantum yields (cf. Figure 4). The S_2 fluorescence decays are generally monoexponential in condensed media, fall in the nanosecond to picosecond range, and can be accurately measured using picosecond laser techniques. Self-quenching of S_2 often occurs at diffusion-limited rates but, unlike T_1, this presents no major difficulty because the S_2 lifetimes are short. Bimolecular quenching only becomes significant in relatively concentrated solutions. The S_2 states of the thiones are therefore amenable not only to intramolecular photophysical studies, but also to photochemical investigations.

The first reports of emission from the S_2 states of larger thiones appeared within a month of one another in 1975. Huber and Mahaney[150] described the observation of $S_2 \rightarrow S_0$ emission from xanthione (**8a**) and almost simultaneously de Mayo, Ware, and co-workers[151] independently reported measurements of the lifetimes and $S_2 \rightarrow S_0$ fluorescence quantum yields of a number of aryl alkyl thiones **20**. These reports were followed by several series of measurements of the photophysical and photochemical properties of a large number of thiones in a variety of media.[8-13] The S_2 lifetimes depend greatly on the solvent employed, and a consistent set of data has been slow to develop. Xanthione (**8a**) is a good example. Hochstrasser and co-workers[152] measured an S_2 lifetime of **8a** in benzene of 12 ± 3 ps by picosecond optical gating methods, whereas Boens and co-workers,[153] de Schryver and co-workers,[154] and Topp and co-workers[156] reported 8 ± 1, 18 ± 2, 11 ± 2 ps, respectively, using time-correlated single-photon counting. Topp and co-workers reported 14 ± 2 ps for the lifetime of S_2 in *n*-hexane by picosecond fluorescence up-conversion[155] and 25 ± 2 ps by time-correlated single photon counting.[156] Maciejewski et al.[50] reported 175 ps in perfluoro-*n*-hexane whereas Topp and co-workers[156] reported 162 ps. The recent extensive tabulations by Topp and co-workers[156] and Boens et al.[153] of the lifetimes of the S_2 state of **8a** in a wide variety of solvents appear to be the most accurate data currently available. From these data one can judge that the S_2 lifetimes reported by Steer and co-workers[50,140,145] and by de Schryver and co-workers[154] using time-correlated single photon counting methods are routinely too large by ca. 10 ps. The S_2 lifetimes reported by Mahaney and Huber,[157] based upon measurements of the $S_2 \rightarrow S_0$ fluorescence quantum yields and a calculation of the $S_2 \rightarrow S_0$ radiative rate constant, are in substantial disagreement with the experimental measurements.

The availability of accurate intrinsic fluorescence lifetime and quantum yield data enables the rate constant for the $S_2 \rightarrow S_0$ radiative decay, k_{RS_2}, and the sum of the rate constants for all nonradiative decay processes of S_2, Σk_{NRS_2}, to be calculated using the analogs of eq 6 and 7. Unlike azulene,[5] solvent-induced relaxation dominates the radiationless decay of the thione S_2 states and masks their intramolecular dynamics in most common solvents (alkanes, CCl_4, benzene).[50,140,154,156] The use of weakly interacting, photochemically inert perfluoroalkane solvents[142] has therefore also been essential in uncovering the intramolecular dynamic behavior of the S_2 states in condensed media. The photophysical decay parameters of those thiones which have been examined to date in perfluoroalkane solvents are summarized in Table IX.

The data in Tables II, VII, and IX reveal a number of important facts. First, the S_2 fluorescence quantum yields and lifetimes are largest for those thiones which are aromatic, rigid, and have the largest S_2–S_1 energy

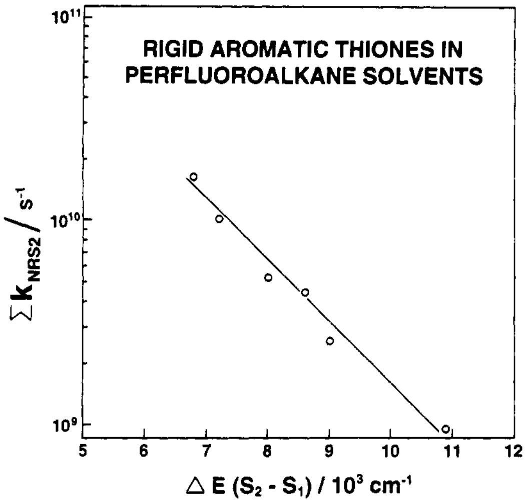


Figure 12. Plot of the logarithm of the sum of the rate constants for the nonradiative decay processes of S_2 vs S_2–S_1 electronic energy gap for several rigid aromatic thiones in perfluoroalkane solution at room temperature.

gaps. As shown in Figure 12, an excellent linear correlation is found between log (Σk_{NRS_2}) and $\Delta E(S_2–S_1)$ within the group of rigid aromatic thiones **7a**, **7b**, **8a**, **8b**, **8d**, and **10a** when data taken in perfluoroalkane solution at room temperature are employed.[50] This has been taken as good evidence that $S_2 \rightsquigarrow S_1$ internal conversion is the major intramolecular nonradiative decay channel in these molecules.[50] Nonrigid aromatic thiones such as **6a** and **11a** (thiobenzophenone) undergo much faster radiationless decay and this has been attributed to activity of their low-frequency internal rotational and out-of-plane bending modes.

Unlike azulene, deuteration slows the radiationless decay of **8a**, substantially.[158] Conventional radiationless transition theory[90] suggests this indicates that high-frequency C–H stretching vibrations act as important accepting modes in S_2's radiationless relaxation. However, this interpretation is complicated by the fact that the deuterium isotope effect is highly position sensitive[158] despite the fact that only small amounts of electron density are transferred to the aromatic rings on $S_2 \leftarrow S_0$ excitation (vide supra). D substitution at the 1 and 8 positions in **8a** ("β" to the thiocarbonyl group) has by far the largest effect. (The effect is masked in alkane solvents.[158]) This has been interpreted by Abrams et al.[158] in terms of a pseudophotochemical mechanism for S_2's relaxation whereby large-amplitude motion of the H atom "β" to the thiocarbonyl group induces radiationless relaxation but produces no net photochemical reaction.

The bi- and tricyclic compounds, **3–5**, differ from the aromatic thiones in their photophysical behavior. Their S_2 states lie at substantially higher energies and their lifetimes are too short (Table IX) to be measured by fluorescence emission methods. Falk and Steer[144,159] estimated the upper-state lifetimes by measuring their very small quantum yields of $S_2 \rightarrow S_0$ fluorescence in perfluoroalkane solutions and calculating the radiative lifetime using the Strickler–Berg formalism. Although such methods provide only an estimate of τ_{S_2}, there can be little doubt that the S_2 lifetimes of **3–5** are too short to enable these states to participate in bimolecular reactions with any substance other than the solvent. This conclusion has important implications for interpreting the UV photochemistry of these thiones (vide infra).

For adamantanethione (**3**) $\phi_f(S_2 \rightarrow S_0)$ is observed to increase modestly on perdeuteration of the molecule.[144] A very fast reversible intramolecular photochemical decay mechanism is apparently operative in the alicyclic thione systems.

Photophysical decay parameters have also been measured for the S_2 states of several cyclic enethiones, **9**, **16b**, **16c**, **17**, and **19**, in perfluoroalkanes and other solvents.[160] These compounds have completely structureless, broad, S_2–S_0 absorption and emission spectra, and it is therefore difficult to establish accurately the energies of their S_1 and S_2 states. Nevertheless, among this group, the rigid molecules with the largest $\Delta E(S_2–S_1)$ appear to exhibit the slowest nonradiative relaxation rates, in qualitative accord with the energy-gap law. (Thiocoumarin (**9**) although rigid has a very small S_2–S_1 energy gap of 6200 cm^{-1} and is the most weakly fluorescent;[136,160] **16c** with a methyl group α to the thiocarbonyl moiety also exhibits a short S_2 lifetime.[160])

