

## THE PROBLEM OF TRIPLET SELF-QUENCHING IN THIOKETONE PHOTOCHEMISTRY

V. RAMESH, N. RAMNATH and V. RAMAMURTHY

*Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012 (India)*

(Received August 6, 1982; in revised form March 23, 1983)

### Summary

The highly efficient quenching of the thioketone triplet state by ground state thioketones with various electronic and structural features was investigated by means of phosphorescence quenching measurements in a number of solvents. Electron-withdrawing groups conjugated to the thioketone chromophore and steric crowding around the lone pair of electrons on the sulphur atom tend to decrease the quenching rate. The ground state thioketone quencher acts as the donor and the excited thioketone phosphorescer acts as the acceptor in the quenching process. Possible involvement of triplet excimers was investigated but no excimer or heteroexcimer emission was observed.

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### 1. Introduction

The thioketone chromophore has been under intense photochemical investigation in recent years. Thioketones produce singlet oxygen and undergo  $\alpha$  cleavage, intramolecular hydrogen abstraction, photoreduction and cycloaddition. These processes occur from the low-lying  $n, \pi^*$  triplet state. Reactions of thioketones from the second excited  $\pi, \pi^*$  singlet state are also known [1]. The photochemical phenomenon of self-quenching, *i.e.* the process of deactivation of a thioketone triplet by a ground state thioketone of the same type, is associated with the  $n, \pi^*$  triplet state of thioketones [2]. This problem of self-quenching leads to energy loss and lowers the quantum yield of the chemical reactions with increasing concentration of thioketone.

While efforts to utilize the thioketone chromophore in phototransformations are in progress corresponding research into the problems that confront its photochemistry and the methods required to surmount them is needed. The operation of triplet self-quenching in thioketones was initially reported by de Mayo and coworkers [2]. Studies on the process for xanthione and related thioketones have been reported more recently [3 - 5].

An understanding of the factors governing the triplet self-quenching process in the thioketones can be reached by measuring the rate of self-quenching (by monitoring the lifetime of the lowest triplet state at various

concentrations) of suitably chosen thiocarbonyl compounds. In the absence of a method of measuring this process, we have undertaken an investigation of the rate of quenching of the triplet thioketone by other thioketones. The thioketones xanthione, thioxanthione, *N*-methylthioacridone and 4,4'-dimethoxythiobenzophenone, among others, phosphoresce at room temperature in fluid solution [5]. The study of the phosphorescence quenching of the triplet states of these thioketones (10 - 13) by a set of suitably tailored ground state thioketones varying in their electronic (1 - 4) and steric features (5 - 9) is reported in this paper. (The thioketone structures are shown in Fig. 1.)

Although the process studied is not rigorously self-quenching, it provides a measure of the interaction between a thioketone triplet and a ground state thioketone. The values obtained for  $k_q$  and the Stern-Volmer constant  $k_q\tau$  can be used to draw conclusions regarding the fundamental nature of the interaction between two thiocarbonyl chromophores. Our results on the electronic and steric factors governing the process, the role of solvents and the search for heteroexcimer and excimer emissions are presented in this paper.

## 2. Experimental details

Thioketones 1 - 13 were synthesized and purified according to methods reported in the literature [6]. Spectrograde acetonitrile, methanol, benzene and cyclohexane were used as solvents.

