

Short Communication

Energy wastage in organic photochemistry: self-quenching in thiones

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Thiones which have low lying $n\pi^*$ excited states (singlet and triplet) possess unique properties which permit unit intersystem yield with high rates of S_1 to T_1 crossing [1]. They also undergo efficient (diffusion-limited) self-quenching in their lowest triplet state [2]. Thus at high concentrations of thiones there is an almost quantitative waste of the energy that is pumped into these thione molecules. Therefore advantageous utilization of the electronic properties of excited thione (T_1) at such high concentrations (10^{-1} M) in photochemical reactions has been difficult. These self-quenching processes, which are also prevalent among excited carbonyls, have considerably lower rates [3] which allow these molecules to undergo unimolecular and bimolecular phototransformations. The self-quenching processes which were initially noticed among aromatics have led to the present concept of excimers and exciplexes (excited state complexes) [4]. However, an understanding of the origin and mechanism of self-quenching in carbonyls and thiones is far from clear. We have attempted to study these processes using xanthione as the model. Our method of study has been to quench the phosphorescence of xanthione by various thiones (Fig. 1) and we present the results in this communication.

1. Results

Xanthione is one of the few molecules that show phosphorescence at room temperature in the liquid phase [5]. Excitation of xanthione in the presence of other thiones was possible owing to the existence of a non-overlapping region in the visible absorption spectrum. The emission due to

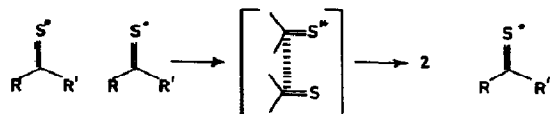


Fig. 1. The quenching mechanism.

TABLE 1
Quenching of xanthione triplet by thiones

| Thione ^a | Triplet energy ^b (kcal mol ⁻¹) | Rate of quenching (M ⁻¹ s) |
|---------------------|--|--|
| 1 | 46.8 | 7.9×10^9 |
| 2 | 50.0 | 1.5×10^{10} |
| 3 | 48.0 | 5.6×10^9 |
| 4 | 48.0 | 4.8×10^9 |
| 5 | 47.5 | 6.0×10^9 |
| 6 | 47.5 | 5.7×10^9 |
| 7 | 53.0 | 7.2×10^9 |
| 8 | 51.2 | 2.8×10^9 |
| 9 | — | 4.5×10^9 |
| 10 | 51.9 | 4.3×10^9 |
| 11 | — | 3.1×10^9 |
| 12 | — | 3.1×10^7 |
| 13 | — | 1.8×10^9 |
| 14 | — | 5.2×10^4 |

^aFor the structures of the thiones see Fig. 2.

^bEstimated from the phosphorescence spectra at 77 K.

xanthione (10^{-4} M) in nitrogen-purged acetonitrile was quenched by a variety of thiones. The rate constants k_q for the primary step were evaluated from the slopes $k_q\tau$ of Stern-Volmer plots knowing the lifetime τ of the xanthione triplet under the same conditions (about $(8.1 \pm 1.5) \times 10^{-7}$ s) [6]. Results are presented in Table 1.

2. Discussion

Perusal of Table 1 reveals that the rates of quenching by all thiones are relatively high (in excess of 10^9 M⁻¹ s). This cannot be due to triplet-triplet energy transfer because all the thiones used here have triplet energies higher (about 50 kcal mol⁻¹) than that of xanthione (about 42 kcal mol⁻¹)[†]. As neither the corresponding carbonyl compounds nor the hydrocarbons quenched the emission of xanthione the quenching presumably involves electronic interaction between thiocarbonyl chromophores (excited and ground state). As no isolable product was obtained when a mixture of xanthione and the thiones 1 - 10 were irradiated under visible light for more

[†]Triplet energies E_{T_1} of all these thiones were estimated from the 0, 0 bands of their phosphorescence spectra at 77 K.

