

SPECTROSCOPIC AND PHOTOCHEMICAL PROPERTIES OF AROMATIC THIOKETONES: XANTHIONE

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Summary

Some aspects of the absorption, emission and photochemistry of xanthione (XS), an aromatic thioketone with a C_{2v} molecular geometry, have been investigated in solution at room temperature and 77 K.

Contrary to the observation in similar aromatic ketones, the first Π, Π^* transition ($^1A_1 \rightarrow ^1A_1$) of thioketones has charge-transfer character as indicated by the results of a CNDO/2-CI calculation. The short lived emission observed at room temperature and at 77 K ($\tau_p(77\text{ K}) = 43\ \mu\text{s}$; $\Phi_p(77\text{ K}) = 0.11$) is polarized parallel to the C=S axis and is assigned as phosphorescence of the lowest $^3(n, \Pi^*)$ state. The exceptionally effective spin-orbit coupling of aromatic thioketones (about two orders of magnitude larger than in the ketone analogs) indicates that a different intersystem crossing mechanism is operative in aromatic thioketones from that of ketones.

The photo-oxidation of XS to xanthone proceeds *via* the lowest n, Π^* triplet state of XS. The photodecomposition is most efficient in oxygen-free alcoholic solutions and involves the excited XS molecule and the solvent.

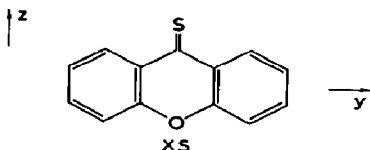
Introduction

The electronic structure of aromatic thioketones appears to be quite similar to the electronic structure of aromatic ketones. Applying a molecular orbital description to simple aromatic ketones and thioketones with a C_{2v} symmetry, one finds that in both compounds the lowest excited singlet S_1 and triplet T_1 are n, Π^* (A_2) states while the second excited singlet state S_2 has a Π, Π^* (A_1) configuration. The absorption spectra of these compounds, however, differ greatly in the position of the longest wavelength transition. This orbitally forbidden n, Π^* band is strongly red shifted in the thioketones [1 - 6]. Apparently, this behavior is due to the fact that the source of the

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non-bonding electron is the $3p_y$ -orbital on sulfur; its lower ionization energy compared with the non-bonding electron of the $2p_y$ -orbital on oxygen decreases the energy gap between the n -orbital and the lowest antibonding Π -orbital. On the other hand, the relatively minor change in the position of S_2 leads to a large energy separation between the lowest n, Π^* and Π, Π^* transitions in thioketones. This property is expected to alter some particularly interesting features of n, Π^* states found in aromatic ketones such as vibronic coupling and spin-orbit coupling between $^{1,3}n, \Pi^*$ and $^{1,3}\Pi, \Pi^*$ states [7]. Therefore, findings on thioketones will also pertain indirectly to ketones.

Its C_{2v} molecular geometry, its chemical stability and the detailed spectroscopic knowledge of its ketone analog [8] makes xanthione (XS) a particularly suitable compound for such a spectroscopic investigation. In the present communication we report on the absorption and emission properties of (XS)



along with some pertinent photochemical findings of this compound.

Experimental

Materials

Xanthione was synthesized from xanthone (Aldrich Chemical Co.) and P_2S_5 in xylene following a published procedure [9]. Xanthione was recrystallized from benzene and it showed a melting point of 155 - 156 °C (lit. [10] 156 °C). All other thioketones which will be mentioned in this study were prepared in the same manner from their corresponding ketones.

3-Methylpentane (3-MP, puriss., Aldrich Chemical Co.) was used after further purification by frontal analysis chromatography through a column of basic alumina (Woelm, W200, basic). EPA (ethanol/isopentane/ether 2:5:5 by vol., American Instrument Co.), ethanol (100% and 95%) and isopropanol (U.S. Industrial Chemicals) were used as received.

