INHIBITION OF SELF-QUENCHING IN THIOKETONES BY MICELLAR COMPARTMENTALIZATION

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Summary

The technique of micellar compartmentalization has been used to inhibit the diffusion-controlled self-quenching process in thioketones. By adjusting the ratio of the bulk concentration of the thioketone solute to the bulk concentration of micelles multiple occupancy of the micelles was avoided. Under these conditions enhanced phosphorescence intensity was observed in nitrogen-purged micellar solutions compared with that in acetonitrile solutions, indicating that the thioketone triplet was indeed protected from deactivation by a ground state thioketone.

1. Introduction

One of the problems that confronts thioketone photochemistry is self-quenching. When a thioketone triplet encounters a ground state thioketone a deactivation of the triplet occurs via a physical or chemical quenching process. Rates of self-quenching of aromatic and aliphatic thioketones have been determined [1 - 3] to be of the order of 10^9 M^{-1} s^{-1}. The efficient diffusion-limited self-quenching therefore makes the advantageous utilization of the thioketone triplet in photochemical reactions difficult as it leads to an almost quantitative wastage of the energy pumped into the system. Therefore it is necessary to inhibit the process of self-quenching so that unimolecular photochemical processes from the triplet state at high concentrations can be achieved without wastage of energy and/or the formation of unfavourable products like disulphides arising from such interactions [4]. The sequestering of thioketones in micelles under conditions where multiple occupancy of a micelle is avoided would compartmentalize the thioketone and eliminate the diffusion-controlled self-quenching process. In this paper we present our studies of the room temperature phosphorescence of thioketones in sodium dodecyl sulphate (SDS), cetyltrimethylammonium bromide (CTAB), poly(oxyethylene)(9.5)*p*-1,1,3,3-tetramethylbutylphenol (Triton X-100) detergents and acetonitrile. The phosphorescence characteristics in acetonitrile

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will elucidate the inherent nature of self-quenching in fluid solutions, and those in detergents will reflect the effect of compartmentalization on self-quenching.

2. Experimental details

In a typical experiment 0.02 M solutions of SDS, CTAB and Triton X-100 in doubly distilled water were prepared. 0.2 ml of a 0.01 M solution of thioketone in ether was pipetted into 20 ml of the 0.02 M detergent solution and stirred overnight in the dark to obtain a 10^{-4} M thioketone solution in the detergents. A 10^{-4} M thioketone solution in acetonitrile was also prepared. The detergent solutions were faintly coloured. In cases where the coloration was too faint UV–visible absorption spectra were obtained to ensure that the thioketone was solubilized in the detergent solutions.

Quartz fluorescence cuvettes fitted with Teflon stoppers were used. 3 ml each of the thioketone solutions were transferred into the cuvettes and nitrogen was bubbled into each solution with the help of a long needle for 30 min. The cuvettes were then stoppered tightly.

Luminescence spectra were recorded on a Perkin–Elmer MPF-44A spectrofluorometer at room temperature.

3. Results and discussion

The aromatic thioketones xanthione, thioxanthione, *N*-methylthioacridone and *p*,*p*′-dimethoxythiobenzophenone, the aryl alkyl thioketone *p*-methoxythiopivalophenone, and the alkyl thioketones thiocamphor, thiofenchone, thiocamphenilone and di-*t*-butylthioketone were investigated. In all cases a 0.02 M detergent solution with 10^{-4} M of thioketone solubilized in it was used. A distribution of the thioketone solute in the micelles can be calculated using Poisson statistics [5], and it is found that multiply occupied micelles are negligible compared with singly occupied and unoccupied micelles. Thus the concentrations used ensured that multiple occupancy of a micelle was avoided.

Figure 1 shows the emission spectra of xanthione and *p*,*p*′-dimethoxythiobenzophenone in acetonitrile, SDS, CTAB and Triton X-100 at room temperature. The emission spectra coincide with spectra reported in the literature [6, 7]. The short wavelength emission corresponds to the fluorescence from the S_2 state and that from the longer wavelength corresponds to phosphorescence from the T_1 state.