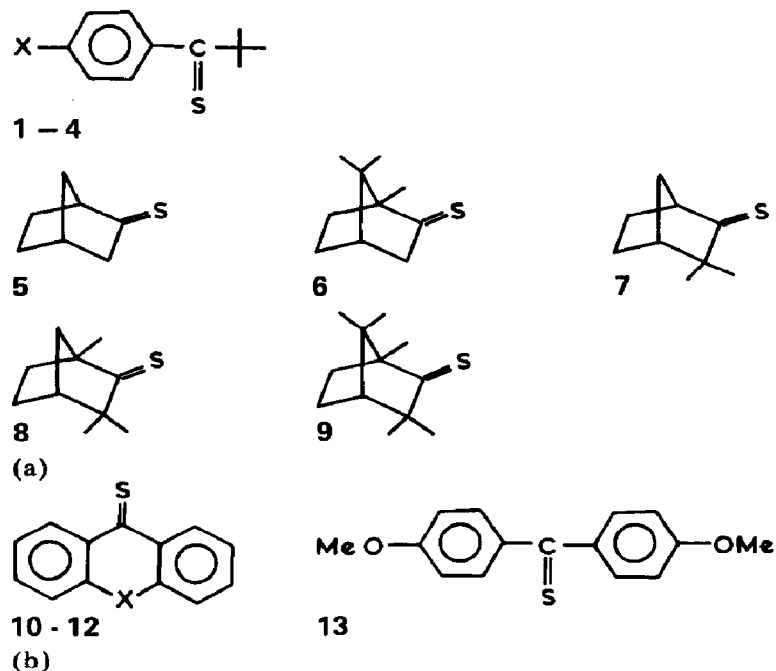


Fig. 1. Structures of (a) the quencher and (b) the phosphorescer thioketones: 1, X  $\equiv$  OCH<sub>3</sub>; 2, X  $\equiv$  H; 3, X  $\equiv$  Cl; 4, X  $\equiv$  F; 10, X  $\equiv$  O; 11, X  $\equiv$  S; 12, X  $\equiv$  N-CH<sub>3</sub>.

In a typical experiment to determine the rate  $k_q$  of quenching, a solution of  $1.5 \times 10^{-5}$  M xanthione in acetonitrile was prepared. 3 ml of the solution were syringed into a quartz cell fitted with a Teflon stopcock, deoxygenated by purging with dried nitrogen gas and stoppered. The phosphorescence of xanthione was quenched by the addition of 0.01 ml portions of the stock solution of the quencher thioketone which was also prepared as a deoxygenated acetonitrile solution.

The plots of  $I_0/I_p$  versus the concentration of the quencher thione, where  $I_0$  is the initial maximum phosphorescence intensity and  $I_p$  is the intensity after quenching, were linear, and the  $k_q$  values were calculated from the slope  $k_q\tau$  and the lifetime  $\tau$  of the phosphorescer. The values of the lifetime of the xanthione triplet in various solvents were taken from the literature [3]. Since lifetime data were not available for thioxanthione, *N*-methylthioacridone and 4,4'-dimethoxythiobenzophenone, the  $k_q\tau$  values are presented.

Care was taken to ensure that the exciting wavelength for the phosphorescers 10 - 13 lay in a region of the absorption spectrum that did not overlap with that of the quencher thioketones. Table 1 gives the details of the exciting and monitoring wavelengths chosen. The triplet energies  $E_T$  of the thioketones were determined from their phosphorescence spectra recorded at 77 K. A Perkin-Elmer MPF-44 A spectrofluorometer was used to record the phosphorescence spectra. The ionization potential data were kindly provided by Professor R. Gleiter and Professor W. Cherry.

TABLE 1

Experimental conditions for the determination of  $k_q\tau$  for various systems

Thioketone phosphorescer	Concentration (M)	Exciting wavelength of the phosphorescer in the presence of the quencher (nm)		Monitoring wavelength of the phosphorescer in the presence of the quencher (nm)	
		1 - 4	5 - 9	1 - 4	5 - 9
10	$1.5 \times 10^{-5}$	430	400	680	680
11	$10^{-5}$	465	300	740	700
12	$10^{-5}$	—	300	—	700
13	$1.5 \times 10^{-5}$	—	360	—	700

A search for heteroexcimer emission was made in each experiment by looking for a new emission peak which increased in intensity with increasing concentrations of the quencher thioketone. The excimer was sought in thioketones 10 - 13. Degassed thioketone solutions of increasing concentrations in the range  $5 \times 10^{-6}$  -  $10^{-4}$  M were prepared and the phosphorescence spectra were recorded at room temperature.

### 3. Results and discussion

The quenching parameters  $k_q$  and  $k_q\tau$  for the quenching of the phosphorescence of xanthione and thioxanthione respectively by the quencher thioketones 1 - 9 in acetonitrile, methanol, benzene and cyclohexane are presented in Tables 2 and 3 (the solvent data are given in Table 4). The  $k_q\tau$  values for the quenching of the phosphorescence of *N*-methylthioacridone and 4,4'-dimethoxythiobenzophenone by 5 - 9 in acetonitrile are presented in Table 5. Since no data are available for the triplet lifetimes of thioxanthione, *N*-methylthioacridone and 4,4'-dimethoxythiobenzophenone only the  $k_q\tau$  values are presented in Tables 3 and 5. However, these can be used to draw general conclusions regarding the mechanism of self-quenching. Quenching of phosphorescers 12 and 13 by thioketones 1 - 4 could not be carried out because the phosphorescence was extremely weak at the required excitation wavelengths. Values of the triplet energy and *n* electron ionization potential for the quencher thioketones are included in Table 2.