Apparatus and Procedure

The spectrofluorimeter employed in this study consisted of a 450 W xenon arc excitation source, a Bausch and Lomb 500 mm, $f/4.4$ monochromator, and a Spex 750 mm, $f/6.8$ analyzing spectrophotometer. The emission spectra were corrected for the response characteristics of the instrument and plotted by computer. The emission lifetimes were measured with an ORTEC Model 9200 fluorescence spectrometer. Absorption spectra were recorded on a Cary 14 spectrophotometer. The quantum yields at 77 K

were determined relative to the quantum yield of 9,10-diphenylanthracene in EPA ($\Phi_f(77\text{ K}) = 0.95$ [11]) with a method analogous to room temperature fluorescence quantum yield determinations. Steady state photolysis was performed with a 150 W medium pressure mercury lamp. The sample cells were equipped with a magnetic stirrer. The photochemical reactions were monitored spectrophotometrically by the disappearance of the reactant. To ensure that the light absorbed by the reactant was constant during the course of the measurements, only a small amount of reactant was used up (O.D. changed from 1.5 to about 1.0). A Plexiglas filter with a cut-off at 350 nm was inserted into the light path to protect photoproducts from further photolysis. When anthracene was used in the energy-transfer experiments a highly concentrated solution was placed as a filter in front of the reaction cell.

Results

Absorption

The absorption spectrum of xanthione (XS) measured at 77 K in 3-MP is displayed in Figs. 1 and 2. The weak, longest wavelength transition (I)

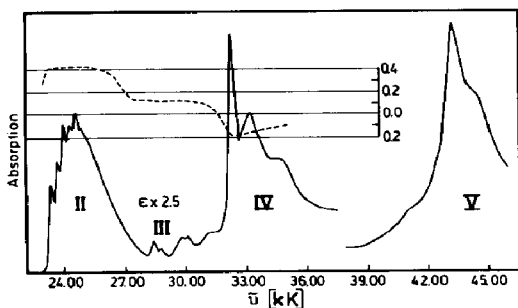


Fig. 1. Absorption spectrum of xanthione in 3-MP at 77 K (the first transition is omitted *cf.* Fig. 2). The insert shows the polarization excitation spectrum monitored at the O—O band of the emission. The roman numerals refer to the transitions listed in Table 1.

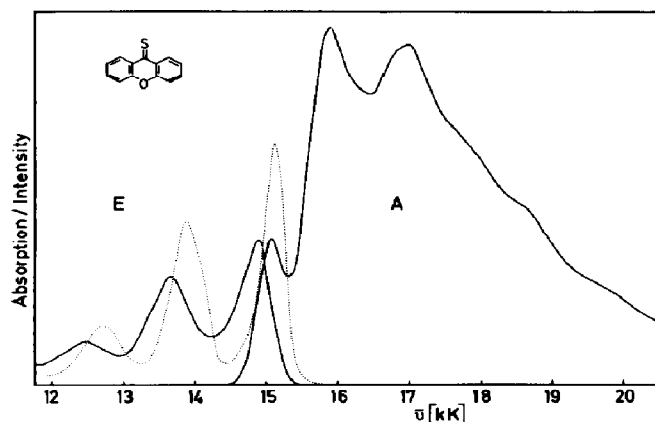


Fig. 2. The first absorption band [$^1A_1 \rightarrow ^1A_2(n, \Pi^*)$] of xanthione and its emission in 3-MP at room temperature. The dotted spectrum shows the emission at 77 K.

