Photophysics and Intramolecular Photochemistry of Thiones in Solution

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Studies of carbonyls occupy a prominent place in the development of our understanding of the spectroscopy, photophysics, and photochemistry of polyatomic molecules. However, recent research suggests that molecules containing carbon, silicon, or germanium doubly bonded to sulfur or to heavier group 16 atoms may prove equally important in the future development of these areas. Among such compounds the thiocarbonyls, which contain the $>C=S$ moiety, have been the subject of considerable study over the past 15 years.

The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) in the thiocarbonyls are constructed from sulfur atomic orbitals of principal quantum number $n = 3$ (vs $n = 2$ for oxygen in carbonyls). Therefore the lowest energy electronic transitions in the thiones occur in the visible, at lower energies than in molecules of comparable size containing only first- or second-row elements. Moreover, the lowest triplet and excited singlet electronic states (T_1 and S_1) most often are located at energies below the threshold for efficient intramolecular photochemical transformations in aromatic and unstrained aliphatic systems. The lowest excited electronic states of many thiones can therefore be relatively long-lived as photophysical rather than photochemical processes dominate their relaxation.

Thiocarbonyls have second excited singlet states (S_2) that are accessible by absorption in the near-UV. Their S_1–S_0 and S_2–S_1 electronic energy gaps are often comparable and relatively large, so that S_2 radiationless decay is slow due to their small S_2–S_1 vibrational overlap (Franck–Condon) factors. Thus, like azulene and its derivatives, intense $S_2 \rightarrow S_0$ fluorescence can often be observed, in violation of what came to be known as Kasha's rule in the early development of photophysics. Unique photochemical reactions can also occur from S_2 in many thione systems.

These and other properties of thiones are remarkable in the sense that many of them run contrary to "expectation" developed from the study of polyatomic organic molecules containing only first- and second-row elements. These differences set the stage for comparisons of the carbonyls with their sulfur and selenium counterparts.

Although work on small thiocarbonyls in the gas phase and larger thiones in the solid phase has been a productive source of information, this Account will focus on recent developments in the photophysics and intramolecular photochemistry of larger thiones in solution. The nature of their electronic transitions in the visible and near-UV and the structures of their associated excited states will be discussed first. This will be followed by a description of their intramolecular relaxation processes, first photophysical and then photochemical. Recent reviews on the spectroscopy of thioformaldehyde,[1] the spectroscopy and photophysics of small thiocarbonyls in the gas phase,[2] and the organic photochemistry of thiones in solution[3-5] are recommended for further background reading. The structures of representative thiones are shown in Figure 1.

Electronic Transitions

The absorption spectra of 4H-1-benzopyran-4-thione (BPT) and adamantanethione (AT), two compounds used as models for the study of thione photophysics and photochemistry, are shown in Figure 2. It is clearly established[6] that the two lowest energy transitions, $T_1 \leftarrow S_0$ and $S_1 \leftarrow S_0$, overlap extensively, the former often appearing as a shoulder or a single distinct band on the long-wavelength side of the latter. The $T_1 \leftarrow S_0$ absorptions are characterized by oscillator strengths that often are only a factor of ca. 10 smaller than those of the companion $S_1 \leftarrow S_0$ absorptions and are significantly red-shifted from the singlet system to permit clean excitation to the triplet. The S_1 state is of primarily $^1(n,\pi^*)$ character ($^1A_2$, assuming C_{2v} local symmetry about the C–CS–C function), whereas the nature of the T_1 state is less clear owing to the close proximity of the two lowest triplets, $^3A_1$ of $^3(\pi,\pi^*)$ character and $^3A_2$ of $^3(n,\pi^*)$ character. The difference in energy between these states, the extent to which they mix, and their sequence in energy can be influenced by the po-

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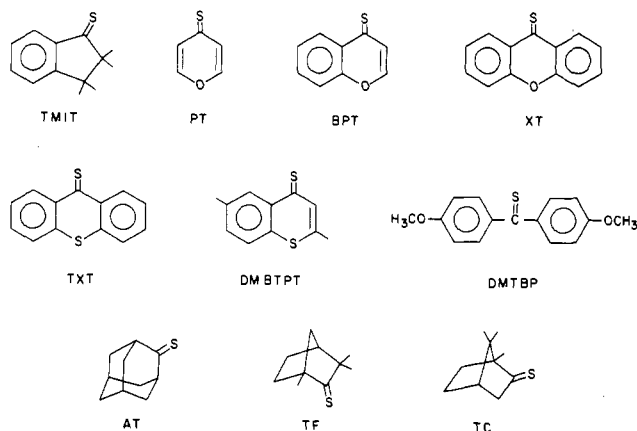(6) Mahaney, M.; Huber, J. R. *J. Mol. Spectrosc.* 1981, *87*, 438.