Illumination of any of the larger thiones in their strong $S_2 \leftarrow S_0$ absorption bands in the UV-blue results in red $T_1 \rightarrow S_0$ phosphorescence. The quantum yield of phosphorescence obtained on $S_2 \leftarrow S_0$ excitation compared with that obtained on $S_1 \leftarrow S_0$ excitation can therefore be used as a means of determining the efficiency of $S_2 \rightsquigarrow S_1$ internal conversion, $\eta(S_2,S_1)$.[143,145,146,148] The same information may be obtained by determining the quantum yield of triplet formation on $S_2 \leftarrow S_0$ compared with $S_1 \leftarrow S_0$ excitation using laser flash photolysis methods.[52,132–138] The existing data are summarized in Tables VII and VIII. In all classes of thiocarbonyl compounds investigated to date, $\eta(S_2,S_1)$ is large, suggesting that $S_2 \rightsquigarrow S_1$ internal conversion is the major radiationless decay route regardless of whether the S_2 lifetime is long (e.g. 880 ps for **10a**) or short (<1 ps for **3–5**). However, experiments in perfluoroalkane solvents reveal subtle additional processes. Accounting for both radiative and nonradiative decay of S_2, Szymanski et al.[145] have shown that $\eta(S_2,S_1)$ is significantly less than 1 in those aromatic thiones which have accessible H atoms in positions "β" to the thiocarbonyl chromophore (e.g. the 1 and 8 positions in **8a**). Deuteration at these positions increases $\eta(S_2,S_1)$ to 1 (within an experimental uncertainty of ca. ±10%); changes in thione structure which tend to tilt these H atoms away from the C=S group (e.g. **6a** and **10a**) have the same effect. Thus, the presence of accessible H atoms in the "β" position appears to be correlated with the existence of a minor $S_2 \rightsquigarrow S_0$ relaxation channel. Again, a pseudophotochemical mechanism involving large-amplitude β-H motion has been proposed.[145] The alicyclic thiones, **3–5**, do not reach S_1/T_1 by direct $S_2 \rightsquigarrow S_1$ internal conversion.[144]

Measurements of τ_{S_2}, $\eta(S_2,S_1)$, and ϕ_T in solvents other than the perfluoroalkanes reveal a number of additional interesting aspects of S_2's radiationless decay. Maciejewski et al.,[140] Szymanski et al.,[145] Falk and Steer,[144] and Das and co-workers[52,133,135,136] all have demonstrated that the lifetime of S_2 is strongly solvent dependent but that $\eta(S_2,S_1)$ and ϕ_T remain large in all solvents. Thus solvent-induced radiationless decay of S_2 results mainly in the population of S_1/T_1, not S_0. However, $\eta(S_2,S_1)$ appears to be slightly smaller in alkanes than in perfluoroalkanes, suggesting that a small fraction of S_2 may be induced to undergo internal conversion to S_0 in more strongly interacting media.[145]

Table X. Lifetimes of the S_2 State of Xanthione (8a) in Various Media

perturber[a]	conditions[b]	$\tau(S_2)$, ps	ref(s)
none (bare molecule)	SSJ, $0 \leq E_{vib} \leq 227$ cm^{-1}	345–350	92, 161
	SSJ, $E_{vib} = 335$ cm^{-1}	295	92
	SSJ, $E_{vib} = 623$ cm^{-1}	265	92
perfluoro-*n*-hexane	SSJ, 1:1 vdW, $E_{vib} = 0$ cm^{-1}	320	92
	SSJ, 1:1 vdW, $E_{vib} = 335$ cm^{-1}	305	92
	liquid solution, AT	162 (175)	156 (50)
n-hexane	SSJ, 1:1 vdW, $E_{vib} = 0$ cm^{-1}	195	92
	SSJ, 1:1 vdW, $E_{vib} = 335$ cm^{-1}	130	92
	liquid solution, AT	25	156
cyclohexane	SSJ, 1:1 vdW, $E_{vib} = 0$ cm^{-1}	145	92
	SSJ, 1:1 vdW, $E_{vib} = 335$ cm^{-1}	130	92
	liquid solution, AT	17	156
benzene	SSJ	*c*	92
	liquid solution, AT	11 (12)	156 (152)

[a] For a more extensive list see references 92 and 156. [b] Abbreviations are as follows: SSJ, supersonic jet; vdW, van der Waals complex; AT, ambient temperature. [c] Not observed in supersonic expansion.

Topp and co-workers[156] have recently measured the lifetime of **8a** in a wide variety of solvents and have found little evidence that would support a nonradiative relaxation mechanism involving Franck–Condon-selective electronic energy transfer to high-frequency vibrational modes of the solvent. Instead, on the basis of differences in the S_2 lifetimes of **8a** in hydrocarbon solvents of varying structures, they proposed that a reversible, H-atom transfer reaction between solvent and excited solute was responsible for the majority of the solvent effect. However this mechanism would appear to be difficult to reconcile with the fact that a very large majority of the solvent-induced decay events results in the population of S_1/T_1, not S_0, and that solvents like CCl_4 have the same effect.

Topp and co-workers[47,92,161] have also made an important contribution to our understanding of the excited-state dynamics of the thiones in their recent reports of measurements of the lifetimes of the S_2 state of **8a** and its van der Waals complexes in a supersonic expansion. In the bare molecule the same mode specificity observed spectroscopically[47] in S_2's nonradiative relaxation appears in its lifetime in selected vibrational states;[92,161] excitation of 335 cm^{-1} and 623 cm^{-1} vibrations results in both an increase in the relative intensity of emission from S_1/T_1 compared with S_2 and a decrease in S_2's lifetime. Similar measurements on 1:1 van der Waals complexes with alkanes and perfluoroalkanes reveal that the perfluorinated compounds cause the S_2 lifetimes to decrease only slightly, whereas the corresponding alkanes cause a very substantial reduction in lifetime and benzene quenches the luminescence almost completely. These observations show remarkable parallels with those obtained when the same compounds are employed as liquid solvents.[156] Representative data are summarized in Table X.

These data, together with the radiative lifetimes from Table IX, reveal that nonradiative relaxation is the major decay chemical for **8a** even when uncomplexed under the isolated, ultracold conditions which prevail in supersonic expansions. Complexation enhances the nonradiative decay rate, and Topp and co-workers[92,161] have shown that the extent of this enhancement is related to the nature of the complexing partner and the zero-point structure of the complex. They also concluded from these studies that vibrational-energy-induced conformational change, limited in rate by vibrational-coupling dynamics, is responsible for the observed increase in nonradiative decay rate when the complex is excited at higher initial vibrational energies.

Evidence of the dynamic behavior of states higher in energy than S_2 is sparse. Excitation of aromatic thiones[145] such as **7a**, **8a**, and **10a** to S_3 results in quantitative relaxation to S_2. Alicyclic thiones[144] such as **3** exhibit no fluorescence when excited in liquid solution to the lowest Rydberg state and may therefore undergo fast intramolecular photochemical reaction at these energies. There are no reports of the dynamic behavior of higher excited states of other classes of thiones.

D. Excited-State Quenching

The fact that the S_2 and T_1 states of the thiones undergo electronic quenching at or near diffusion-limited rates by a wide variety of substances (including ground state thione and oxygen) is one of the major difficulties associated with studying their photochemistry and photophysics in fluid media. In studies of the reactions and interactions of triplet thiones, oxygen must be rigorously excluded. Thione concentrations must also be kept very low (often $<10^{-6}$ M) in order to prevent triplet decay from being dominated by self-quenching interactions. Indeed, the inefficiencies in photochemical reactions between triplet thiones and reactive addends have been traced to the energy wastage associated with competition by self-quenching at high thione concentrations.[162-165] Such inefficiencies can, however, be diminished by incorporating the thiones in micelles.[166] These requirements are relaxed when studying the short-lived second excited singlets. However, studies of S_2 are complicated by the facts that the thione nonradiative decay rates are extremely sensitive to the nature of the solvent (vide supra) and that quenching by many common solvents occurs at diffusion-limited rates.

Irrespective of the mechanism of the electronic quenching process and the nature of the quencher, the second-order rate constants for quenching of both the S_2 and T_1 states of thiones in homogeneous fluid media have generally been obtained either from Stern–Volmer plots using eqs 5a and 5b or from equivalent competitive scavenging methods. Such plots are consistently observed to be linear, as shown in Figures 13 and 14. (Complications arise in S_2 quenching when the transient

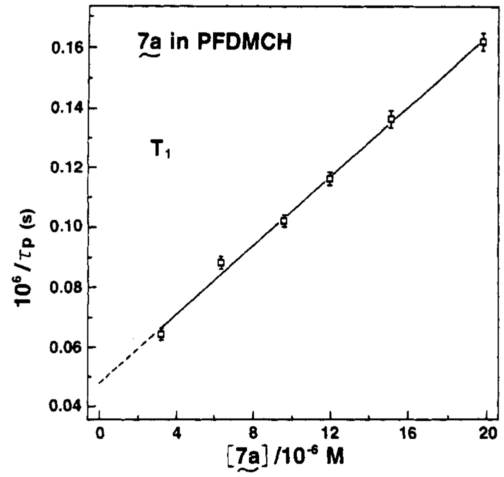


Figure 13. Stern–Volmer plot of $1/\tau_p$ vs thione concentration for **7a** in perfluoro-1,3-dimethylcyclohexane, illustrating the self-quenching of thione triplets in fluid solution.