The most striking observation is that the weak phosphorescence in acetonitrile is enhanced by a factor of almost 4 in SDS and Triton X-100. This could be attributed to the fact that whereas the diffusion-controlled self-quenching, in addition to other quenching processes such as impurity quenching and triplet–triplet annihilation, deactivate the triplet thioketone

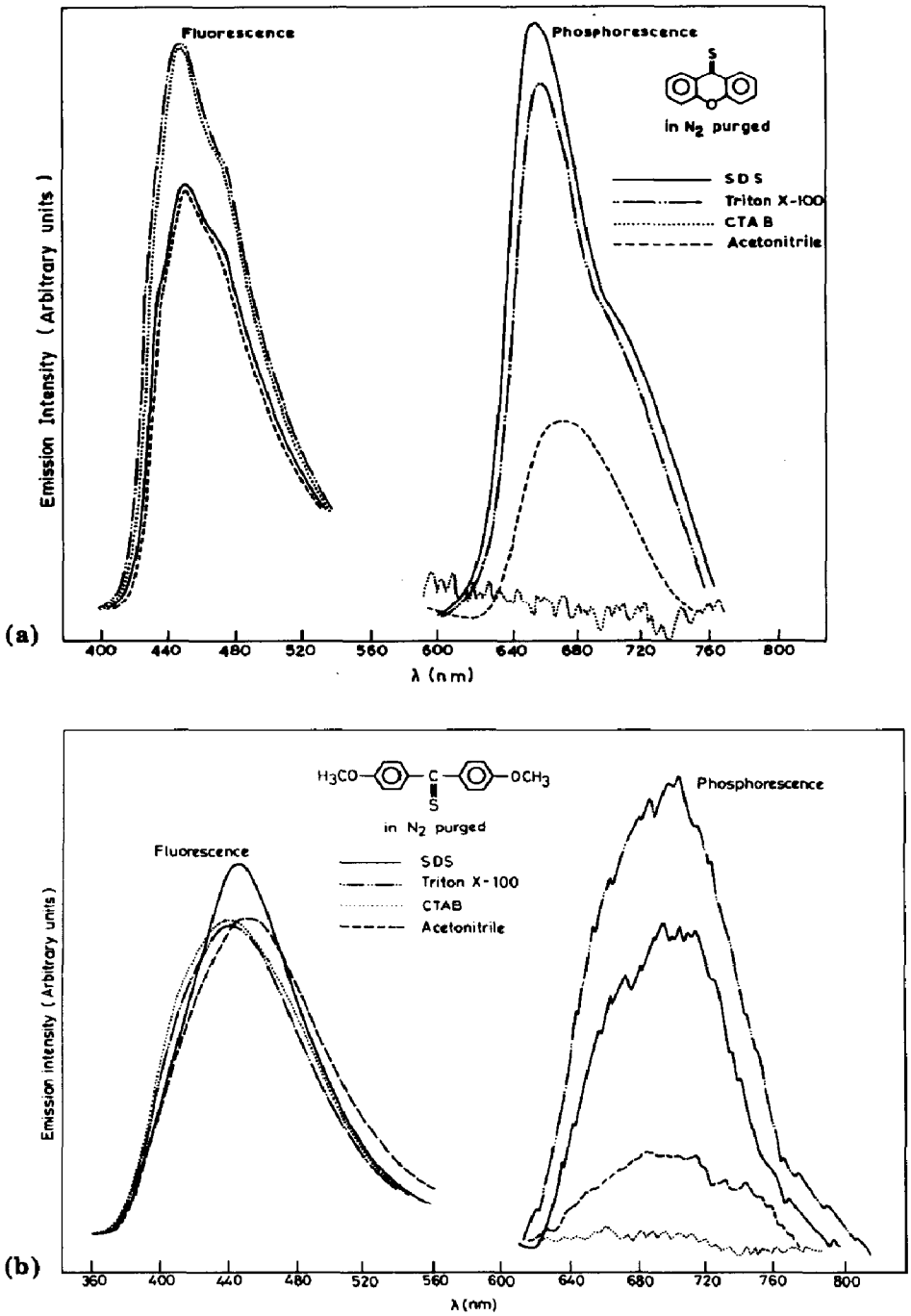

Fig. 1. (a) Emission spectrum of xanthione (10^{-4} M) in nitrogen-purged acetonitrile, SDS (0.02 M), CTAB (0.02 M) and Triton X-100 (0.02 M) at room temperature (excitation wavelength, 400 nm; phosphorescence spectrum recorded at a sensitivity 3.3 times that of the fluorescence spectrum); (b) emission spectrum of *p,p'*-dimethoxythiobenzophenone (10^{-4} M) in nitrogen-purged acetonitrile, SDS (0.02 M), CTAB (0.02 M) and Triton X-100 (0.02 M) at room temperature (excitation wavelength, 360 nm; phosphorescence spectrum recorded at a sensitivity 10 times that of the fluorescence spectrum).

species in acetonitrile, the micellar environment protects the compartmentalized thioketone triplet from encountering another thioketone. The increase in phosphorescence intensity in micellar solutions is an indication of the inhibition of self-quenching. However, the intensity of the fluorescence emission from the S_2 state is not strongly affected as is expected.

It should be noted that S_2 emission is observed in CTAB whereas phosphorescence is quenched completely. This, we believe, could be due to enhancement of the rate of a radiationless process by the bromide ion. Further, we have observed that fluorescence and phosphorescence are devoid of any fine structure and are sensitive to nitrogen purging, with phosphorescence being the more sensitive of the two. However, phosphorescence was observed even in aerated detergent solutions of the thioketones [8].