(*cf.* Fig. 2) carries an oscillator strength $f = 3.0 \times 10^{-4}$ and is located in the visible region of the spectrum. (Owing to its limited solubility at low temperature this transition could only be recorded at room temperature). The apparent O–O band lies at $\sim 15,030 \text{ cm}^{-1}$. The four peaks and three shoulders correspond to vibrational frequencies of 800 cm^{-1} and 1100 cm^{-1} . Replacement of 3-MP with ethanol leads to a blue shift ($\sim 450 \text{ cm}^{-1}$) of band I. The second electronic transition appears as a strong band ($f = 0.20$) containing well-defined vibrational structure. The vibrational frequencies of this band appear at $330, 660, 970, 1250$ and 1540 cm^{-1} relative to the O–O band. Transition III, with its O–O band at $\sim 28,000 \text{ cm}^{-1}$ is weak ($f = 0.035$) while transition IV exhibits an f value of 0.23 . Table 1 summarizes the pertinent results of the absorption spectrum of XS.

TABLE 1

Absorption spectrum of xanthione in 3-methylpentane

Band	Assignment/ polarization	Transition	Energy $\tilde{\nu}_{0,0}(77 \text{ K})$	Energy $\tilde{\nu}_{0,0}(298 \text{ K})$	$\epsilon_{\text{max.}}(298 \text{ K})$	Oscillator strength (298 K)
I	${}^3A_2(n, \pi^*) \leftarrow {}^1A_1$	(Z)	14,990 ^a	15,030 ^a	8	2.5×10^{-5}
	${}^1A_2(n, \pi^*) \leftarrow {}^1A_1$	—		15,840	20	3.0×10^{-4}
II	${}^1A_1(\pi, \pi^*) \leftarrow {}^1A_1$	(Z)	23,410	23,650	16,000	0.20
III	${}^1A_1(\pi, \pi^*) \leftarrow {}^1A_1$	(Z)	28,050	28,730	2,000	0.035
IV	${}^1B_2(\pi, \pi^*) \leftarrow {}^1A_1$	(Y)	32,380	32,580	15,500	0.23
V	${}^1B_2(\pi, \pi^*) \leftarrow {}^1A_1$	(Y)	43,290	43,590	51,500	0.85

^aPhosphorescence O–O band (*cf.* Fig. 2).

The polarized excitation spectrum as monitored at the O–O band of the emission ($15,000 \text{ cm}^{-1}$) shows that band II is polarized parallel to band III but is perpendicularly polarized to band IV.

Emission

The emission spectrum of XS is 3-MP at 77 K is shown in Fig. 2. The spectrum, with its O–O band at $15,100 \text{ cm}^{-1}$, is characterized by a vibrational frequency of 1150 cm^{-1} . This behavior is in qualitative agreement with the emission observed by Nurmukhametov *et al.* [4]. The extremely weak emission at room temperature is very similar to the spectrum at 77 K with the exception of a red shift. Upon excitation into band II the polarization of the emission is positive ($P = 0.34$) throughout the spectrum.

In a rigid glass matrix (EPA) at 77 K, the xanthione emission is quenched by anthracene as shown in a Stern–Volmer plot in Fig. 3(a).

The emission quantum yields Φ_p and the emission lifetimes τ_p of XS are listed in Table 2. In a degassed ethanol solution τ_p was measured to be 700 ns. With an air saturated solution ($[O_2] = 1.87 \times 10^{-3}$ [12]) a lifetime $\tau_p = 150 \text{ ns}$ was found. Thus, the emitting state is quenched by oxygen with a quenching constant $k_Q = 3.5 \times 10^9 M^{-1} s^{-1}$.

TABLE 2

Emission quantum yield and emission lifetime of xanthione

Solvent	$\Phi_p(77\text{ K})$	$\tau_p(77\text{ K})$ (μs)	$\tau_p(298\text{ K})$ (μs)
3-MP	0.11 ± 0.02	43 ± 5	—
EtOH/EPA	0.15 ± 0.03	48 ± 6	0.70