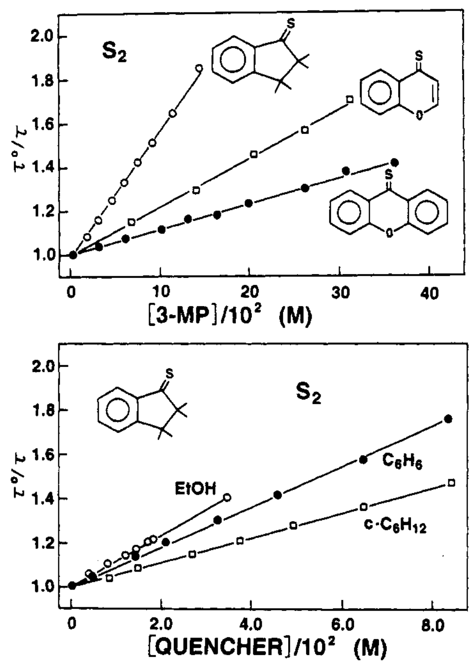


Figure 14. Stern–Volmer plots of the quenching S_2–S_0 fluorescence of several thiones by 3-methylpentane (top), and of **10a** by several quenchers (bottom) all in perfluoroalkane solvents at room temperature.

effect becomes important, vide infra.) In the case of self-quenching and quenching by oxygen, the rate constants thus obtained have magnitudes characteristic of diffusion-limited processes (i.e. ca. 10^{10} M^{-1} s^{-1} in typical fluid solvents at room temperature) for all but the most sterically crowded thiones. Exothermic triplet–triplet energy transfer, triplet quenching by di-*tert*-butylnitroxyl radical, and triplet–triplet annihilation also frequently occur at diffusion-limited rates. The nature of the solvent (in particular its viscosity), the temperature, and the structures and diffusion coefficients of the excited thione and quencher are therefore important parameters in determining the magnitudes of the quenching rate constants. Extensive tabulations of the values of the rate constants for quenching of the thiones in their S_2[140,142,173] and T_1[49,52,133-137,146,162,163,172] states have been provided by several research groups.

The mechanisms of triplet quenching have been extensively studied using both phosphorescence quenching and transient absorption methods. In the case of triplet self-quenching a mechanism involving the formation of triplet excimers was proposed initially by de Mayo and co-workers[167,168] and has been amplified by Ramamurthy and co-workers[162,163] and Maciejewski and co-workers.[164,165] No spectroscopic evidence of triplet excimers has been found to date, implying that, if formed, triplet thione excimers or heteroexcimers decay primarily by nonradiative means. However, good indirect evidence for the intermediacy of triplet excimers has been uncovered recently by Maciejewski[164,165] who showed that small amounts of dimeric product arise from triplet self-quenching of **6a**, **7a**, and **8a** in highly purified, inert perfluoroalkane solutions (vide infra), and that the quantum yield of consumption of the thione is a linear function of the fraction of triplets which are self-quenched. Ramamurthy, Das, and co-workers[135,163] have demonstrated that the triplet self-quenching rate constants of **11** and **14** decrease on proceeding from their electron-withdrawing to their electron-releasing para substituents. This trend and the effects of steric crowding were interpreted in terms of donor–acceptor interactions between the thiocarbonyl groups in the excited complex, with the ground-state molecule acting as the electron donor.

Exothermic energy transfer from sterically unhindered thione triplets to acceptors such as ferrocene, *all-trans*-1,6-diphenyl-1,3,5-hexatriene, and molecular oxygen also occurs at near diffusion-limited rates.[52,132-136,138,169,170] In the case of quenching by $O_2(^3\Sigma_g^-)$ the products, $O_2(^1\Delta_g)$ and ground-state thione, are formed with unit efficiency, proving that energy transfer, not chemical interaction, is the first step in the photooxidation of thiones in solution. Unlike aromatic hydrocarbons,[171] oxygen quenching of the thione triplets generally proceeds at greater than the spin statistical rate.[52,135,172] That is, $k_Q > {}^1/_9 k_{diff}$ where k_Q is the observed second-order quenching constant and k_{diff} is the calculated rate constant for a diffusion-controlled process. The factor of ${}^1/_9$ is expected on simple spin-statistical grounds[171] when only singlet products are formed via an encounter complex, $^{1,3,5}(T\cdots O_2)$, which contains nine spin sublevels. The fact that $k_Q > {}^1/_9 k_{diff}$ in the thione systems indicates that oxygen quenching is more complex than this simple mechanism describes. Several alternatives have been advanced.[52,135,172]

Ramamurthy, Das, and co-workers[52,134,135] have also shown that the di-*tert*-butylnitroxyl radical is a very efficient quencher of the triplets of **11**, **14**, and **18**. Electronic energy transfer is improbable in these systems, and a charge-transfer quenching mechanism was ruled out on the grounds that no variation in k_Q was observed on changing the electron-donating/electron-accepting properties of the substituents. On this basis an electron-exchange mechanism was suggested for nitroxyl radical quenching of these triplet thiones.

Quenching of the S_2 states of many thiones also occurs at diffusion-limited rates in fluid solution. However, Maciejewski[173,174] has shown that in these cases transient effects which have their origins in the time evolution of quencher concentration gradients must be taken into consideration when interpreting the quenching kinetics. Transient effects have the greatest impact on the quenching kinetics when the lifetime of the excited state is short and/or the solvent viscosity is large and lead to nonlinear Stern–Volmer plots and nonexponential transient decays when the concentration of quencher is sufficiently large. The transient effect is therefore an important factor in describing the quenching of the S_2 states of thiones even in nonviscous solvents because the excited state is so short-lived and its quenching is often diffusion limited. By systematically varying the viscosity of inert perfluoroalkane solvents, the lifetime of the excited thione, and the quencher diffusion coefficient (size and structure), Maciejewski et al.[173,174] showed that the quenching process involves only short-range interactions. Transient effects completely dominate the quenching of the shortest-lived S_2 states by quenchers with the smallest diffusion coefficients in these systems (k_Q as large as 1.2×10^{11} M^{-1} s^{-1}). The Smoluchowski–Collins–Kimball model[174,175] provides a satisfactory theoretical description of the process.

A further review of the mechanisms of T_1 and S_2 interactions with reactive addends will be included in later segments of this article.

E. Miscellaneous

The visible electronic spectra of thioketene, H_2CCS, and its D_2 isotopomer have been reported,[176] and an in-plane bent upper state structure ($^1A''$) has been deduced from the observed vibronic activity. The lack of rotationally discrete structure in the spectrum and the complete absence of fluorescence suggest that the upper state is predissociated. This conclusion is consistent with the observation of an intense absorption due to the HCCS radical immediately following flash photolysis of thioketene in the gas phase. The photophysical properties of the triplets of three substituted thioketenes in fluid solution have also been reported.[137] The triplets are very short-lived ($\tau_p < 5$ ns) and are apparently formed from S_1 in low quantum yield despite the fact that the S_1 states are photostable under these conditions. Pseudoisomerization along the in-plane C=C=S bending coordinate is suggested to promote rapid $S_1 \rightsquigarrow S_0$ internal conversion and $T_1 \rightsquigarrow S_0$ intersystem crossing in these molecules.

The electronic absorption and laser-induced emission excitation spectra of thioacrolein, $H_2CCHCHS$, have been reported by Moule and co-workers.[177,178] The trans isomer is more stable than the cis in the ground state, but the cis form is predicted to be slightly favored in T_1 ($^3A''$). The barrier to internal rotation between the two isomers is calculated to be slightly higher in T_1 (ca. 2800 cm^{-1}) than in S_0, consistent with increased electron density between C(1) and C(2) in the triplet. The laser-induced emission excitation spectra contain contributions from both fluorescence and phosphorescence and result exclusively from absorption by the trans isomer. A search for emission resulting from absorption by the less stable cis form was unsuccessful.

Phosphorescence has also been observed on excitation of thioacetaldehyde[179] and thioacetone[37,179] in their overlapping $S_1 \leftarrow S_0$ and $T_1 \leftarrow S_0$ absorptions. The lifetimes of their triplets are ca. 10 μs in the low-pressure limit, but Stern–Volmer plots of τ_p^{-1} vs pressure are highly nonlinear, suggesting that collision-induced radiationless decay may be occurring in these systems. The features in the excitation spectra due to methyl torsional vibrations are clearly resolved in mild supersonic expansions,[37] and this, combined with emission lifetime measurements, should be a powerful tool for examining the effects of internal rotation on the excited-state dynamics of both thioacetaldehyde and thioacetone.

V. Physical Photochemistry of Larger Thiocarbonyls

Molecules containing the thiocarbonyl group are known to undergo reduction, oxidation, dimerization, cycloaddition to unsaturated addends, and a variety of cleavage reactions on excitation to one or more of their S_2, S_1, and T_1 states in condensed media. Several excellent, comprehensive reviews of this work have appeared recently.[9-13] These reviews and the original research on which they are based have focused mainly on the organic and physical organic aspects of the photochemistry. In keeping with this focus, emphasis has been placed on the identities and yields of the final products as a function of thione and addend structure, the identities and lifetimes of the intermediates formed, and mechanisms of the reactions, and their synthetic utility. The experimental work has been supplemented and supported by a number of useful theoretical studies.[180-183]

Our purpose here is not to re-review this literature. Instead, we intend to concentrate on those systems for which either good computational studies of the excited-state surfaces or detailed experimental studies of the electronic spectroscopy and photophysics are available to support the photochemistry. The number of such systems is relatively small.