The triplet self-quenching processes which are prevalent among ketones and aromatic compounds have been investigated [8] and have been found to have self-quenching rate constants in the range  $10^5 - 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . These relatively low rates of self-quenching allow these molecules to undergo unimolecular and bimolecular transformations. Thioketones, however, have self-quenching constants of the order of  $10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and these comparatively high rates can be attributed to the intrinsic nature of the thioketone chromophore. A closer examination of the data presented in Tables 2, 3 and 5 provides an insight into the mechanism of self-quenching.

TABLE 2

Rate of quenching  $k_q$  of the xanthione triplet ( $E_T \approx 43.7 \text{ kcal mol}^{-1}$ ) by arylalkyl and bicyclo[2.2.1]heptane thioketones in various solvents

Quencher thioketone data			$k_q$ ( $\text{M}^{-1} \text{ s}^{-1}$ ) for the following solvents			
Quencher	$E_T^a$ (kcal mol $^{-1}$ )	$IP(n)^b$ (eV)	Methanol	Acetonitrile	Benzene	Cyclohexane
1	45.4	7.83	$8.6 \times 10^9$	$7.6 \times 10^9$	$4.6 \times 10^9$	$4.7 \times 10^9$
2	46.2	7.92	$7.8 \times 10^9$	$7.5 \times 10^9$	$4.6 \times 10^9$	$3.4 \times 10^9$
3	45.8	8.39	$6.1 \times 10^9$	$4.2 \times 10^9$	$3.9 \times 10^9$	$2.7 \times 10^9$
4	45.8	7.99	$3.4 \times 10^9$	$2.2 \times 10^9$	$2.3 \times 10^9$	$0.9 \times 10^9$
5	52.2	8.32	$6.6 \times 10^9$	$4.7 \times 10^9$	$1.1 \times 10^9$	$1.0 \times 10^9$
6	51.8	8.17	$7.9 \times 10^9$	$5.6 \times 10^9$ <sup>c</sup>	$5.4 \times 10^9$	$3.8 \times 10^9$
7	52.0	8.15	$8.8 \times 10^9$	$7.7 \times 10^9$ <sup>c</sup>	$7.4 \times 10^9$	$5.4 \times 10^9$
8	52.0	8.10	$0.9 \times 10^9$	$1.2 \times 10^9$ <sup>c</sup>	$1.2 \times 10^9$	$0.7 \times 10^9$
9	52.2	8.01	$2.4 \times 10^9$	$1.5 \times 10^9$	$1.6 \times 10^9$	$1.0 \times 10^9$

<sup>a</sup>Estimated from the phosphorescence spectra at 77 K.

<sup>b</sup>*n* electron ionization potential.

<sup>c</sup>Value differs from that given in ref. 4, probably because of impurities in the samples of thioketones used previously.

TABLE 3

$k_q\tau$  values for the thioxanthione triplet ( $E_T \approx 43.7$  kcal mol<sup>-1</sup>) quenched by arylalkyl and bicyclo[2.2.1]heptane thioketones in various solvents

Quencher thioketones	$k_q\tau$ for quenching of the thioxanthione triplet (M <sup>-1</sup> ) in the following solvents			
	Methanol	Acetonitrile	Benzene	Cyclohexane
1	$16.7 \times 10^2$	$52.6 \times 10^2$	$42.6 \times 10^2$	$39.1 \times 10^2$
2	$18.2 \times 10^2$	$56.5 \times 10^2$	$32.7 \times 10^2$	$29.5 \times 10^2$
3	$13.9 \times 10^2$	$33.1 \times 10^2$	$17.1 \times 10^2$	$21.8 \times 10^2$
4	$8.9 \times 10^2$	$17.3 \times 10^2$	$10.5 \times 10^2$	$9.6 \times 10^2$
5	—	$1.1 \times 10^2$	$1.8 \times 10^2$	$1.4 \times 10^2$
6	$1.0 \times 10^2$	$1.4 \times 10^2$	$1.5 \times 10^2$	$0.9 \times 10^2$
7	$1.1 \times 10^2$	$1.0 \times 10^2$	$1.0 \times 10^2$	$0.9 \times 10^2$
8	$0.8 \times 10^2$	$0.7 \times 10^2$	$1.0 \times 10^2$	$0.7 \times 10^2$
9	$4.0 \times 10^2$	$2.3 \times 10^2$	$5.0 \times 10^2$	$4.3 \times 10^2$