Thioxanthione and *N*-methylthioacridone in detergent solutions exhibit similar characteristics. In these cases phosphorescence observed in the region 680 - 800 nm for thioxanthione and 600 - 760 nm for *N*-methylthioacridone is in agreement with emission regions reported in the literature [6, 9], and the enhancement of the emission intensity in SDS and Triton X-100 is a factor of 2 - 3. There is no emission in nitrogen-purged acetonitrile solutions of *p*-methoxypivalophenonethione but a weak phosphorescence emission between 650 and 750 nm was observed in micellar solutions. We were unable to detect phosphorescence from nitrogen-purged micellar or acetonitrile solutions of alkyl thioketones at room temperature. This could possibly be due to the low rate of phosphorescence of these compounds.

In order to demonstrate that micellar sequestering of the thioketone is indeed responsible for the inhibition of self-quenching and thereby causes an enhancement in the phosphorescence intensity we designed two experiments using xanthione and *p,p'*-dimethoxythiobenzophenone.

In the first experiment the detergent concentration was varied and the thioketone concentration was kept constant at 10^{-4} M (Fig. 2). Phosphorescence was observed near and above the critical micelle concentration (CMC) in SDS, while in Triton X-100 the phosphorescence intensity increased gradually and became nearly constant above the CMC. This observation is consistent with our hypothesis that compartmentalization of the thioketone occurring near and above the CMC inhibits self-quenching and enhances the phosphorescence intensity.

In the second experiment the detergent concentration was kept constant at 0.02 M (above the CMC) and the thioketone concentration was varied from 5×10^{-5} to 4×10^{-4} M. This was done with a view to gradually increasing the ratio of the bulk concentration of the thioketone solute to the bulk concentration of the micelles so that multiple occupancy of the micelles is induced [5]. Under these conditions the effectiveness of the inhibition of self-quenching decreases and hence a decrease in phosphorescence is expected. (An inevitable drawback of this experiment is the inner filter effect which would contribute to the decrease in the phosphorescence intensity with increasing concentration. However, we employed concentration ranges and concentration intervals small enough to minimize such effects. Further, we