Figure 1. Structures of and abbreviations for some of the thiones referred to in this Account. TMIT, 2,2,3,3-tetramethylindanthione; PT, 4*H*-pyran-4-thione; BPT, 4*H*-1-benzopyran-4-thione; XT, xanthione; TXT, thioxanthione; DMBTPT, 2,6-dimethyl-4*H*-1-benzothiopyran-4-thione; DMTBP, *p,p'*-dimethoxythiobenzophenone; AT, adamantanethione; TF, thiofluorenone; TC, thiocamphor.
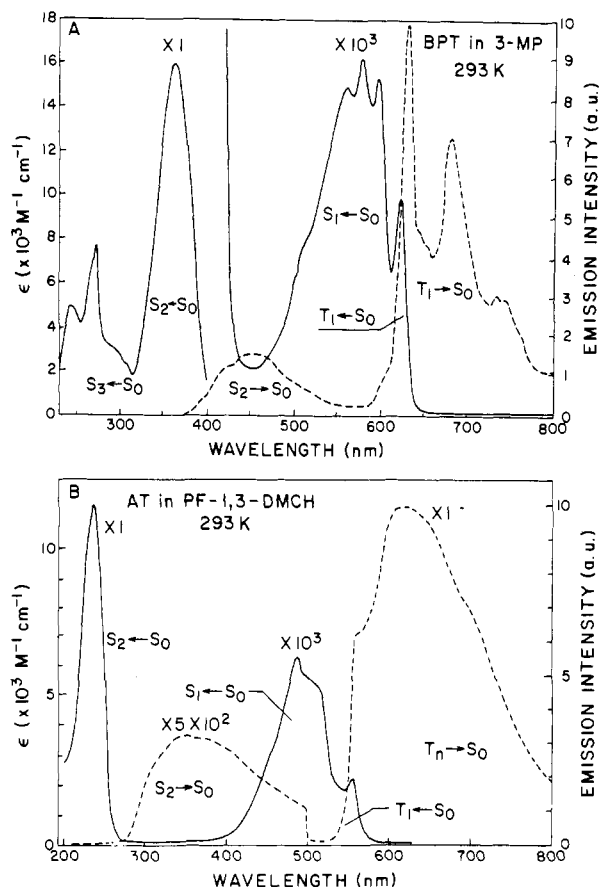

Figure 2. (A) Absorption and emission spectra of 4*H*-1-benzo-pyran-4-thione (BPT) in 3-methylpentane at 293 K. (B) Absorption and emission spectra of adamantanethione (AT) in perfluoro-1,3-dimethylcyclohexane (PF-1,3-DMCH) at 293 K.

larity of the solvent.[7]   In inert, weakly interacting solvents such as perfluoroalkanes the $^3(n,\pi^*)$ state ($^3A_2$ in C_{2v} local symmetry) appears to be of lower energy in most thiones.

The lowest energy allowed transition most often occurs in the near-UV in the thioketones and is associated with a $\pi \rightarrow \pi^*$ electron promotion largely localized on

the $>C=S$ function. These $^1A_1 \leftarrow {}^1A_1$ transitions (C_{2v} symmetry) are broad and exhibit poorly resolved vibrational structure even in inert perfluoroalkane solutions[8,9] or in low-temperature matrices.[6]

Gas-phase absorption spectra of aliphatic thiones in the $190 < \lambda < 230$ nm region[10,11] reveal the presence of three other transitions possessing clearly identifiable vibrational structure. Based upon the results of large-scale CI calculations on H_2CS,[12] these are assigned to electric dipole allowed Rydberg (atom-like) $\tilde{C}(^1B_2) \leftarrow \tilde{X}(^1A_1)$, $(^1A_1) \leftarrow \tilde{X}(^1A_1)$, and $(^1B_2) \leftarrow \tilde{X}(^1A_1)$ transitions involving, respectively, $n \rightarrow 4s$, $n \rightarrow 4p_y$ and $n \rightarrow 4p_z$ one-electron promotions on sulfur. The $(^1A_2) \leftarrow \tilde{X}(^1A_1)$ transition involving the $n \rightarrow 4p_x$ electron promotion is predicted to occur at ca. the same energy, but it is electric dipole forbidden and has not been observed. These transitions are not readily identifiable in the aromatic thiones and, in solution, broaden asymmetrically to higher energies.[13] Careful examination of the spectra of bicyclic and tricyclic thiones in perfluoroalkane solutions, however, reveal the residua of these transitions.[10] Although these Rydberg states are not accessed directly by excitation of the thiones in their $\pi \rightarrow \pi^*$ absorptions at $\lambda > \lambda_{max}$, the $^1A_1$, $^1(\pi,\pi^*)$, states may nevertheless possess considerable Rydberg character through Rydberg–valence conjugate mixing.[12,13]