TABLE 4

Data for solvents used in Tables 2 and 3

Solvent	Methanol	Acetonitrile	Benzene	Cyclohexane
Xanthione triplet lifetime <sup>a</sup> (s)	$1.3 \times 10^{-6}$	$2.78 \times 10^{-6}$	$3.22 \times 10^{-6}$	$5.88 \times 10^{-6}$
Viscosity <sup>b</sup> ( $\times 10^{-3}$ P)	5.45	3.45	6.03	8.98
Polarity $Z^b$ (kcal mol <sup>-1</sup> )	83.6	71.3	54.0	—

<sup>a</sup>From ref. 3.

<sup>b</sup>From ref. 7.

TABLE 5

$k_q\tau$  values for the 4,4'-dimethoxythiobenzophenone triplet ( $E_T \approx 42$  kcal mol<sup>-1</sup>) and the *N*-methylthioacridone triplet ( $E_T \approx 44.3$  kcal mol<sup>-1</sup>) quenched by bicyclo[2.2.1]heptane thioketones in acetonitrile

Quencher thioketone	$k_q\tau$ (M <sup>-1</sup> ) for quenching of the following triplets	
	<i>N</i> -methylthioacridone triplet	4,4'-dimethoxythiobenzophenone triplet
5	$1.2 \times 10^2$	$8.2 \times 10^3$
6	$1.3 \times 10^2$	$8.1 \times 10^3$
7	$1.2 \times 10^2$	$6.6 \times 10^3$
8	$0.8 \times 10^2$	$2.5 \times 10^3$
9	$2.8 \times 10^2$	$2.1 \times 10^3$

The triplet energies of the arylalkyl thioketones 1 - 4 ( $E_T \approx 46$  kcal mol<sup>-1</sup>) and the bicyclo[2.2.1]heptane thioketones 5 - 9 ( $E_T \approx 52$  kcal mol<sup>-1</sup>) are higher than those of the phosphorescers ( $E_T \approx 43$  kcal mol<sup>-1</sup>). Consequently quenching at ambient temperatures via triplet-triplet energy transfer

is not expected to be important. The results shown in Table 2 reveal that the rate of quenching by thioketones 1 - 9 is slightly less than diffusion limited in all cases and in all four solvents investigated. This is unexpected in view of the rates of self-quenching of some thioketones reported earlier [2 - 5]. Further, the quenching rates  $k_q$  and  $k_q\tau$  are found to be dependent on the thioketones in both the arylalkyl and the dialkyl series. The results for the arylalkyl thioketones 1 - 4 (Tables 2 and 3) reveal that the rate of quenching varies with the substitution on the aryl ring. This is true in all four solvents for phosphorescers 10 and 11. It is observed that, while electron-withdrawing groups lower the rate, electron-releasing groups enhance it. Correlations of  $k_q$  and  $k_q\tau$  with the  $n$  electron ionization potentials and with the Hammett parameters  $\sigma$  and  $\sigma^+$  were attempted but a non-linear relation was obtained. However, the quenching rates were found to be dependent on the  $n$  electron ionization potentials. It is evident that the presence of an electron-withdrawing group on the aryl moiety which lowers the availability of electrons of the ground state thioketone and increases the  $n$  electron ionization potential results in a decrease in the rate of quenching. Similarly the presence of an electron releasing group which enhances the availability of electrons on the thiocarbonyl chromophore and lowers the  $n$  electron ionization potential results in an increase in the rate of quenching. These observations reveal that the ground state thioketone acts as the donor in the quenching process.

The results for the bicyclo[2.2.1]heptane thioketones throw more light on the nature of the orbitals involved in the ground state donor. As with the arylalkyl series we attempted to correlate  $k_q$  and  $k_q\tau$  with the  $n$  electron ionization potentials. The results for xanthione are discussed first, followed by those for thioxanthione and the other thioketones.