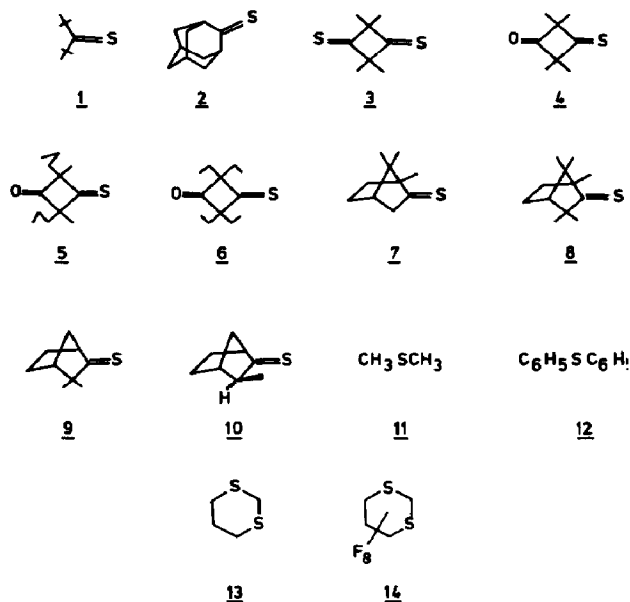


Fig. 2. Structures of the molecules investigated.

than 10 days, the interaction outlined between the excited xanthione triplet and ground state thiones results in a considerable wastage of energy. In all these thiones the electronic interaction could involve a common mechanism. To unravel the mechanism of self-quenching in thiones we have used in our study the phenomenon of steric hindrance which is normally used in physical organic chemistry for an understanding of relative molecular orientation.

For an effective electronic interaction between excited and ground state thiones involving n , π and π^* orbitals there are at least eight possible orientation modes; four of these are in phase and the rest are out of phase. It is evident from the structural features of 1 - 10 that the in phase orientation is not possible and will not result in good electronic overlap to give quenching of the xanthione triplet. This is exemplified by the cases 3 - 6 in which increased steric crowding for in phase orientation has a negligible effect on the rate of quenching. Therefore, it is clear that out of phase orientation is the preferred mode for quenching. With such an orientation there are four possible electronic overlap interactions (Fig. 3) that may lead to quenching. Comparison of the quenching rates of 7 - 10 reveals that introduction of steric crowding around the n phase of quenchers results in decreased quenching rates (compare 7 and 8). Furthermore, it must be noted that the rate of quenching decreases with increased steric crowding on the n phase of quenchers, *i.e.* $8 < 9 < 7$. Therefore, it is evident that the lone pair on the sulphur atom of ground state thione is responsible for the quenching of the xanthione triplet. The ability of sulphides 11 - 14 to quench the triplet xanthione supports this view. The availability of a lone pair of electrons seems to be responsible for quenching as with 12 and 14; where quenching is

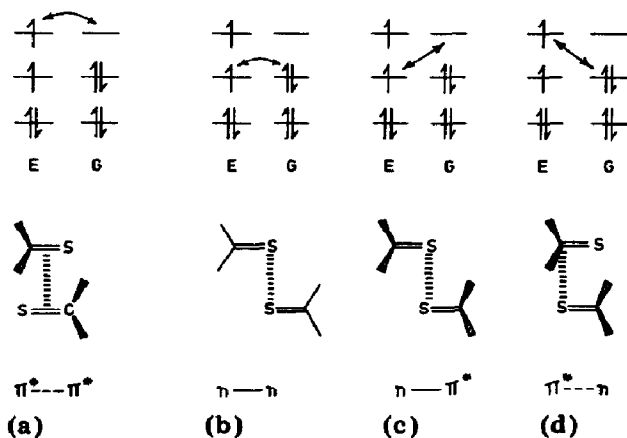


Fig. 3. Excited thione-thione out of phase interaction (E = excited state, G = ground state).

reduced by appropriate substitutions the rate is much lower than that in 11 and 13. The increased rate of quenching in thiones in relation to that in carbonyls must be due to the difference in the nature of orbitals involved, *i.e.* 3p and 2p respectively, with a consequent decrease in ionization potential. It is obvious from the results presented that the excited thione behaves as an electrophile. From the nature of the electronic state ($n\pi^*$) involved, we can conclude that it is the singly occupied n orbital of the sulphur atom of excited xanthione that interacts with the lone pair of the ground state thione. We can visualize the interaction that may be responsible for self-quenching as in Fig. 3(b).

In conclusion, we have shown that ground state thiones are excellent quenchers of triplet thiones involving the interaction of n orbitals of excited and ground state thiones. The interaction yields no chemical products and thus results in energy wastage.

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