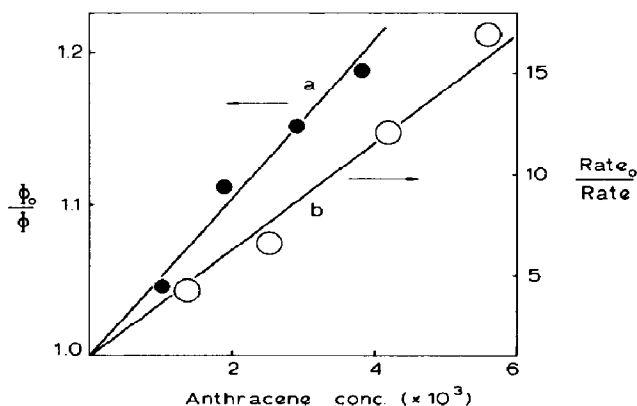


Fig. 3. Stern-Volmer plots of the xanthione emission Φ_0/Φ at 77 K in EPA and of the photo-oxidation reaction in ethanol at room temperature (R_0 is the disappearance rate of xanthione without anthracene).

Photolysis

Steady state photolysis ($\lambda_{xc} > 350\text{ nm}$) of XS in ethanol solution at 298 K produces xanthone (X) in a quantitative yield. Xanthone was identified by its absorption spectrum at 298 K and its characteristic emission spectrum at 77 K [8]. Experiments in degassed, air-saturated, and oxygen-saturated solutions indicate that the reaction rate of the photolysis process decreases as the oxygen concentration increases (*cf.* Table 3). In all cases, the disappearance of XS follows first order kinetics. The photoreaction in isopropanol and in *t*-butyl alcohol proceeds very similar to the one in ethanol. However, in non-alcoholic solutions such as 3-MP, photolysis is very slow leading to a major product which was not identified but which is definitely not X. The addition of small amounts of alcohol to 3-MP solutions results in a strongly increased photochemical rate. The photodecomposition rates relative to degassed ethanol solution are summarized in Table 3 and the percentage conversions of XS to X are listed in Table 4. When anthracene was added to the ethanol solution of XS the rate was greatly suppressed. This behavior is shown with a Stern-Volmer plot in Fig. 3(b). It might be noteworthy that excitation of XS in aerated ethanol solutions directly into its n, π^* band employing a He-Ne laser ($\lambda = 6328\text{ \AA}$) also gives a quantitative yield of X.

TABLE 3

Relative photochemical rates, normalized to ethanol solution, at 298 K with excitation wavelength $\lambda_{\text{exc.}} > 350$ nm ($S_0 \rightarrow S_2\Pi, \Pi^*$) excitation)

Solvent	Degassed ^a	Air (sat.)	Oxygen (sat.)
Ethanol (100%) ^b	1.00	0.065	0.023
Isopropanol	1.22	0.12	0.080
3-MP	0.085	0.0084	0.0060

^aPurged with N₂.

^bThe same results were obtained with ethanol (95%).

TABLE 4

Percentage conversion of xanthione to xanthone at 298 K with excitation wavelength $\lambda_{\text{exc.}} > 350$ nm

Solvent	Excitation wavelength (nm)	Degassed ^a (%)	Air (sat.) (%)	Oxygen (sat.) (%)
Ethanol (100%) ^b	> 350	80	95 - 100	95 - 100
Ethanol (100%)	633		95 - 100	
3-MP	> 350	< 10	20	20

^aPurged with N₂.

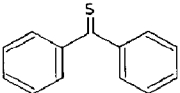
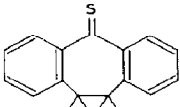
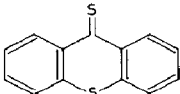
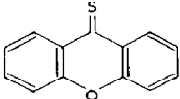
^bIsopropanol gives the same results as ethanol.