There is a poor correlation between the rate of quenching and the  $n$  electron ionization potential. For example thiofenchone, which has a low ionization potential for  $n$  electrons, exhibits a lower rate of quenching than northiocamphor which has a high ionization potential. These results can be rationalized by invoking steric factors. It can be seen that complete blocking of the  $n$  orbitals, as occurs in thiofenchone and dimethylthiocamphor, decreases the rate of quenching compared with that of thioketones 5, 6 and 7 where the  $n$  lobe of the sulphur atom is not completely blocked by methyl groups. As expected, this is also true for the quenching of the 4,4'-dimethoxythiobenzophenone, thioxanthione and *N*-methylthioacridone triplets (Tables 3 and 5).

On the basis of these observations we conclude that the lone pair of electrons in the  $n$  orbital of the ground state thioketone is involved in quenching and that the ground state quencher thioketone is the donor species in the electronic interaction leading to self-quenching.

#### 4. Solvent effects

To seek further evidence for the possible involvement of a donor-acceptor type of interaction during the quenching process described above

the quenching constants were measured in various solvents (acetonitrile, benzene, methanol and cyclohexane). The  $k_q\tau$  values measured for 11 - 13 cannot be used to draw conclusions regarding solvent-dependent quenching processes as the lifetimes of the quenchers themselves may be solvent dependent. Examination of Table 2 reveals that  $k_q$  for the thioketones 1 - 9 is generally larger for solutions in methanol and lower for solutions in benzene and cyclohexane. This variation could arise from differences in either the viscosity or the polarity of the medium. However, the measured rates of quenching in all solvents are lower than the diffusion rates which implies that viscosity may not be the limiting factor in these cases. It should be noted that recent measurements have revealed that the self-quenching rates for xanthione and *N*-methylthioacridone are diffusion limited in various solvents [3, 4]. However, the rates that are measured here are not for self-quenching but for the quenching of excited thioketones by other thioketones. It is not obvious why the latter are less than diffusion limited.

The rate of quenching by all thioketones except 8 is higher in methanol than in benzene. Similarly, the rate of quenching in acetonitrile is lower than that in methanol but higher than that in benzene. Both methanol and benzene have similar viscosities ( $5.45 \times 10^{-3}$  P and  $6.03 \times 10^{-3}$  P respectively) but their polarities  $Z$  are significantly different ( $83.6 \text{ kcal mol}^{-1}$  and  $54.0 \text{ kcal mol}^{-1}$  respectively). In the limited number of solvent systems studied the rates of quenching appear to be directly related to the  $Z$  values of the solvents which is an indication that the solvent polarity plays a significant role in the quenching process.

## 5. Search for excimer and heteroexcimer emissions

The phenomenon of self-quenching has been noted earlier in ketones and some aromatic molecules [8]. Although the mechanism of self-quenching in ketones is not yet understood, triplet excimer formation has been proposed for the aromatics and emissions from such excimers have been recorded [9]. The formation of a triplet excimer as a consequence of efficient self-quenching has also been suggested for thioketones [2 - 4]. We attempted to observe heteroexcimer emission in a number of thioketones, and the results are presented in this section.

As pointed out earlier, the phosphorescer concentration was kept constant ( $10^{-5}$  M) and the quencher thioketone was added at concentrations in the range  $10^{-4}$  -  $10^{-3}$  M to observe a decrease in the phosphorescence intensity. The interaction between two thioketone chromophores was expected to lead to the formation of a heteroexcimer. We searched for a new emission whose intensity would increase with the addition of further quencher for all the systems in all four solvents, but failed to observe such an emission at room temperature. We then looked for a possible excimer emission at various concentrations of xanthione, thioxanthione, *N*-methylthioacridone and 4,4'-dimethoxythiobenzophenone in all four solvents but none was observed. We conclude that, if an excimer or heteroexcimer is

formed, it is either deactivated via a radiationless process or the emission is too weak to be detected by the spectrofluorometer used in this work.

## 6. Conclusion

The present study has revealed that the n orbital of the ground state thioketone chromophore acting as the donor is involved in the quenching process. The quenching process is affected by substitution of electron-withdrawing groups in arylalkyl thioketone systems and steric crowding around the thioketone chromophore blocking the n lobes. Although structural manipulations of the thioketone chromophore reduce the quenching rate, complete inhibition of the process is not achieved. The technique of micellar compartmentalization has recently been shown to inhibit the process [10] and this may provide a solution to the problem of self-quenching.

## Acknowledgments

We are grateful to Professor P. Balaram for allowing us to use the spectrofluorometer. The Department of Atomic Energy and the Department of Science and Technology, Government of India, are thanked for financial support.

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