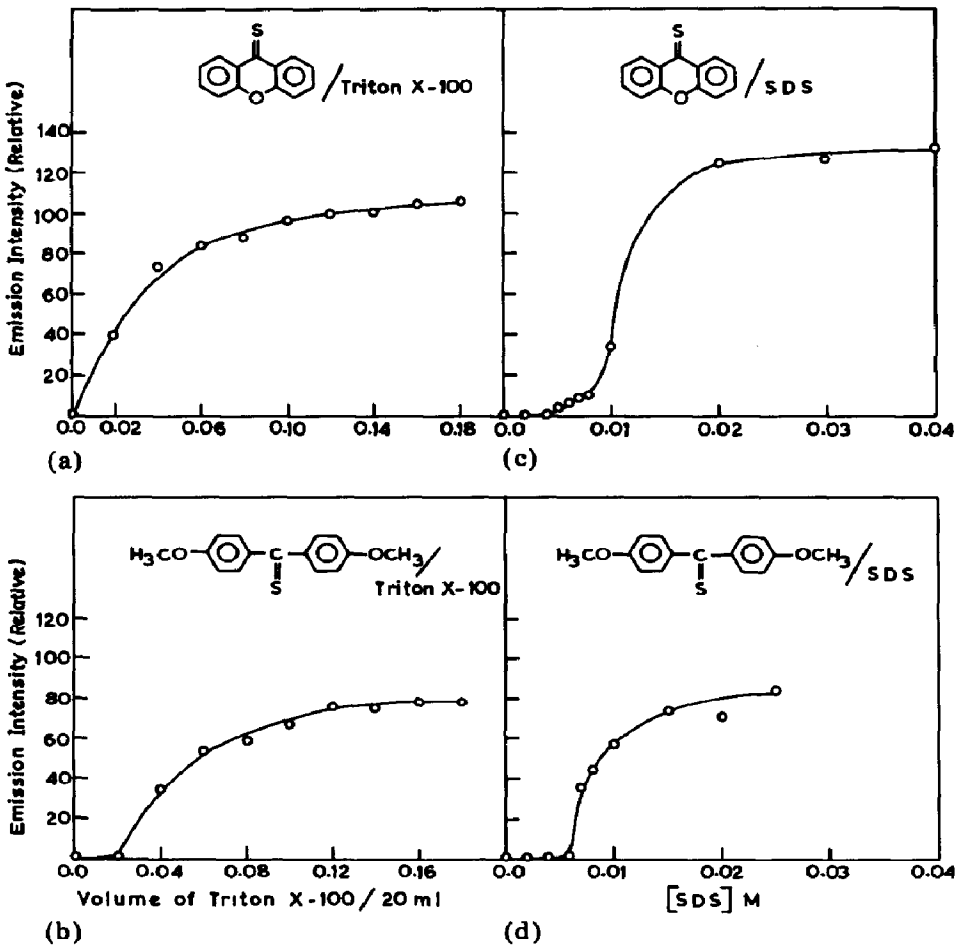

Fig. 2. Variation in the detergent concentration at a constant thioketone concentration (10^{-4} M). The emission intensity was recorded at the phosphorescence emission maxima. The observed critical micelle concentrations are (a) 0.48 vol.%, (b) 0.50 vol.%, (c) 0.011 M and (d) 0.008 M.

have also carried out the same experiment for acetonitrile solutions so that comparison with detergent solutions could be made.) Figure 3 illustrates the results of these experiments which are in agreement with expectations. The decrease in phosphorescence intensity is less drastic in detergent solutions than in acetonitrile solutions. This indicates that self-quenching in higher concentrations of thioketone solutions can be inhibited by micellar compartmentalization. Micelle-stabilized room temperature phosphorescence is a topic of current interest [8, 10 - 12]. Earlier workers have utilized this technique in arenes and substituted naphthalene systems, and we have been able to apply it successfully to thiocarbonyls to demonstrate that micellar sequestering of thioketones would surmount the problem of self-quenching in thiocarbonyl photochemistry.