Discussion

The first electronic transition is the orbitally forbidden $^1A_2 (n, \Pi^*)$ transition [2, 4, 5]. Its oscillator strength is 3.0×10^{-4} and its extinction coefficient $\epsilon_{\text{max}} \approx 20$. These values are of the same magnitudes as the corresponding parameters of the ketone analog (*cf.* Table 5). In ketones with a C_{2v} molecular symmetry, the intensity of this band may be explained on the basis of a Herzberg-Teller (HT) electronic-vibronic coupling mechanism. The orbitally forbidden n, Π^* transition "steals" intensity from the strongly allowed $^1A_1 (\Pi, \Pi^*)$ transition *via* non-totally symmetric vibrations. If, however, the geometry of the molecule deviates slightly from planarity (*i.e.* from C_{2v} symmetry), the n, Π^* transition acquires intensity through mixing between the n -orbital and Π orbitals [13, 14]. Considering the large energy gap ΔE between the n, Π^* and Π, Π^* transitions in thioketones (ΔE (XS) ≈ 8600 cm^{-1}), the HT coupling mechanism is expected to be quite inefficient for this type of molecule. Therefore, it is anticipated that the intensity of the n, Π^* band is mainly due to the breakdown of the C_{2v} molecular symmetry. In Table 5 we have listed a series of similar thioketones in order of increasing planarity—thiobenzophenone as the least planar molecule on the top, XS as the most planar molecule at the bottom. As expected the oscillator

TABLE 5

The oscillator strengths f of the lowest n, π^* and π, π^* transitions of thioketones and their energy separation ΔE in 3-MP solvent at room temperature.

Molecule	$f(n, \pi^*) \times 10^4$ ^a	$f(\pi, \pi^*)$ ^a	$\Delta E(\text{cm}^{-1})$
	20 ^b	0.20	14,700
	18	0.30	15,700
	6.9	0.13	6000
	3.0 ^c	0.21	7700

^a Estimated error $\pm 10\%$.

^b Benzophenone $f(n, \pi^*) \approx 30 \times 10^{-4}$ see ref. [14].

^c Xanthone $f(n, \pi^*) \approx 4.0 \times 10^{-4}$.

strength $f(n, \pi^*)$ increases strongly as the molecule becomes less planar. Contrary to this behavior a pure HT mechanism predicts a significant decrease of $f(n, \pi^*)$ [†]. (It is interesting to note that the oscillator strengths $f(n, \pi^*)$ of benzophenone ($f \approx 30 \times 10^{-4}$) and xanthone ($f \approx 4 \times 10^{-4}$) parallel those of the sulfur analogs).

The apparent O–O band of the n, π^* (${}^1A_1 \rightarrow {}^1A_2$) transition at 15,030 cm^{-1} is relatively weak ($\epsilon = 8$) compared with the maximum ($\epsilon = 20$) of the transition and is separated by 800 cm^{-1} from the latter. The rest of the vibrational structure conforms to the C=S stretch frequency $\nu = 1050 \text{ cm}^{-1}$ in accordance with earlier observations on thiobenzophenone ($\nu = 1000 \text{ cm}^{-1}$) [5]. Several reasons discussed below as well as results from similar studies lead us to conclude that the apparent O–O band is due to the $S_0 \rightarrow T_1$ absorption. Consequently the O–O band of the n, π^* transition has to be placed at 15,830 cm^{-1} and the energy gap $\Delta E(S_1 - T_1)$ becomes 800 cm^{-1} .

[†] For a rough estimate we have assumed that $f^{\text{HT}}(n, \pi^*) \approx C(f(\pi, \pi^*)) / \Delta E^2$ where $f(\pi, \pi^*)$ is the oscillator strength from which intensity is borrowed and C is a constant factor. With these assumptions one obtains $f^{\text{HT}}(n, \pi^*)$ (thiobenzophenone) / $f^{\text{HT}}(n, \pi^*)$ (XS) $\approx 1/4$.