We begin by introducing two general caveats for readers of the photochemical literature. Researchers have often wished to investigate the unusual wavelength-dependent photochemistry of the thiones. As noted in earlier sections of this review, near-UV excitation most frequently populates S_2 and this state may be sufficiently long-lived (albeit <1 ns) to undergo either intramolecular or intermolecular reactions. Excitation in the visible populates the coupled $S_1/T_2/T_1$ states. In this case the lowest triplet is almost always formed rapidly in high yield and is taken to be the photochemically reactive species. However, because S_2 decays efficiently to T_1 in most thiones, any differences in photochemical reactivity of S_2 and T_1 can only be ascertained by comparing the nature and the quantum yields of the products formed on UV excitation with those formed in the visible. If different products are formed at different wavelengths, one may safely conclude that the photochemistries of S_2 and T_1 are *qualitatively* different. However, frequently both UV and visible excitation yield the same products, requiring that relative quantum yields of formation of the products or of consumption of the reactants be measured to determine the differences in reactivity of the two states.

Here, care must be exercised because the long-lived triplet states are self-quenched at or near diffusion-limited rates. Even at low thione concentrations self-quenching can compete effectively with parallel photochemical reactions of the triplet when these reactions are inhibited by activation barriers or severe steric effects. Although the S_2 states are also often self-quenched at diffusion-limited rates, this only becomes a factor at much higher thione concentrations because S_2 is so much shorter-lived. Care must therefore be taken in assessing the apparent wavelength dependence of the quantum yields of product formation and thione consumption when such measurements have been made at different thione concentrations. This is particularly the case when considering the yields of reaction products derived from free radicals or potentially scavengeable diradicals since ground-state thione can also act as an efficient radical trap (vide infra).

A second caveat concerns the nature of the excited-state responsible for reaction on the low-lying excited-state surfaces. As previously discussed, the S_1, T_1, and T_2 states of the thiones are often of similar energy. Therefore, because the solvatochromic properties of π,π^* states are different from those of n,π^* states, changing solvents can bring T_2 into closer proximity with S_1 and T_1 and, in some cases can cause T_1 and T_2 to invert. The reactive species responsible for the visible photochemistry of the thiones has, however, often been presumed to be the $^3(n,\pi^*)$ state irrespective of the nature of the solvent. Other possibilities such as reaction from thermally populated S_1 have also not been explored in any detail.

A. Cleavage Reactions

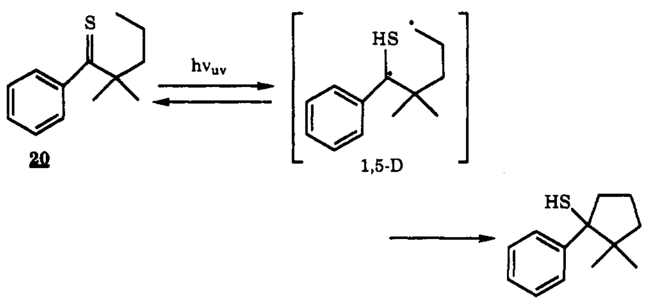
Norrish type I (α) cleavage is a well-known and efficient process in the S_1 and T_1 states of a wide variety of carbonyl-containing compounds. It is often followed by elimination of CO from the resulting acyl radicals, a process which is usually a major pathway in gas-phase systems. However, α cleavage does not occur in the T_1 (or S_1) states of unstrained thiocarbonyls unless a heteroatom is located in an α position, and dethiacarbonylation has never been observed. UHF-MINDO/3-CI calculations predict that activation barriers to α-bond cleavage are higher on the S_1 and T_1 surfaces of model thiones than in the corresponding ketones,[181,183] consistent with these observations. Efficient α-cleavage on the T_1 surface is observed experimentally in strained thioketones which have substantially higher energies. This is also consistent with calculations which predict lower activation barriers to α cleavage with increasing strain in model compounds. Thus, initial α cleavage to form 1,4-diradicals occurs in the T_1 states of substituted cyclobutanethiones[182,184–187] and cyclobutanedithiones[134,182,187] such as **18**. α Cleavage also occurs on visible excitation of the arylalkylcyclopropenethiones,[188,189] but in these cases both the initial 1,3-diradicals and the corresponding thioketene carbenes are calculated to be accessible on energetic grounds. This is consistent with the observation of carbene reaction products in various solvents. Ring-closed thiacarbenes are also thought to be intermediates in the photolysis of **18**.

In all cases UHF-MINDO/3-CI calculations[181–183] reveal that the activation barriers on the S_1 and T_1 surfaces are associated with avoided crossings between the bound $^{1,3}(n,\pi^*)$ states and a $^3(n,\sigma)^*$ state which is unbound with respect to α cleavage. In the substituted cyclobutanethiones, the cyclopropenethiones, and compounds **18a–e**, these activation barriers are sufficiently low that barrier crossing competes with other radiative and nonradiative decay processes of the triplets at room temperature. Accordingly, the unquenched lifetimes of the strained triplets are short at room temperature (less than or equal to ca. 0.5 μs for substituted cyclobutanethiones and dithiones[134,182]) and phosphorescence is not observed. Emission from T_1 appears[182] on cooling to 77 K, at which temperature barrier crossing is suppressed. Chandra and Sumathi[183] have also predicted that perpendicular motion of the thiocarbonyl carbon atom is an important feature of the α-cleavage reaction coordinate on the T_1 but not the S_1 surfaces. The photochemical consequences of this prediction have not been elucidated experimentally.

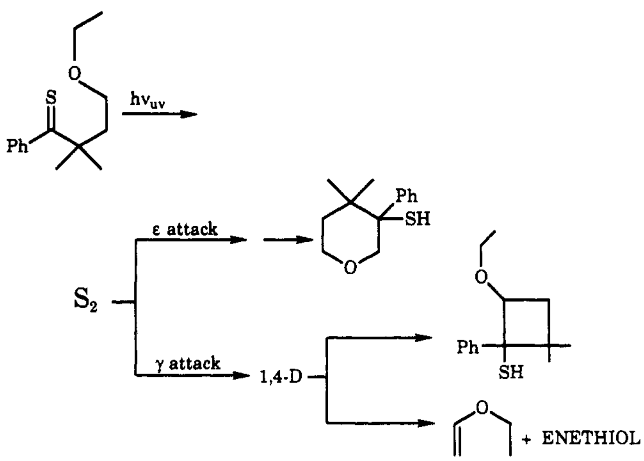
Despite the tidy picture of α cleavage in the strained thioketones which theory and experiment apparently produce, a number of unresolved questions remain. First, Ramamurthy and co-workers[190,191] have interpreted the results of quenching and sensitization experiments on several four-membered-ring β-dithiolactones in terms of α cleavage from their S_1, not T_1 states. However, no photophysical data are available to support this suggestion, and there appears to be no fundamental reason why these thiones should behave "anomalously" in their S_1/T_1 states. Second, calculations predict that the T_2, $^3(\pi,\pi^*)$ states of the strained thiones play no significant role in the photochemistry, whereas T_2, S_1, and T_1 are known to be of approximately the same energy in many thioketones (vide supra). The role of T_2 either directly or indirectly (i.e. by mixing with S_1 and T_1) has yet to be ascertained; a matter which is particularly unsettling because many of the experimental photophysical measurements on these strained thiones have been made in benzene solution. T_1–T_2 inversion is known to occur in benzene in some thiones.[91] The possible role of $S_1 \rightleftarrows T_1$ equilibrium also has not been investigated, although a significant population of S_1 must be present under conditions of steady-state illumination at room temperature owing to the small S_1–T_1 electronic energy spacings in these systems.[148] Finally, the activation energies associated with the increase in the rate of α cleavage, and the decrease in the intensity of phosphorescence with increasing temperature have not been measured. The latter are required to ascertain the accuracy of the barrier calculations which, of course, apply only to isolated molecules.

When their structures permit, intramolecular photoreactions other than α cleavage occur in unstrained thioketones. The aryl alkyl thiones such as **20**[151,192,193] are related compounds[194–197] have been thoroughly studied by de Mayo and co-workers. The same products are sometimes obtained from illumination in both the visible and the near-UV absorptions, but product quantum yields are invariably higher when exciting at the higher energy and it is therefore clear that the same product can sometimes be obtained by two entirely different pathways. Sensitization experiments reveal that reaction is initiated from the lowest triplets when exciting in the visible, whereas excitation in the UV produces S_2. Intramolecular H abstraction competes successfully with radiationless relaxation of the intact S_2 excited molecule in these aryl alkyl thiones. The S_2 lifetimes are short (<0.5 ns by $S_2 \rightarrow S_0$ fluorescence decay[151,197]), and the abstractions are barrier free, thus demonstrating that these states act as powerful electrophiles.