Excited-State Structures

All thiones possess C_{2v} local symmetry about the four-atom C–CS–C moiety in their electronic ground states. These four atoms may or may not be coplanar in the excited states, however, if the results of vibrational analyses of the absorption spectra of tetraatomic thiocarbonyls[1,2] can be used as a guide. In the T_1 and S_1 states of the latter, the C–S group may assume an equilibrium out-of-plane conformation characterized by deformation angles ranging from 0 to almost 40° and inversion barrier heights of up to ca. 3400 cm^{-1}, both increasing with increasing electronegativity of the substituents on the thiocarbonyl group. In both the aliphatic and aromatic thiones, however, present scant evidence suggests that the S_1 and T_1 states may tend toward planar equilibrium conformations about the C–CS–C moiety. Moreover, unlike the tetraatomic thiocarbonyls, Franck–Condon factors derived from the profiles of the absorption and emission spectra suggest[6] that the equilibrium C–S bond lengths in the S_1 and T_1 states of the larger thiones are similar to those of the ground states.

The situation for the S_2 states may be quite different. Here, even for stable aromatic thiones such as xanthione, S_2–S_0 absorption and emission profiles[6] suggest that the excited-state geometries are considerably distorted relative to their ground states. In unconjugated aliphatic thiones the $\pi \rightarrow \pi^*$ transitions must be localized on the C–S group, resulting in a lowering of the C–S bond order from 2 in S_0 to 1, nominally, in S_2. The C–S stretching frequency drops markedly in the

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Table I
$S_2 \rightarrow S_0$ Fluorescence Quantum Yields and S_2 Decay Parameters of Several Aromatic Thiones

compd	solvent[a]	$\phi_f°(S_2 \rightarrow S_0)$	$\tau°(S_2)$, ps	$k_{nr} \times 10^{-9}$, s^{-1}	$k_r \times 10^{-7}$, s^{-1}
XT	PFMCH	0.014 ± 0.002	175 ± 5	5.7	8.0
	3-MP	(3.0 ± 0.3) × 10^{-3}	38 ± 7	25	7.5
	C$_6$H$_6$	(1.0 ± 0.2) × 10^{-3}	12 ± 3[b]	83	8.3
BPT	PFMCH	0.023 ± 0.002	210 ± 5	4.8	11
	3-MP	(2.3 ± 0.2) × 10^{-3}	24 ± 7	40	9.6
TMIT	PFMCH	0.14 ± 0.015	880 ± 10	0.97	16
	3-MP	0.013 ± 0.002	77 ± 10	13	17

[a] PFMCH, perfluoromethylcyclohexane; 3-MP, 3-methylpentane; C$_6$H$_6$, benzene. [b] Reference 35.

excited state, and the application of approximate frequency–bond length correlations[14] suggests that the C–S bond may be elongated on excitation by up to 0.5 Å in extreme cases.[15] Smaller displacements are expected on $S_2 \leftarrow S_0$ excitation in aromatics due to delocalization. The question of excited-state out-of-plane displacements of the S atom relative to the carbon skeleton is as yet unresolved, although some evidence of out-of-plane ring displacement has been inferred from spectral intensities in aromatic systems.[16]

Dynamics and Mechanisms of Excited-State Decay

General. Elucidation of the dynamics of the decay of the excited states of thiones in fluid solutions is complicated by the facts that, for sterically unhindered[17,18] thiones, (i) self-quenching of both S_2 and T_1 is almost always diffusion limited,[19-22] (ii) oxygen quenching of T_1 is $\geq^1/_9$ of the diffusion-limited rate,[23,24] and (iii) nonchemical quenching of S_2 by most common solvents[9,25] is extremely efficient. In the presence of oxygen, the corresponding ketones and/or sulfines are often observed as products.[17,26] Complications due to oxygen quenching can, of course, be eliminated by carrying out experiments in degassed solutions. However, the observation that self-quenching occurs at the diffusion-limited rate in fluid solutions introduces the need either to extrapolate measured quantum yield and excited-state lifetime data to infinite thione dilution in order to obtain the "unquenched" values of these parameters or otherwise to use measured second-order rate constants to correct observed lifetimes and quantum yields for self-quenching effects. Fortunately, linear static and dynamic Stern–Volmer plots have been obtained for all self-quenching processes investigated

