Short Communication

The nature of the red emission of aromatic thioketones

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Aromatic thioketones have recently aroused interest among photochemists [1, 2] and spectroscopists [2 - 5]. Although much information has been gathered about emission behaviour of this class of compounds, there still remains some uncertainty whether the red emission is, as proposed, phosphorescence [2 - 5] or, in spite of indirect evidence, fluorescence. A decision based on emission lifetime measurements, the usual method for distinguishing between the singlet (S_1) or triplet (T_1) character of the emitting state [6], is not applicable here, since the measured lifetime (700 - 900 ns) is consistent with a symmetry forbidden $S_1 \to S_0$ (n, π^*) transition as well as with a $T_1 \to S_0$ transition involving strong spin-orbit coupling, a property expected in these sulphur compounds [3 - 6].

With a quenching study of the red emission of xanthione (XS) and thiobenzophenone (TBP) at room temperature we were able to add another piece of evidence allowing us to assign this emission with confidence as phosphorescence. In order to measure the weak emission, a fully computerized spectrofluorimeter equipped with a red sensitive photon counting system (RCA C31034 photomultiplier tube) was employed. From the 0-0 band of the room temperature emission spectra of TBP and XS in deaerated ethanol solution a good estimate of the energy of the emitting state is obtained. These values and the energies of the first excited singlet states are listed in Table 1 together with the corresponding values of anthracene and ferrocene which were selected as quenchers. The lifetime of the emitting state, necessary for the determination of the quenching rate constant k_Q, was measured by means of a pulsed nitrogen laser (Mod. 100 Lambda Physik, Göttingen) in conjunction with a cooled RCA 7102 photomultiplier tube as detector.

As is demonstrated by the Stern–Volmer plot in Fig. 1, the red emission of XS is quenched very efficiently by both ferrocene and anthracene. Within experimental error a quenching rate constant $k_Q = (5.8 \pm 0.4) \times 10^9 \ M^{-1} \ s^{-1}$ is obtained for both quenchers. The emitting state of TBP, which is located below that of XS, is quenched by ferrocene

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TABLE 1

Compound	$\Delta E(S_0 - S_1)^a$ (cm^{-1})	$\Delta E(S_0 - T_1)^b$ (cm^{-1})	$\tau_p(298)$ (ns)	$k_Q\,[M^{-1}\,s^{-1}]$	
				Anthracene	Ferrocene
				$\Delta E(S_0 - S_1)$ 25000	
				$\Delta E(S_0 - T_1)$ 14700[c]	14,000 ± 1000[d]
Xanthione	15,380	14,850	900 ± 50	$(5.8 \pm 0.4) \times 10^9$	$(5.8 \times 0.4) \times 10^9$
Thiobenzophenone	15,950	13,300	710 ± 30	no quenching	$(1.1 \pm 0.3) \times 10^9$

[a]From the 0-0 band of the absorption.
[b]From the 0-0 band of the emission.
[c]J. B. Birks, Photophysics of Aromatic Molecules, Wiley–Interscience, New York, 1970.
[d]W. Herkstroeter, J. Am. Chem. Soc., 97 (1975) 4161; M. Kikuchi, K. Kikuchi and H. Kokubun, Bull. Chem. Soc. Japan, 47 (1974) 1331; ref. 8.
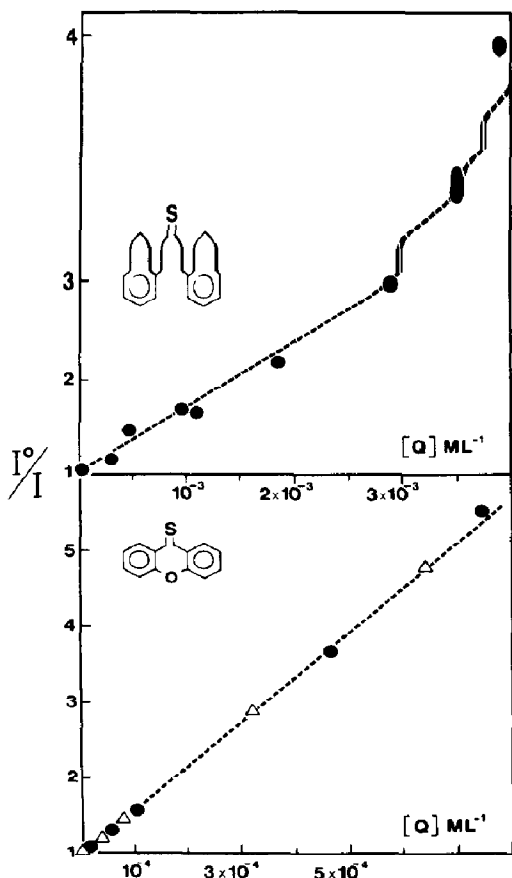
Fig. 1. Stern—Volmer plots of the red emission (I° intensity without quencher) of xanthione (top) and thiobenzophenone (bottom) in ethanol solution at room temperature. ●, Ferrocene as quencher; △, anthracene as quencher.

(cf. Fig. 1) with k_Q = (1.1 ± 0.3) × 10^9 M^{-1} s^{-1}. These quenching rate constants agree well with the k_Q values normally found for triplet—triplet energy transfer processes [7]. Moreover, in a very recent study on triplet state quenching by ferrocene, Farmilo and Wilkinson [8] have shown that ferrocene quenches triplet states having energies E_T ⩾ 15,000 cm^{-1} with k_Q = (6 ± 1) × 10^9 M^{-1} s^{-1}, whereas the quenching ability is strongly reduced if E_T falls below 14,000 cm^{-1}. Since all these findings on triplet state quenching parallel our observation on the aromatic thioketones XS and TBP, we are led to conclude that the emitting state of these compounds is indeed a triplet state, and consequently the red emission is $T_1(n\pi^*) \rightarrow S_0$ phosphorescence [9]. It is noteworthy that no quenching of the TBP emission by anthracene was detectable. It seems that this result should be expected, since the anthracene triplet lies at 14,700 cm^{-1}, just falling between the S_1 and T_1 states of TBP. It does show, however, that there is no effective quenching of the thioketone singlet state.

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9 Given this result, a better estimate of E_T of XS is now available from the $S_0 \rightarrow T_1$ absorption–phosphorescence cross-point. In 3-methylpentane solution this point is found at $14,960$ cm^{-1}. Owing to a strong broadening of the absorption bands in ethanol this information is not easily discernible, but the similar position of the 0-0 band of the emission in ethanol ($14,850$ cm^{-1}) and in 3-methylpentane ($14,900$ cm^{-1}) suggests here an $E_T \sim 14900$ cm^{-1}. For TBP which shows a more pronounced Stokes shift, E_T is expected to be about $14,000$ cm^{-1}.