It is worthwhile to consider band II in some detail since it has been shown that the photochemical behavior of thioketones is different upon excitation into the first or the second excited state [15 - 17]. The strong absorption band II ($f = 0.20$) exhibits sharp vibrational structure. The weak O—O band is followed by a 330 cm^{-1} progression of increasing intensity. This type of Franck—Condon envelope is typical of the vibrational pattern of electronic transitions which are accompanied by distortion of molecular geometry. In agreement with the result of a CNDO/2-CI calculation[†] band II is assigned as a ${}^1A_1 \rightarrow {}^1A_1$ (Π, Π^*) transition polarized along the C=S axis. Consideration of the changes in the electron density distribution between the ground and excited states (*cf.* Fig. 4) reveals a striking difference in the character of the second transition between aromatic ketones and thioketones. In the former compounds this transition is localized mainly in the rings while in the thioketones it appears as a typical intramolecular charge-transfer transition involving strong transfer of the charge from the thiocarbonyl sulfur to the adjacent carbon atom. Thus, the second transition in aromatic thioketones is strongly localized similar to the n, Π^* transition. (In similar aromatic ketones the charge-transfer band is found around $40,000\text{ cm}^{-1}$. The lower ionization potential of sulfur shifts this band in thioketones considerably to the red [8, 13]).

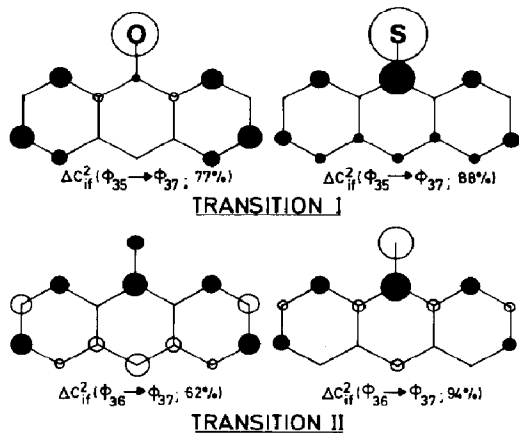


Fig. 4. Relative change of the electron densities ΔC_{if}^2 ($i = \text{initial state}$, $f = \text{final state}$) of the first transition I (n, Π^*) and the second transition II (Π, Π^*) in xanthone (left side) and in xanthione (right side). (Results from the CNDO/2-CI calculation).

The assignments of the higher energy transitions based on the polarization results and the CNDO/2-CI calculation are listed in Table 1.

The emission behavior of aromatic thioketones is a particularly interesting feature. At both room temperature and 77 K the emission spectrum is

[†]Configuration interaction was limited to the 25 lowest, singly excited states. Program and parameterization used are described in detail in a recent publication: J. R. Huber and J. E. Adams, *Ber. Buns. Phys. Chem.*, 78 (1974) 217.

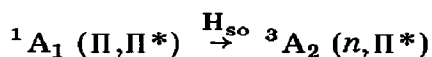
characterized by a 1150 cm^{-1} vibrational spacing which agrees with the C=S stretch frequency of 1140 cm^{-1} found in the i.r. spectrum of thiophosgene [18]. This characteristic and the observed red shift of the emission in going from polar to non-polar solvents supports the n, Π^* assignment of the emitting state. However, the assignment of the multiplicity of this state raises some questions. The small energy difference between $^1(n, \Pi^*)$ and $^3(n, \Pi^*)$ states in the thioketones (small exchange integral due to small overlap of the n_s -AO and Π^* -MO) plus emission lifetimes that fall in the range of either long-lived (symmetry forbidden) singlets or short-lived triplets do not allow application of the diagnostic criteria usually applied for the multiplicity assignment of the emitting state [19]. In addition the emission polarization along the z -axis may arise from either a $^1(n, \Pi^*)$ or a $^3(n, \Pi^*)$ state, in the former *via* vibronic coupling to $^1A_1(\Pi, \Pi^*)$, in the latter through spin-orbit coupling with $^1A_1(\Pi, \Pi^*)$ [13, 14].