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Table II
T_1 Decay Parameters of PT, BPT, and XT in PF-1,3-DMCH at Room Temperature

parameter	PT	BPT	XT
$\tau_{T_1}°$, μs	43 ± 4	16 ± 2	8.2 ± 0.4
$\phi_p^b(T_1)$	0.47 ± 0.07	0.13 ± 0.03	0.064 ± 0.013
$\phi_p(S_2)/\phi_p(T_1)$	0.70 ± 0.07	0.59 ± 0.05	0.6^a
$\phi_p(S_1)/\phi_p(T_1)$	0.70 ± 0.07	0.69 ± 0.06	0.85^b
$\phi_d°$	≤6 × 10^{-4}	≤5 × 10^{-4}	≤5 × 10^{-4}
k_{sq}, ×10^{-9} M^{-1} s^{-1}	13.6 ± 0.6	6.9 ± 0.9	6.2 ± 0.9
$E(T_1)$, kJ mol^{-1}	206	193	181
k_r, ×10^{-3} s^{-1}	11 ± 3	7.4 ± 1.8	7.6 ± 1.9
$\sum k_{nr}$, ×10^{-4} s^{-1}	1.2 ± 0.3	5.4 ± 1.3	11 ± 3
$k_d \times 10^{-2}$ s^{-1}	≤0.2	≤0.5	≤0.7

^{a} Estimated by comparison with BPT. Measurement impossible due to insufficient solubility in perfluoroalkane solvents. ^{b} Reference 54.

to date, and extensive tabulations of self-quenching rate constants in a variety of solvents are available.[17-25]

The participation of solvent in the *electronic* relaxation of excited thiones is particularly interesting. The role played by the solvent in inducing nonphotochemical, nonradiative decay is particularly important for thione S_2 states.[25] Table I provides representative data that illustrate the sensitivity of both the $S_2 \rightarrow S_0$ fluorescence quantum yields, $\phi_f(S_2 \rightarrow S_0)$, and S_2 lifetimes, $\tau(S_2)$, to the nature of the solvent. Also presented are $S_2 \rightarrow S_0$ radiative and S_2 apparent nonradiative decay rate constants calculated from $k_r = \phi_f/\tau_f$ and $k_{nr} = (1 - \phi_f)/\tau_f$, respectively. Without exception the largest $\phi_f(S_2 \rightarrow S_0)$ and the longest $\tau_f(S_2)$ in room temperature fluid solutions are obtained in the perfluoroalkanes. For aromatic thione solutes such as tetramethylindanthione and xanthione the quantum yield of net photochemical consumption of thione is small, even in alkane solvents, and superficially at least photochemistry would therefore appear to contribute in only a minor way to the overall S_2 decay rate (cf. the different behavior of bridged bicyclic and tricyclic systems, however[3]). Thus, the large effects of solvent on k_{nr} show that solvents other than the perfluoroalkanes play an important, indeed dominant, role in determining the rate of nonphotochemical radiationless S_2 decay in aromatic systems.

On the other hand, the perfluoroalkanes can act as efficient vibrational thermalizers but at the same time cause minimal perturbation of the S_2 electronic decay rate. Indeed, the perfluoroalkanes appear to act as inert heat baths[26] of the type originally envisaged by Robinson and Frosch.[27] Carrying out experiments on perfluoroalkane solutions thus permits a more accurate picture of the nature of the purely *intramolecular*

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electronic decay process of excited thiones to be uncovered.

T_1. The characterization of T_1 is readily accomplished in fluid solutions either by monitoring $T_1 \rightarrow S_0$ phosphorescence or by observing triplet–triplet absorption in laser flash photolysis.[19,24] Decay parameters typical of photostable T_1 states are given in Table II. 4H-Pyran-4-thione is remarkable in that it exhibits a phosphorescence quantum yield of 0.47 on direct $T_1 \leftarrow S_0$ excitation.[28] To our knowledge this is the largest phosphorescence quantum yield ever measured for an organic compound in fluid solution at room temperature. 4H-Pyran-4-thione is exceptional among the thiones examined to date because it has a large T_1 radiative rate constant as a consequence of effective spin–orbit coupling to the singlet manifold and a relatively small $T_1 \rightsquigarrow S_0$ nonradiative rate constant owing to the Franck–Condon prohibition associated with the large T_1–S_0 energy gap (vide infra).

Most triplet thiones, however, decay by predominantly nonradiative means in the absence of reactive intermolecular interactions. Solvent induction of this mode of decay is also important, as can be deduced from the increase in the apparent nonradiative rate constant in solvents other than the perfluoroalkanes. The same sort of solvent effect was first noted many years ago by Parker et al.[29] in experiments on the much longer-lived triplets of aromatic ketones. However, in neither the ketones nor the thiones has the exact mechanism of solvent-enhanced radiationless decay been established since, for example, no spectroscopic evidence of ground- or excited-state association with solvent has been found.