Scheme I



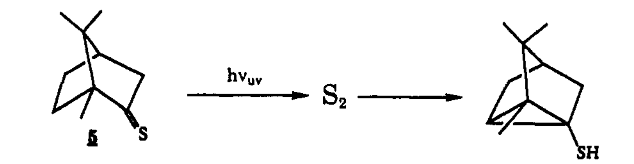
Scheme II



By systematically varying the nature of the substituents in **20**, including both ethers[195,196] and λ aryl groups,[197] de Mayo and co-workers demonstrated that intramolecular abstraction occurs preferentially from the δ position, when H is available there, but only on excitation to S_2 (Scheme I). Singlet 1,5-diradicals are formed which either disproportionate to reform starting material or cyclize to form the corresponding cyclopentanethiol. When the δ carbon is replaced by an ethereal oxygen atom,[196] abstraction occurs at either the ϵ position (giving six-membered ring thiols) or the γ position. In the latter case ring closure of the resulting 1,4-diradical yields cyclobutanethiol whereas Norrish type II β cleavage yields vinyl ethers (Scheme II). Weak $S_2 \rightarrow S_0$ emission is seen in these systems; the fluorescence quantum yields and lifetimes of the S_2 states have been measured directly in some cases.[151] The resulting S_2 radiative and nonradiative decay constants together with the product quantum yields may then be used to obtain the overall rate constants for product formation. The results reveal that net product formation constitutes an interesting but relatively minor intramolecular radiationless decay path in these systems. The inefficiency in net product formation can be traced to competition from both the radiationless decay of the intact S_2 state and reformation of the parent thione by disproportionation of the intermediate diradicals.

The only abstractable H atoms in the λ aryl alkyl thiones are β to the thiocarbonyl group. $S_2 \leftarrow S_0$ excitation of these thioketones[197] results in the formation of 1,3-diradicals and the ultimate production of cyclopropanethiols. Similar β-H-transfer reactions are seen in the bicyclic thiones **4** and **5** in which selective deuteriation was used to prove that only the *endo*-β-hydrogen atom is transferred following UV excitation

Scheme III



en route to the final cyclopropanethiol (homothioenol) products[198,199] (Scheme III). Selective deuteriation has also been used to show that large amplitude motion of H atoms "β" to the thiocarbonyl group is associated with the direct radiationless decay of the S_2 state of the aromatic thione, **8a**, to the ground state.[158] The sum of the chemical evidence therefore supports the conclusion that the excited states of thiones of all varieties are ubiquitous abstractors of H atoms and that the S_2 states are particularly powerful in this respect. These conclusions are also borne out by studies of the intermolecular H-abstraction reactions of thione excited states in a variety of media (vide infra).

B. Intermolecular H Abstraction

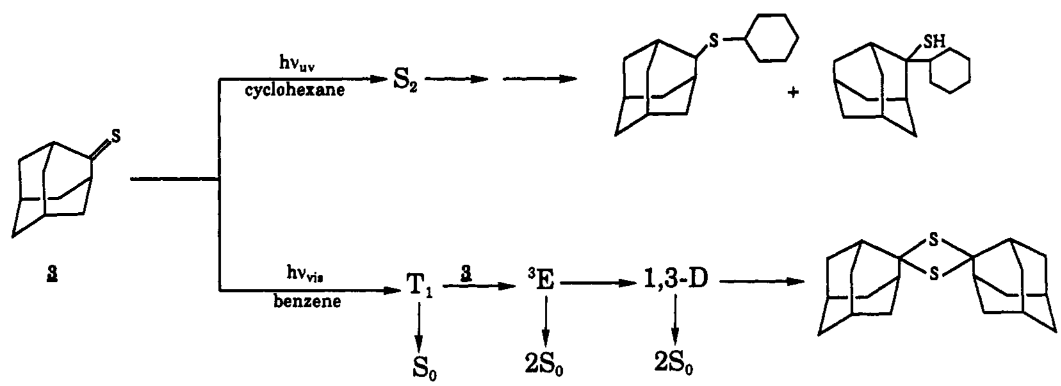
Reduction of the thiocarbonyl group can occur when thiones are excited to any of their S_2, S_1 or T_1 states in hydrogen-donating media. The ease of reduction is related both to the structure and electronic state of the thione and to the H-donating ability of the donor.

Adamantanethione (**3**) has been described as a model compound for studies of such abstraction reactions.[200,201] When **3** is illuminated in benzene in the visible the reactive intermediate is the lowest triplet state and the only product is the 1,3-dithietane dimer[202] (Scheme IV). When 2-adamantanethiol is added to the solution in high concentration (ca. 1 M), the only product is the disulfide.[203] Abstraction of the labile sulfhydryl hydrogen atom by T_1 initiates the chemistry. Deuteriation of the thiol showed that only one deuterium is incorporated per molecule of disulfide, and this and other results were interpreted in terms of a chain reaction in which the reversible addition of a thiyl radical to ground-state thione is the key chain-propagation step. The identities of the free-radical intermediates were established by EPR using spin-trapping techniques.[203]

When **3** is excited in its strong $S_2 \leftarrow S_0$ UV absorption band in alkane solvents, 1,3-dithietane dimer is produced together with sulfides and thiols.[200,201] The latter result from net insertion of the thione into C–H bonds of the solvent (Scheme IV). Chemical scavenging experiments were employed to trap reactive precursors of the insertion products. A species of ca. 200-ps lifetime was inferred from these measurements,[201,204] and de Mayo and co-workers assigned it to the S_2 state of **3**. Experiments in which the thione was illuminated in mixtures of cyclohexane and cyclohexane-d_{12} were interpreted[201] in terms of a mechanism involving initial H(D) abstraction by S_2 to form caged radical pairs. Observed product yields in these experiments led de Mayo and co-workers to propose that an unusually large, viscosity-dependent fraction of the caged radical pairs combined to give the sulfide and thiol products. The small fraction of thiyl radicals which escape the cage are scavengeable (by ground-state thione as well as other radical traps) and lead to sulfide and disulfide.

The available photophysical data[144,159] are at odds with parts of this interpretation. The $S_2 \rightarrow S_0$ fluo-

Scheme IV



rescence quantum yields of **3** (and of the bicyclic thiones **4** and **5**) are very small even in inert perfluoroalkane solvents. By measuring these fluorescence quantum yields and estimating the $S_2 \rightarrow S_0$ radiative decay rate constants by the Strickler–Berg method,[205] Falk and Steer[144] showed that the lifetimes of the initially populated S_2 states of **3–5** are all < 1 ps. Although reaction with the solvent is still possible, the fluorescent S_2 state is too short-lived to participate in intermolecular reactions even when the reaction partners are present in relatively large concentrations. This result has important implications in the interpretations of the results of cycloaddition experiments involving the "S_2 state" of **3** (vide infra). The identity of de Mayo's scavengeable 200-ps intermediate in the UV photolysis of **3** remains uncertain.

Irrespective of the mechanism of the photochemistry initiated by $S_2 \leftarrow S_0$ excitation of these bridged bi- and tricyclic thiones, the fact that almost the same quantum yields of phosphorescence are obtained on initial excitation to both S_2 and S_1 in a variety of solvents indicates that a large majority of S_2 states decay nonradiatively by some means to the lower $S_1/T_2/T_1$ surfaces.[144] This conclusion is supported by measurements[144] of ϕ_D, the quantum yields of net consumption of these thiones; for $S_2 \leftarrow S_0$ excitation at infinite dilution $\phi_D^0 = 0.04$ for **3** in perfluoroalkanes and 0.11 in cyclohexane. However, the very short lifetimes of the S_2 states and the large S_2–S_1 energy gaps in these compounds indicate that this relaxation route does *not* involve direct $S_2 \rightsquigarrow S_1$ internal conversion. Instead, S_2 must decay indirectly to the coupled $S_1/T_2/T_1$ surfaces by a process which does not involve net consumption of thione, but which might involve reversible photochemistry (frustrated intramolecular β-H transfer or intermolecular H transfer in alkanes?) or the population of a lower, bound, dark, (doubly?) excited state of unknown identity. Further work is clearly required before this system is fully understood.

Aromatic thiones also undergo photoreduction by intermolecular H abstraction. The early work of Oster et al.[206] and Ohno and Kito[207,208] on thiobenzophenone (**11a**) has been reviewed by de Mayo[13] and by Rao.[10] A free-radical mechanism, initiated by H-atom abstraction from the solvent is operative on both S_2 and S_1 excitation. Differences between **11a** and benzophenone itself have been traced to the fact that ground-state thiobenzophenone (like many thiones) is an excellent radical trap.[203] Although it would be interesting to be able to carry out studies which parallel the vast literature on the corresponding ketone, thiobenzophenone has proved to be a difficult compound to study comprehensively because it fluoresces only weakly from S_2 in solution at room temperature and its photochemistry is complex.