The assignment of the emitting state of XS as a triplet is based on the following reasons: (a) the measured emission lifetime $\tau_p(77\text{ K}) = 43\ \mu\text{s}$ in 3-MP is in good agreement with the calculated phosphorescence lifetime. Using the well known relationship [19]:

$$\tau_p^0 = \frac{1.5}{n^2} \times \frac{g_u}{g_l} (\tilde{\nu}^2 f)^{-1}$$

where $\tilde{\nu}$ is the position of O-O band in cm^{-1} , n the refractive index of the solvent, f (2.5×10^{-5}) is the oscillator strength of the "odd" band at $15,030\text{ cm}^{-1}$ and g_u and g_l are the multiplicities of the ground and excited state, we obtain $\tau_p^0 = 460\ \mu\text{s}$. This result, together with $\Phi_p = 0.11$ and the assumption $\Phi_{\text{isc}} \approx 1$ leads to $\tau_p(77\text{ K}) \approx 50\ \mu\text{s}$; (b) the oxygen quenching constant of the emitting state in ethanol $k_Q = 3.5 \times 10^9\ \text{s}^{-1}M^{-1}$ agrees well with $k_D/9$ ($k_D \approx 3 \times 10^{10}M^{-1}\ \text{s}^{-1}$ is the bimolecular rate constant) found in aromatic hydrocarbons and aromatic ketones [20, 21]; (c) the observed energy transfer between the emitting state and anthracene ($T_1 \approx 14,700\text{ cm}^{-1}$) in a rigid glass at 77 K, where the mean distance is $d \geq 60\ \text{\AA}$ between the donor and acceptor molecule, makes any mechanism other than triplet-triplet energy transfer unlikely. (The energy transfer constant k_A of $^3\text{XS} + ^1\text{A} \xrightarrow{k_A} ^3\text{A} + \text{XS}$ derived from the plot in Fig. 3(a) is $k_A \approx 10^6M^{-1}\ \text{s}^{-1}$). In a recent investigation of thiocarbonyl compounds [6], De Mayo *et al.* reached a similar conclusion on the emitting state.

At this point it seems worthwhile to compare the intersystem crossing process (ISC) of ketones and thioketones under the assumption that in both molecules the route



is dominant. The radiative phosphorescence lifetime τ_p^0 , which is a measure of the effectiveness of the ISC, shows that this process is nearly two orders of

magnitude more effective in XS than in the ketone analog X (τ_p^0 (XS) = 460 μ s; τ_p^0 (X) \approx 35 ms[†]). A similar result was obtained with thiobenzophenone [6] and thioxanthone [22]. Within the framework of LCAO-MO theory, Plotnikov [23] has recently shown that for ISC between n, Π^* and Π, Π^* states the matrix element $\langle {}^1\Psi (\Pi, \Pi^*) / H_{so} / {}^3\Psi (n, \Pi^*) \rangle = \beta$ can be approximated by the expression:

$$\beta = C'_\mu C_\mu \frac{\alpha^2 Z_\mu^4}{12(n_\mu^*)^3} = C_\mu \zeta_\mu$$

where α is the fine structure constant, Z_μ is the effective nuclear charge on the μ th atom, n_μ^* is the effective principle quantum number for non-bonding electrons, C'_μ is the coefficient of the p atomic orbital in the non-bonding orbital on the μ th atom, and C_μ is the coefficient of the p orbital in the Π MO. Applying first order perturbation theory to spin-orbit coupling (SOC), the reciprocal of the radiative phosphorescence lifetime is expressed as:

$$1/\tau_p^0 = 0.67 \frac{\tilde{\nu}^3 (T_1 - S_0)}{\tilde{\nu} (S_0 - S_2)} \frac{C_\mu^2 \zeta_\mu^2}{\Delta E(S_2 - T_1)^2} f (S_0 - S_2)$$