The most detailed photophysical decay data for thione triplets have been obtained by Maki and co-workers[30,31] and by Burland,[32] who have used low-temperature optically detected magnetic resonance and phosphorescence techniques to determine the zero-field splitting parameters and triplet sublevel decay characteristics of xanthione, 4H-pyran-4-thione, and related molecules. Very large values of the zero-field splitting parameter, D^* (>10 cm^{-1}), have been convincingly attributed to an unusually large *spin–orbit coupling* contribution to the molecular spin Hamiltonian. The presence of a "heavy" S atom, together with the relatively strong interaction of the x and y sublevels of the $^3A_2$ state with those of the nearby $^3A_1$ state, accounts for the observed effects in each case. Calculations confirm that the $^3A_1$ state in xanthione should lie within ca. 1000 cm^{-1} of the $^3A_2$ state,[33] and independent experimental evidence[7] based upon the dependence of triplet spectroscopic and photophysical properties on solvent polarity provides additional support for this suggestion. The exact energies of higher triplet states have, however, not been determined.

S_1. The S_1 states of H_2CS, Cl_2CS, and other small thiocarbonyls decay radiatively with large quantum yields ($\phi_f \rightarrow 1$) in the gas phase under collision-free conditions.[1] By contrast, the quantum yields of prompt
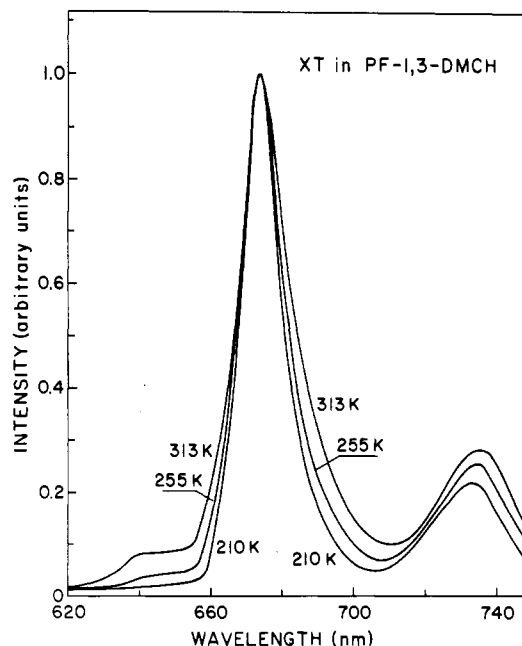

Figure 3. Emission spectrum of xanthione (XT) in PF-1,3-DMCH in the $\lambda > 620$ nm region as a function of temperature. The spectra have been normalized to the peak intensity to facilitate comparison. The thermally activated fluorescence is centered at 640 nm.

fluorescence of larger thiones in solution are generally immeasurably small owing to their rapid rates of $S_1 \rightsquigarrow T_1$ intersystem crossing ($k \sim 5 \times 10^{10}$ s^{-1} in xanthione[34,35]). Only indirect evidence of the photophysical behavior of S_1 is thus available.

Fortunately, it is possible to deduce some essential information about S_1 in aromatic systems by observing both thermally activated fluorescence[36] from S_1 and phosphorescence from T_1 during steady-state excitation within the singlet manifold. The relatively small S_1–T_1 electronic energy gaps and greater-than-microsecond unquenched T_1 lifetimes permit a significant photostationary-state population of S_1 to be established at room temperature as a result of $S_1 \rightleftharpoons T_1$ interconversion. Careful examination of the emission spectra of the aromatic thiones reveals the presence of a temperature-sensitive feature (cf. Figure 3), assigned to thermally activated fluorescence from S_1, which lies to the blue of the phosphorescence. In xanthione,[36] the apparent activation energy for the production of this S_1 "delayed fluorescence" is identical with the solvent-modified S_1–T_1 electronic energy gap, and the emission lifetimes of S_1 and T_1 are equal, as required. A detailed analysis[36] has yielded estimates of the apparent rate constants for the $S_1 \rightleftharpoons T_1$ interconversion processes in xanthione. For adamantanethione, a similar temperature-sensitive emission is assigned to a second triplet that exists in thermal equilibrium with T_1.[37]

Earlier investigations[2–5] indicated that the quantum yield of $S_1 \rightsquigarrow T_1$ intersystem crossing was unity for large thiones in solution. However, recent careful measurements have shown that the quantum yield of

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phosphorescence obtained on steady-state excitation to S_1, $\phi_p{}^\circ(S_1)$, is slightly smaller than that obtained on direct excitation to T_1, $\phi_p{}^\circ(T_1)$, at room temperature.[38] Molenkamp et al.[34] have shown that the lifetime of the S_1 state of xanthione is very short (ca. 20 ps) in a matrix at temperatures near 1 K. Therefore, the quantum yield of *prompt* $S_1 \rightsquigarrow T_1$ intersystem crossing must be nearly unity, in keeping with the large rate constant for $S_1 \rightsquigarrow T_1$ compared with other competing S_1 decay processes. However, $\phi_p{}^\circ(S_1)$ can still be less than $\phi_p{}^\circ(T_1)$ owing to relaxtion via $S_1 \rightsquigarrow S_0$ when a significant *photostationary*-state population of S_1 is established in experiments conducted under conditions of continuous illumination at room temperature.