Table XI. Quantum Yields of Net Photochemical Consumption of Several Aromatic Thiones at Infinite Dilution in Perfluoroalkane and Alkane Solvents at Room Temperature

thione	solvent[a]	$\phi_D^0(T_1)$	$\Delta\phi_D^0(S_2)$[b]	ref(s)
6a	PFDMCH	$\leq 4 \times 10^{-4}$	$<1 \times 10^{-4}$	165
	3-MP	0.035		49, 146
7a	PFDMCH	$\leq 2 \times 10^{-4}$	$<5 \times 10^{-5}$	164, 165
	3-MP	0.025	≤ 0.0025	49, 146, 210
8a	PFDMCH	$\leq 2 \times 10^{-5}$	$<5 \times 10^{-6}$	165
	3-MP	0.008		49, 146

[a] Abbreviations are as follows: PFDMCH, perfluoro-1,3-dimethylcyclohexane; 3-MP, 3-methylpentane. [b] Increment in ϕ_D^0 due to consumption of the thione in its S_2 state.

Recent work has focused on the photochemistry of the series of aromatic pyranthiones, **6a**, **7a**, and **8a**, whose photophysics and electronic spectroscopy have been more thoroughly studied. The photochemical properties of xanthione (**8a**) were first investigated by Huber and co-workers[73,209] who showed that its rate of reduction was much faster in alcohols than in 3-methylpentane or acetonitrile solvents. The reactive state was assigned to the lowest triplet irrespective of the excitation wavelength. The initial photochemical step involves hydrogen abstraction from the solvent and formation of a caged radical pair. Subsequent competition between recombination of the caged radicals and reaction of the thioketyl radical with ground-state thione leads to products at rates which could be modeled quantitatively.[209]

Subsequent studies have shown that the nature of the solvent also has a dramatic effect on the rates of relaxation of the S_2 states of a wide variety of aromatic thiones[50,140,154,156,157] and that intermolecular interactions dominate the relaxation mechanism(s) in all but the most weakly solvating media (the perfluoroalkanes[142]).

The quantum yields of net consumption of thione, ϕ_D, have been measured on $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ excitation of varying concentrations of **6a**, **7a**, and **8a** in a variety of solvents.[164,165] Extrapolation of these data to infinite dilution give ϕ_D^0 (Table XI) whose values reflect the net chemical consumption of the thione in the absence of self-quenching interactions (vide infra). The values of ϕ_D^0 are very small in highly purified perfluoroalkanes, and are the *same*, within an experimental error of ±20%, for initial excitation to both S_2 and S_1. These facts show that the excited states of **6a**, **7a**, and **8a** accessed in the UV-visible are very unreactive in solvents which possess no abstractable H atoms (or other reactive centers) and that S_2 is consumed to no greater extent than T_1. Although the values of ϕ_D^0 are at least 2 orders of magnitude larger when the photolyses of these thiones are carried out in 3-methylpentane, the absolute magnitudes of ϕ_D^0 are still relatively small. For **7a** the same values of ϕ_D^0 (within ±10%) are again obtained on both UV and visible excitation.[210] Hydrogen abstraction by the triplet must therefore be responsible for the larger values of ϕ_D^0 in the hydrocarbon solvent. However, even in hydrocarbon solvents, *net* photochemical reaction cannot account for a significant fraction of the decay of either S_2 or T_1.

On the other hand, fluorescence lifetime and quantum yield measurements have demonstrated that the S_2 states of **7a**, **8a**, and other rigid aromatic thiones decay nonradiatively by factors of up to 1 order of magnitude *faster* in alkanes than in the corresponding perfluoroalkanes.[50,140,156] Topp and co-workers[156] interpreted this and the variations in S_2 lifetimes of **8a** with alkane structure in terms of a mechanism involving reversible hydrogen-atom abstraction. However, the quantum yields of phosphorescence produced on $S_2 \leftarrow S_0$ excitation of **8a** are not significantly different in 3-methylpentane and perfluoroalkane solvents (Table VII),[145,146] indicating that the primary effect of the alkane is to accelerate the rate of S_2 nonradiative decay to S_1/T_1. Topp observed the same effect in 1:1 van der Waals complexes of **8a** with hydrocarbons,[47,92] and similar effects are also seen in solvents such as benzene, CCl_4, and other chlorofluorocarbons[140] where H atom abstraction is not possible. Unless H abstraction produces caged radical pairs which combine almost quantitatively on the S_1/T_1 surfaces of the parent thione (which would be most unusual), a reversible hydrogen-atom abstraction mechanism would appear not to be responsible for accelerating the rate of S_2's nonradiative decay in alkane solvents. Decay via an intermediate exciplex[140] is feasible, but no spectroscopic evidence of such a species has yet been found. Further work to clarify these matters is clearly required.

The experimental work on both intramolecular and intermolecular hydrogen abstraction outlined above finds support in a number of theoretical studies on model systems. In an interesting early paper Formosinho[211] showed that the measured rates of intermolecular hydrogen abstraction from 2-propanol and ethanol by the lowest triplet of thiobenzophenone (**11a**)[167] could be accurately evaluated by considering the reaction in terms of a radiationless transition. This involves calculating the tunnel-effect probability of a transition from the T_1 potential surface of the thione and the C–H vibrations in the reactant state to the potential surface of the C–S and S–H bonds in the products. Large H/D isotope effects are predicted and this is consistent with observations in a number of triplet hydrogen abstraction reactions.[197,209]

Natural correlation diagrams together with ab initio SCF-CI calculations have been employed by Bigot[212] to describe the potential energy profiles along several hydrogen-atom abstraction paths in a model system consisting of excited thioformaldehyde and methane.

The same model system has also been treated using semiempirical MINDO/3 methods by Sumathi and Chandra.[213] Although neither study can be expected to provide accurate activation barriers, both provide qualitative insight into aspects of the reaction coordinates. In the n,π^* states, abstraction is only feasible when the hydrogen atom approaches the S atom in the plane of the thiocarbonyl chromophore. Hydrogen abstraction by the π,π^* state is possible at either the S or the C atom of the chromophore and is favored by approach in a plane which is perpendicular to the molecular plane, i.e. in the plane of the π^* orbital. The latter is in agreement with the observation that only *endo*-β-H atoms undergo intramolecular transfer on excitation to the S_2 states of **4** and **5**.[198,199] In all cases the barrier heights are extremely sensitive to the distance between the donor hydrogen atom and the accepting atom of the chromophore at the transition state.

C. Dimerization

Dimers are ubiquitous products of the photolysis of alicyclic,[202,214] aromatic,[164,165] and dibenzyl[215] thiones in unreactive media. Sensitization experiments have proved that the reactions initiated by excitation in the visible involve the lowest triplet states. Only dimers with 1,3-dithietane structures have been isolated. However, the corresponding 1,2-dithianes are expected to be less thermally stable and, if formed, might be difficult to quantitate. Dimer quantum yields from photolysis in the visible are invariably low, even when the reactions are carried out in solutions of high thione concentration where $T_1 \cdots S_0$ self-quenching encounters are exclusively responsible for the triplet decay. An efficient energy-wastage process is therefore operative along the photochemical route to these products. The nature of the intermediates involved has been a subject of ongoing interest.

de Mayo and co-workers[202,214] have proposed that both triplet excimers and short-lived 1,4-diradical intermediates precede the formation of dimer in the visible photolysis of adamantanethione (**3**, Scheme IV). Although only one intermediate was required to rationalize the kinetics, arguments based on the ring-closing propensities of the several possible sulfur-containing 1,4-diradicals led them to propose that the diradical is preceded by a triplet excimer. (Only 1 in 7000 $T_1 \cdots S_0$ encounters leads to product formation. Both radiationless decay of the triplet excimer and homolysis of open-chain conformations of the 1,4-diradicals reform reactant thione.) de Mayo and co-workers[204] also analyzed the kinetics of dimer formation resulting from UV photolysis of **3** in terms of an excimer derived from $S_2 \cdots S_0$ interaction. However, this interpretation should be viewed with caution in light of the subsequent revelation[144] that the fluorescent S_2 state of **3** has a subpicosecond lifetime.