where $\Delta E(S_2 - T_1)$ is the energy separation between the perturbing singlet state ${}^1A_1 (\Pi, \Pi^*)$ and the emitting triplet state, and the $\tilde{\nu}$'s are the energies in wavenumbers of the transitions given in parenthesis. Since this expression gives reasonable results for the phosphorescence lifetimes of ketones, it should do the same for thioketones if, as expected, a similar ISC mechanism is operative. Using the values $\zeta(O) = 47.7 \text{ cm}^{-1}$ for a carbonyl oxygen and $\zeta(S) = 27.1 \text{ cm}^{-1}$ for a thiocarbonyl sulfur [19, 23] and $C^2(O) = 0.063$ and $C^2(S) = 0.50$ as taken from the CNDO/2 calculation one gets $\tau_p^0(S)/\tau_p^0(O) = 5$. This result is in vast disagreement with the experimental finding.

Contrary to the latter it predicts a considerably longer phosphorescence lifetime for the sulfur compound than for its oxygen analog. (A similar result is obtained with benzophenone and thiobenzophenone using the data of recent studies [6, 14] and with thioxanthone and thioxanthione [22]). This result indicates that SOC is more complex in thioketones than in ketones. Therefore, one should be cautious in proposing that the extremely effective ISC in thioketones is due to a heavy atom effect, because sulfur is not a "real" heavy atom and the extremely large energy difference between the emitting triplet and the allowed perturbing singlet state $\Delta E(S_2 - T_1) \approx 8600 \text{ cm}^{-1}$ negates the increase in the SOC matrix element due to the increase in the atomic number. Moreover, possible mixing of the ground state with the low-lying triplet states must be considered only a minor source for such a strong

[†] The phosphorescence lifetime τ_p of X was found to be $\tau_p(77 \text{ K}) = 25 \text{ ms}$ and the phosphorescence quantum efficiency $\Phi_p(77 \text{ K}) = 0.70$. (Benzophenone e.g. shows a $\tau_p^0 = 6 - 10 \text{ ms}$ [14]).

SOC. The contribution of d -orbitals on the sulfur to the mixing process is more likely to influence SOC. In C_{2v} symmetry, the d_{xz} orbitals can mix with the Π orbitals, while d_{yz} orbitals are allowed to mix with n -orbitals. It is therefore expected that the mixing will lead to an increase in SOC; however, it is unlikely that these orbitals can dominate the ISC process. At this time it seems that the still scarce data available on thioketones do not allow a reasonable explanation for the very effective ISC mechanism in thioketone molecules.

In the light of the conclusion that the emission of XS is phosphorescence, the experimental findings on the photo-oxidation* of XS to X strongly suggest that the photoreactive state is the lowest triplet state. Oxygen as well as anthracene suppresses this reaction (*cf.* Table 3 and Fig. 4); oxygen about twice as effectively as anthracene. The rates in isopropanol are slightly faster than in ethanol while in non-alcoholic solvents such as 3-MP, the photo-oxidation and the photodecomposition in general is about 13 - 15 times slower. (At 77 K the photochemistry is also ineffective in an alcoholic environment as indicated by the same phosphorescence lifetimes τ_p measured in EPA and 3-MP). The addition of small amounts of alcohol to the 3-MP solution, however, results in a dramatic increase of the photo-oxidation rate. This, together with the observation that the sulfur is also exchanged by oxygen in degassed solutions lead us to believe that the reaction occurs between XS and the alcoholic solvent, but on structural reasons, not by the well known α -hydrogen abstraction mechanism of alcoholic solvents by aromatic ketones [24]. In the present case it is possible that the mechanism consists of an addition of alcohol in the triplet state of XS followed by hydrolysis (OH^-). The latter step seems feasible since small amounts of water are always present in alcoholic solvents. A more detailed photochemical study is now in progress.

Acknowledgements

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*Photo-oxidation on thiobenzophenone has been reported in ref. [15]. The quantum yield of this process in ethanol solution was found to be 0.056.

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