S_2. In the absence of strong intermolecular interactions, the second excited singlet states of the thiones can begin their return to the ground state by executing one or more of the following processes: (i) intramolecular photochemical transformation, (ii) thermal conversion to S_1 or S_0, and (iii) intersystem crossing to T_1, T_2, or other accessible triplet states. For the aromatic thiones intramolecular reaction is very inefficient, judging by the low quantum yields of net consumption of thione in dilute degassed perfluoroalkane solutions ($\phi_d < 10^{-2}$), and contributes negligibly to the rate of S_2 relaxation. For some aliphatic, alicyclic, and arylalkyl thiones, intramolecular H transfer results in the formation of small, but significant quantum yields of stable or semistable photoproducts.[39–43] (Interestingly, H-atom motion without the formation of net photochemical product also appears to contribute significantly to the internal conversion of S_2 to S_0 (vide infra).[44])

The decay of S_2 directly to the triplet manifold was proposed on the basis of some early photochemical kinetic studies of adamantanethione.[45] However, despite strong evidence for such processes in other systems,[46] subsequent mechanistic investigations[47] have apparently ruled out direct $S_2 \rightsquigarrow T_n$ decay in adamantanethione. No further evidence for such a decay mechanism has been obtained in any subsequent study involving thiones in solution.

Both $S_2 \rightarrow S_0$ fluorescence and $T_1 \rightarrow S_0$ phosphorescence are observed, albeit with differing intensities, following $S_2 \rightarrow S_0$ excitation in most thiones, and the corrected excitation spectra replicate the $S_2 \rightarrow S_0$ absorption spectra exactly. Moreover, the *quantum yield* of $T_1 \rightarrow S_0$ phosphorescence obtained on $S_2 \leftarrow S_0$ excitation, $\phi_p{}^\circ(S_2)$, most often lies between ca. 0.5 and 1.0 times the value obtained on direct $T_1 \leftarrow S_0$ excitation, $\phi_p{}^\circ(T_1)$.[7,28,44] This result confirms laser flash photolysis measurements showing smaller than unit

Table III
Parameters Describing the Decay of Xanthione and Some Deuteriated Derivatives Excited to Their Second Excited Singlet States

compd	$\phi_f{}^\circ \times 10^2$	$\tau^\circ(S_2)$, ps	$k_{nr} \times 10^{-9}$, s^{-1}
XT-h_8	1.3 ± 0.1	183	5.4
XT-1,4,5,8-d_4	3.8 ± 0.3	571	1.7
XT-1,3,4,5,6,8-d_6	4.2 ± 0.4	602	1.6
XT-d_8	3.8 ± 0.4	626	1.5

^{a} Error of ± 10 ps in each case.

quantum yields of triplet formation following excitation to S_2 in several aliphatic,[19] alicyclic,[48] ene,[49] and arylalkyl[18] thiones. A similar effect is seen in the efficiency of singlet oxygen generation by T_1 following excitation to S_2 compared with S_1.[24] The implication is that more than half (and sometimes nearly all) the S_2 molecules decay via $S_2 \rightsquigarrow S_1$ internal conversion, and thence to T_1 via $S_1 \rightsquigarrow T_1$ intersystem crossing. In perfluoroalkanes an excellent correlation (the energy gap law) is observed between log (k_{nr}) of S_2 and the S_2–S_1 electronic energy separation for a series of structurally rigid, apparently photostable aromatic thiones.[50] This observation provides additional support for the suggestion that $S_2 \rightsquigarrow S_1$ is the major decay path in aromatic systems. The facts that $\phi_p{}^\circ(S_2)$ is often considerably smaller than $\phi_p{}^\circ(T_1)$ whereas $\phi_p{}^\circ(S_1)$ and $\phi_p{}^\circ(T_1)$ seldom differ by more than 10 or 15%,[38] however, indicate that in some cases S_2 also decays to a second state that is poorly coupled to the triplet manifold. By elimination, this should be some portion of the ground-state surface.[38,44,49,50]

Deuterium substitution studies on xanthione and adamanthanethione are revealing. In xanthione[44] (Table III) deuterium substitution at C(1) and C(8) decreases k_{nr} of S_2 by a factor of ca. 3 whereas substitution at all other ring carbons decreases k_{nr} by a factor of only ca. 1.1. The latter is of the magnitude expected if a change in C–H(D) stretching frequency is responsible for lowering the Franck–Condon factor associated with $S_2 \rightsquigarrow S_1$ internal conversion.[51] The factor of ca. 3 resulting from C(1) or C(8) deuteriation is of the magnitude normally found for primary isotope effects and is thus associated with a large H-atom displacement (perhaps reversibly forming an unstable biradical intermediate) in the course of S_2's relaxation to a considerably distorted portion of the S_0 surface. Similar deuteriation effects have been observed in the bicyclic and tricyclic thiones and have been used to ascertain the course of intramolecular photochemical processes following excitation to S_2 (vide infra).[41,42] Thus parallel $S_2 \rightsquigarrow S_1$ and $S_2 \rightsquigarrow S_0$ processes can take place, the latter occurring by a pseudophotochemical mechanism involving large-amplitude H-atom displacement toward the S atom.