Ramamurthy and co-workers[162,163] studied the quenching of the triplet states of **8a**, **8b**, **8c**, and **11b** by a variety of aromatic and alicyclic thiones having higher triplet energies. The results were interpreted in terms of the formation of triplet thione heteroexcimers which are stabilized by donor–acceptor interactions of the thiocarbonyl groups (cf. section IV.D). Maciejewski and co-workers[164,165] showed that, contrary to earlier

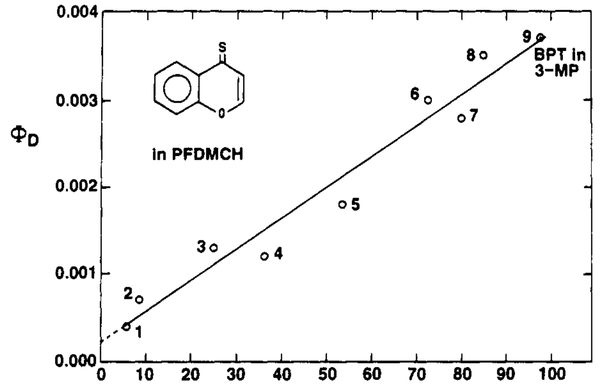


Figure 15. Graph of the quantum yield of net photochemical consumption of **7a** in perfluoro-1,3-dimethylcyclohexane at various increasing concentrations of thione. The circled point is for **7a** (BPT) in 3-methylpentane (from ref 165).

reports,[162,209,216] dimers are also produced in small yields on photolysis of the aromatic thiones **6a**, **7a**, and **8s** in both perfluoroalkane and 3-methylpentane solvents. In perfluoroalkanes ϕ_D is a *linear* function of the fraction of triplets self-quenched (Figure 15) at thione concentrations up to about 10^{-3} M ($\leq$99% self-quenching). Interestingly, the value of ϕ_D for high concentrations of **7a** in 3-methylpentane falls on the same line. This indicates that when self-quenching dominates the triplet decay process, the only significant net product arises from dimerization. Hydrogen abstraction consumes insignificant amounts of thione under these conditions. These results were interpreted in terms of a mechanism involving the formation of triplet excimers whose efficiencies of dimer formation increase in the order **8a** $\ll$ **7a** < **6a**. Finally Maciejewski and coworkers[165] showed that $S_2 \leftarrow S_0$ excitation of **7a** in perfluoroalkane solvents produces no measurable change in product quantum yield (when normalized to the same triplet yield) compared with excitation to S_1/T_1 at thione concentrations where self-quenching dominates T_1 decay. Product formation must therefore arise exclusively from the interaction of triplet-state and ground-state thione under these conditions, irrespective of whether initial excitation is to S_2 or S_1/T_1.

Although both diradicals and excimers have been proposed as intermediates in thione dimerization no direct spectroscopic evidence of their existence, for example emission or transient absorption, has yet been obtained. A search for such evidence would be well received.

D. Cycloaddition

The 1964 paper by Kaiser and Wulfers[217] on the UV photolysis of thiobenzophenone in the presence of olefins contains the first report of a cycloaddition reaction of a thiocarbonyl. Since then a very large number of thione–adduct systems have been investigated. Thiobenzophenone and related compounds (**11**),[10-13,218-225] xanthione and related compounds (**8**),[225-232] the α,β-unsaturated thiones such as thiocoumarin(**9**),[233-235] and adamantanethione (**3**)[204,214] have been most thoroughly examined. Their photocycloaddition reactions with olefins, dienes and polyenes, allenes and cumulenes, and alkynes constitute the bulk of this literature, but reactions with imines,[236] ketenimines,[226,237] and nitriles,[223] and a number of other adducts[232] have also been reported. The wavelength dependence of these reactions has been systematically investigated in order to ascertain differences, if any, in the photochemistry of the thione S_2 and T_1 states. This research has been thoroughly reviewed by de Mayo,[13] Ramamurthy,[12] Coyle,[11] and Rao.[10] We shall focus here mainly on the characterization of the intermediates involved in these reactions, and other "physical" aspects of the photochemistry.

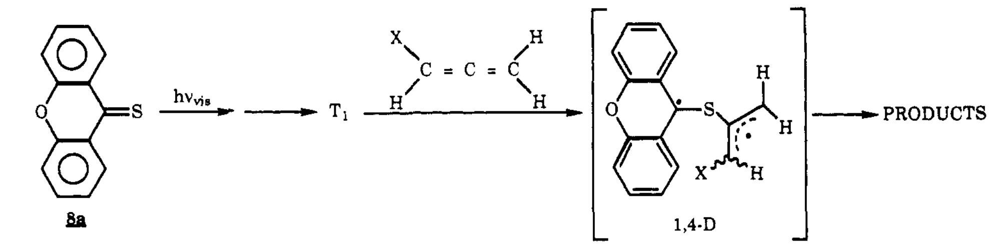
When excitation occurs in the visible the triplet state of the thione is responsible for initiating any observed cycloaddition. Excitation in the near-UV produces S_2 whose cycloaddition reactions can be both qualitatively and quantitatively different from those of the triplet. In addition to S_2 and T_1, a number of chemically distinct reactive intermediates, including diradicals, zwitterions and exciplexes, have been proposed. Most attempts to trap these species or to observe them spectroscopically have been unsuccessful, and their nature has therefore usually been inferred from steric, electronic, and stereochemical considerations.

Triplet thiones generally react with monoolefins in a regioselective but nonstereoselective manner to give the corresponding thietanes as final products. The existence of diradical intermediates in this process has been inferred from (i) the observation of geometrical isomerization in the recovered olefin, (ii) the formation of 1,4-dithianes (by trapping of the initial 1,4-diradical adduct by high concentrations of ground state thione), (iii) the observation that the orientation of the [2 + 2] addition corresponds to that expected from the closure of the more stable 1,4-diradical, and (iv) the recent observation of the scavenging of a 1,4-diradical by electron transfer from methyl viologen.[225] However, although the quenching of the triplet by the olefin may be efficient[136,224,235] (particularly for electron-rich olefins), the quantum yields of cycloaddition products are invariably quite small. These inefficiencies in product formation and variations in k_Q with olefin ionization potential have led some authors[224,231,235] to propose that a triplet exciplex precedes diradical formation. Radiationless decay of such an exciplex as well as decomposition of the diradical would then be responsible for the observed unproductive deactivation of the triplet thione.

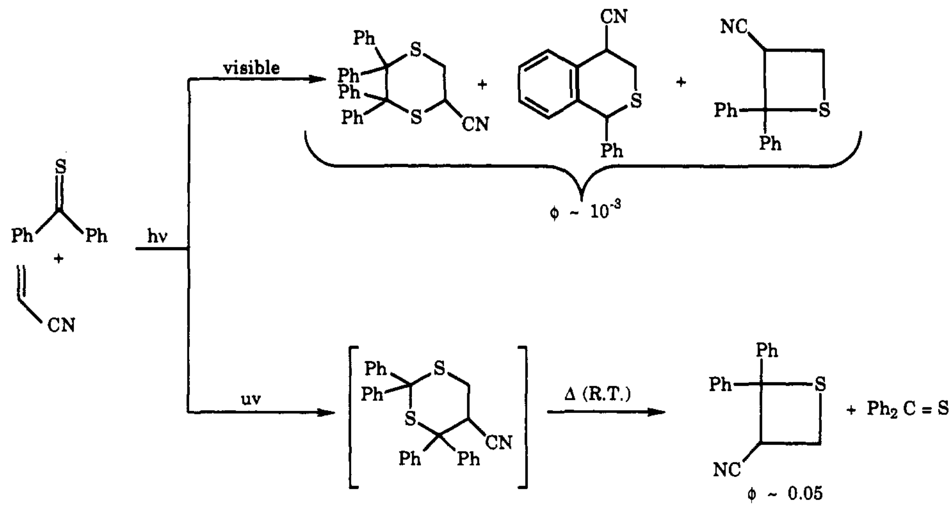
If formed, triplet exciplexes can be stabilized by charge-transfer interactions between the thione and the olefin. The experimental evidence supporting the existence of a charge-transfer-stabilized triplet exciplex arises from the observation in several systems[224,231,234] that the logarithm of the rate constant for triplet quenching is proportional to the ionization potential of the olefin. However, although such plots of log k_Q vs IP are linear,[224,225] their small negative slopes reveal that charge transfer itself contributes in only a minor way to stabilizing the complex. If formed, such exciplexes would therefore need to be stabilized by electron exchange.

Using transient absorption and ground-state depletion methods, Bos, Varma, and co-workers[225] have interpreted the cycloaddition of triplet **8a**, **8b**, **11a**, and related compounds to various allenes, acetylenes, and trienes in terms of the formation of 1,4-diradicals (Scheme V) and have considered in detail if diradical

Scheme V



Scheme VI



formation is preceeded by an exciplex. In the reaction of the triplets of **8a** with phenylallene, addition of methyl viologen results in the formation of a second transient, the methyl viologen radical cation, which can be observed at wavelengths free from interference by the thione triplet. Kinetic arguments based upon deuterium isotope effects and comparisons of the photochemical and thermal reactions of thiones with allenes of differing structure led Bos and Varma to conclude that (i) the methyl viologen radical cation is formed by electron transfer to the 1,4-diradical not to an exciplex, (ii) the diradical has a lifetime of ca. 90 ps in CH_2Cl_2 solution at room temperature, and (iii) an independently acting exciplex plays no significant role in the reaction mechanism. The short intrinsic lifetime of the diradical, which is ultimately responsible for the inefficiency of net cycloaddition, was attributed to efficient local spin–orbit coupling caused by large spin densities of both unpaired electrons on the S atom.