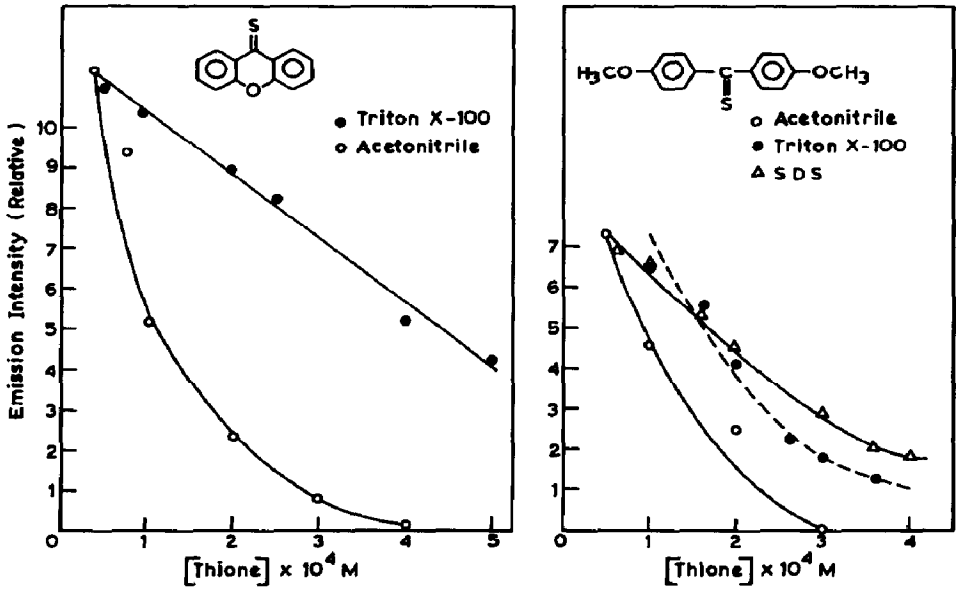

Fig. 3. Variation in the thioketone concentration at constant detergent concentration (0.02 M). The emission intensity was recorded at the phosphorescence emission maxima.

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References

1 D. R. Kemp and P. de Mayo, *J. Chem. Soc., Chem. Commun.*, (1972) 233.
2 A. H. Lawrence and P. de Mayo, *Mol. Photochem.*, *5* (3) (1973) 361.
3 U. Bruhlmann and J. R. Huber, *Chem. Phys. Lett.*, *54* (1978) 606.
R. Rajee and V. Ramamurthy, *J. Photochem.*, *11* (1979) 135.
4 A. H. Lawrence, C. C. Liao, P. de Mayo and V. Ramamurthy, *J. Am. Chem. Soc.*, *98* (1976) 3572.
K. Muthuramu and V. Ramamurthy, *J. Org. Chem.*, *45* (1980) 4532.
5 N. J. Turro, M. Grätzel and A. M. Braun, *Angew. Chem., Int. Edn. Engl.*, *19* (1980) 681.
6 M. Mahaney and J. R. Huber, *Chem. Phys.*, *9* (1975) 371 - 378.
7 D. S. Blackwell, C. C. Liao, R. O. Loutfy and P. de Mayo, *Mol. Photochem.*, *4* (2) (1972) 171 - 188.
8 N. J. Turro, Kou-Chang Liu, Ming-Fea Chow and P. Lee, *Photochem. Photobiol.*, *27* (1978) 523 - 529.
9 A. Saferzadeh Amiri, D. A. Condirston, R. E. Verrall and R. P. Steer, *Chem. Phys. Lett.*, *77* (1981) 99.
10 K. Kalyanasundaram, F. Grieser and J. K. Thomas, *Chem. Phys. Lett.*, *51* (1977) 501.
11 L. J. Cline Love, M. Skrillec and J. G. Habarta, *Anal. Chem.*, *52* (1980) 754.
12 M. Skrillec and L. J. Cline Love, *Anal. Chem.*, *52* (1980) 1559.