Rydberg States. Little is known about the photophysical properties of UV-accessible Rydberg states in the thiones. Discrete vibrational structure is seen in the gas-phase Rydberg absorptions of all aliphatic and alicyclic compounds examined to date.[10,11,52] Moreover,

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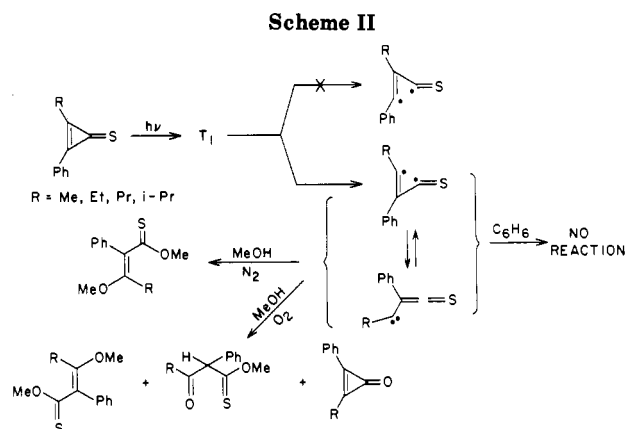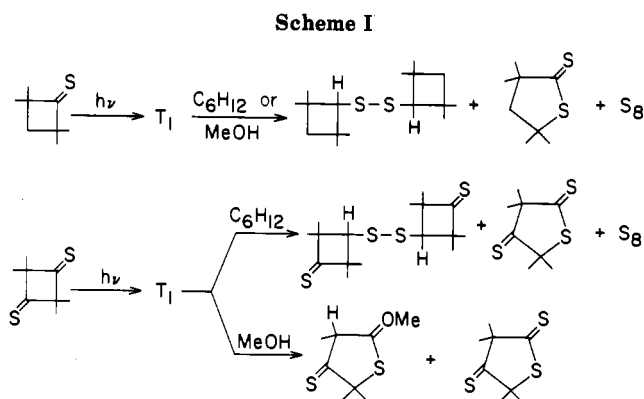
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Scheme I   **Scheme II**

clear internal rotational features are seen in the spectra of thiocarbonyls with free methyl rotors (e.g., thioacetone[11] and thioacetaldehyde[52]), and well-resolved rotational fine structure has been photographed in the gas-phase $\tilde{C} \leftarrow \tilde{X}$ spectrum of H_2CS.[53] The available evidence, particularly rotational line-width estimates for the $\tilde{C}$ state of H_2CS, thus suggests that those thione Rydberg states accessible in the near-UV may be relatively long-lived (up to 100 ps) in the gas phase and may exhibit unique photochemistry. While the lifetimes of these states are likely to be considerably shorter in solution, they still might be measurable with femtosecond laser techniques.

Photochemistry

Both S_1 and T_1 are of relatively low energy (typically 160–200 kJ mol^{-1} above S_0). In aromatic and unstrained cyclic thiones these states lie well below the threshold for intramolecular photochemical transformation. Thus, for example, in perfluoroalkanes at infinite dilution the quantum yield of net photochemical consumption of $4H$-1-benzopyran-4-thione[54] is $\leq 5 \times 10^{-4}$. Nevertheless, interesting photochemistry can be initiated with visible light in strained systems.

Cyclic and bicyclic ketones undergo efficient initial α-cleavage, but the corresponding thiones tend to resist such a process. Among the various thiocarbonyls investigated, both cyclobutanethiones[55–62] and cyclopropenethiones[63–65] are known to be photochemically active. Cyclobutanethiones substituted at the α,α'-positions with cyclic and acyclic moieties and at the 3-position with dicyanomethylene, cyanocarboethoxy-

methylene, carbonyl, thiocarbonyl, and phenylimino groups have been studied. Sensitization and quenching experiments[61] have established that these molecules react via T_1. Norrish Type I α-cleavage in the cyclobutane-1,3-dithione system initiates the train of photochemical events leading to the products shown in Scheme I.[60] Both diradical and thiacarbene intermediates have been proposed on the basis of the structures of the final products obtained when the photolysis is carried out in the presence of oxygen or in reactive solvents. MINDO/3 calculations[62] suggest that direct conversion from T_1 to both the diradical and the thiacarbene is possible in α-alkyl-substituted cyclobutane-1,3-dithiones. However, α-alkyl-substituted monothiones are predicted to cleave only to the 1,4-diradical. Both predictions are in accord with experiment.