Excitation of diaryl thiones such as **11a** in the near UV at room temperature results in cycloaddition to electron-poor olefins and yields thietanes as final products. Unlike that of the triplets, however, the reaction is both regiospecific and stereospecific with complete retention of configuration both in the thietane and in the recovered olefin. Extensive studies of the thiobenzophenone–acrylonitrile system[219–221] reveal that the S_2 state of the thione initiates the reaction, but that the thietanes are obtained from the thermal decomposition of 1,3-dithianes which are the primary products (Scheme VI). A short-lived exciplex which opens to permit the incorporation of a ground-state thione has been proposed to account for the formation of the 1,4-dithiane product.[219] In the case of adamantanethione (**3**)[204,214] and di-*tert*-butyl thioketone (**1d**)[238,239] exciplex formation has also been proposed to account for the relatively large quantum yields of thietane formation, the lack of regioselectivity and the high stereoselectivity in the reaction. In the case of **3** at least, this interpretation should be viewed with caution given the fact that the fluorescent S_2 state of adamantanethione is too short-lived to participate directly in intermolecular cycloaddition reactions.[144,159] No direct kinetic or spectroscopic evidence of either diradicals or exciplexes has been reported in any of the S_2 cycloaddition reactions investigated to date.

Recently Ramamurthy and co-workers[233–235] have investigated the photocycloaddition reactions of a number of α,β-unsaturated thiones such as **8**, **16**, **17**, and **19** whose photophysics have also been studied.[136,160] The photocycloadditions of these enethiones parallel those of the corresponding saturated thiones. Addition occurs to the thiocarbonyl function, not to the carbon–carbon double bond, and both exciplex and diradical intermediates have been proposed. Regrettably, the photophysical data for the S_2 states of these enethiones are either incomplete or, in some cases, in disagreement.[160,234] Solvent effects, which are known to play a very important role in aromatic and alicyclic thiones of similar structure, have not been investigated systematically. There are also indications that some of these compounds may be photochemically unstable in their S_2 states.[160] A detailed, comprehensive picture of the photochemistry and photophysics initiated on $S_2 \leftarrow S_0$ excitation of these compounds has yet to emerge.

Several theoretical analyses of the thermal and photochemical cycloaddition reactions of thiocarbonyls have also been undertaken. These include both a systematic ab initio study of thermal [4 + 2] cycloaddition reactions of thiones to dienes,[240] and a recent analysis of both thermal and photochemical cycloadditions using MINDO/3 parameters within the frontier molecular orbital framework.[241] Using model thiones, the latter approach satisfactorily rationalizes the observed products of thione–olefin cycloaddition reactions for both T_1 and S_2 reactants. In particular the model[241] convincingly rationalizes all three levels of selectivity in the photocycloaddition of α,β-unsaturated thiones to olefins having electron-withdrawing substituents, i.e. preference for C=S over C=C reaction site, the regiochemistry of the products (2,3- vs 2,4-disubstituted thietane) and the preferred orientation of the substituents (cis vs trans). The analysis reveals that secondary orbital interactions play a decisive role in this selectivity.

Finally, we note that the source of the inefficiency of product formation observed in thione photocycloaddition reactions remains an open question. There can be little doubt that diradicals participate as distinct intermediates in these reactions, but whether their reversion to starting materials is solely responsible for the low quantum yields of products is unresolved. The evidence for the participation of exciplexes is not conclusive, and the caveat of Turro and Ramamurthy[242] concerning other possible energy-wasting pathways should be considered.

E. Oxidation

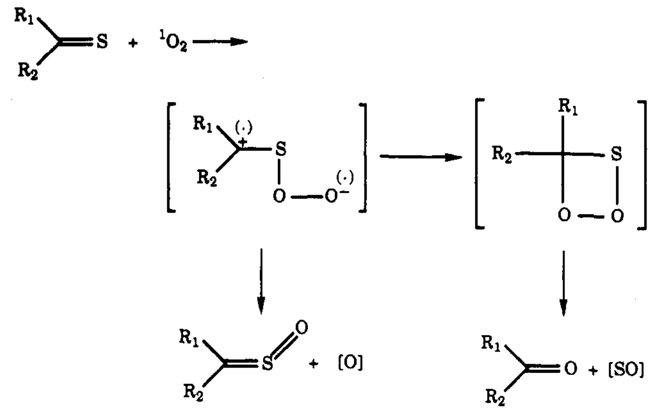
Although the fact that the oxidation of thiocarbonyl compounds is accelerated in room light has been known for decades, the systematic study of thione photooxidation processes is of relatively recent vintage. Studies of aliphatic and aromatic thiones having a variety of structures[169,170,242–250] reveal that photooxidation is initiated by interactions of the lowest triplet with ground-state oxygen. Initial excitation to either S_2 or S_1 produces the same net result. In solution the products invariably include the ketone, but the corresponding sulfine is also produced in comparable yield in some systems. Photooxidation can be frustrated in the solid state.[247,248] No reaction is observed on illumination of **1d** in a molecular inclusion complex of deoxycholic acid.[247] Channels of dimensions appropriate for the diffusion of oxygen into the solid appear to be required if photooxidation of the pure crystalline material is to occur.[248]

The initial step in the photooxidation involves the generation of O_2 ($^1\Delta_g$) with overall unit efficiency by energy transfer from the triplet to O_2 ($^3\Sigma_g^-$) (cf. section IV.D).[52,132,164,170] The singlet oxygen then attacks ground-state thione at the S atom. Both zwitterions/diradicals and ring-closed 1,2,3-dioxathietanes (Scheme VII) have been proposed as intermediates.[169,170,244–246,249,250] The relative yields of sulfine and ketone have been correlated with the electronic and steric properties of the parent thiones.[169,170]

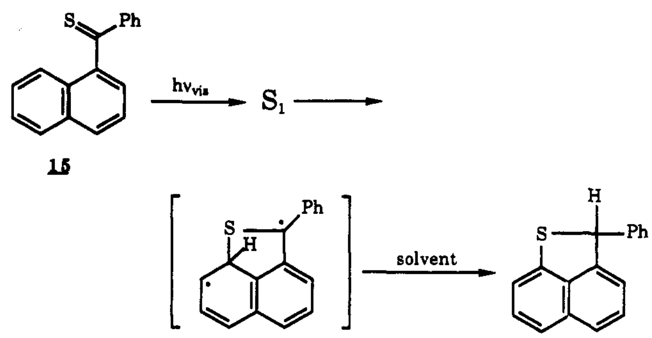
F. Miscellaneous

Both photophysical and photochemical studies of a number of polycyclic thiones having a free peri position have been reported.[138,149,251] 1-(Thiobenzoyl)naphthalene (**15**) and related compounds are known to undergo pericyclization on excitation in the visible to give thiophane derivatives (Scheme VIII). The formal 1,3-hydrogen migration required is known, in at least one case, to involve an intermolecular process.[149] Unlike most thiocarbonyls, however, the initial intramolecular

Scheme VII



Scheme VIII



process appears to occur on the S_1, not the T_1 surface. From the growth of T_1 absorption under picosecond flash excitation,[138] the lifetime of the S_1 state of **15** in benzene was estimated to be ≤50 ps. The resulting triplet is short-lived ($\tau_T^0 \approx$ 80–130 ns) and is accompanied by an unknown longer-lived transient which is not derived from T_1.

The formation of desulfurized dimeric product in the photolysis of 2,6-diphenylpyran-4-thione (**6d**) has also attracted attention.[252] The usual triplet dimerization route to give 1,3- (or possibly 1,2-) dithietanes does not appear to be operative in this case. Instead, the reaction appears to be initiated by abstraction of hydrogen from a suitable donor (e.g. solvent), followed by an attack of the resulting free radical on ground-state thione and subsequent elimination of sulfur-containing moieties.

Thione photolysis has also been used to generate a number of theoretically interesting, structurally unstable or semistable sulfur-containing species. Most recently Quast et al.[253] have reported the generation of a number of 3,3-disubstituted alkylidenethiiranes by photolysis (in the azo chromophore) of tetraalkyl-1-pyrazoline-4-thiones as precursors. Elimination of molecular nitrogen is expected to yield unstable thioxyallyl diradicals which could either close to produce the elusive cyclopropanethiones or, as observed, rearrange to give alkylidenethiiranes as final products. The photolysis of the heterocumulene, S=C=C=C=C=S, in a low-temperature matrix also affords one of the few examples of elimination of CS from a thiocarbonyl.[254]

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