In the arylalkylcyclopropenethiones[63–65] an unusual, although inefficient, regioselective α-cleavage is observed (Scheme II), which is likely a consequence of the close approach of the ground-state surface of the less stable alkyl-substituted diradical/carbene primary intermediates to the triplet-state surface of the parent thione. UHF MINDO/3 calculations[65] demonstrate that the unsubstituted cyclopropenethione triplet has a highly unsymmetric geometry consisting of an elongated C–C bond, a delocalized thiaallyl fragment, and a pyramidal radicaloid carbon (which eventually becomes the carbene center). Such a structure favors the notion that α-cleavage of the long C–C bond leads to a thioketene carbene, with the pyramidal carbon becoming the ultimate carbene center. In the case of the arylalkylcyclopropenethiones, the (n,π^*) triplet is likely to have an unsymmetrical geometry in which the more stabilizing aryl group remains in the ring plane attached to the thiaallyl fragment. The alkyl group is expected to be at the pyramidal carbon that forms the elongated bond to the sulfur-bearing carbon. Cleavage of the latter would lead to the observed products. Thus the structure of the substituted triplet thione, rather than that of the thioketene carbene, determines the photobehavior. By comparison with the corresponding cyclopropenone, which eliminates CO to give acetylenes, the excited-state behavior of the thione is unexpected.

Excitation in the $S_2 \leftarrow S_0$ absorption in the near-UV provides sufficient energy to induce a host of possible photochemical reactions. Both intermolecular and intramolecular hydrogen abstractions from S_2 have been thoroughly studied.[3–5] However, although photorearrangements in carbonyls are well documented,[66–68] those

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Scheme III
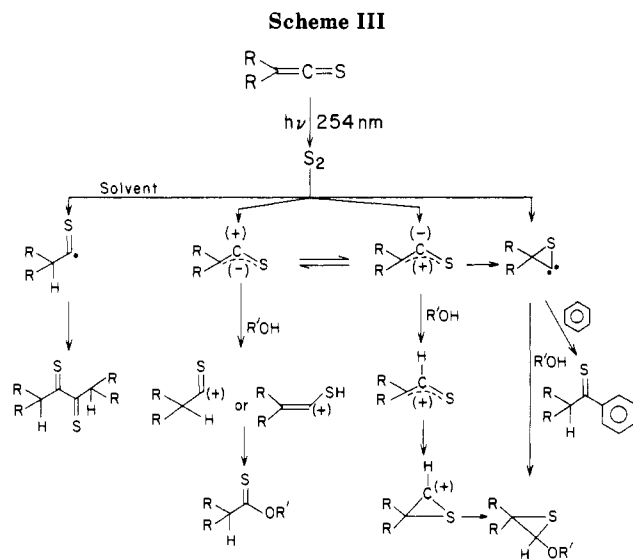
in thiocarbonyls have been reported only rarely.

Although it was originally reported that di-*tert*-butylthioketene is inert toward photolysis,[69] the systematic study of several thioketenes[70,71] has indicated that they undergo an interesting skeletal rearrangement on the S_2 surface. Disubstitution at the thioketene carbon generally results in a clean transformation whereas the presence of an α-hydrogen leads to extensive polymerization. The proposed mechanism involves zwitterions as well as thiirenylcarbene as intermediates, as shown in Scheme III.

A comparison of the excited-state behavior of thioketenes with those of ketenes, allenes, and other heterocumulenes[72,73] is revealing. The latter possess

zwitterionic minima in their excited-state surfaces. In this respect the excited-state behavior of thioketene is similar to that of other cumulene systems. However, the differences are many. The major photochemical relaxation pathway of an excited ketene is to extrude carbon monoxide, while allenes undergo diverse reactions that include concerted cyclization to cyclopropenes and 1,2-shifts to vinyl carbenes. Thioketenes, on the other hand, undergo photoreaction from the S_2 state, and neither eliminate carbon monosulfide nor undergo concerted cyclization to thiirene.

Concluding Remarks

The thiocarbonyls exhibit excited-state dynamic behavior that is quite different from their well-studied analogues, the carbonyls. Reports of the synthesis of stable silathiones, germathiones, selenoketones, and other molecules containing group 14 atoms doubly bonded to group 16 atoms have become more frequent in recent years. We therefore look forward to improving our understanding of molecular photochemistry and photophysics through the study of these species in the future.

Note Added in Proof. Readers may wish to consult two recent papers: Motyka, A. L.; Topp, M. R. *Chem. Phys.* **1988**, *121*, 405 for further information on the nonradiative decay of xanthione and some molecular complexes in a supersonic jet, and Maciejewski, A. *J. Photochem. Photobiol., Sect. A* **1988**, *43*, 303 concerning the role of T_1 self-quenching in the photochemical decay of aromatic thiones.

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