Preliminary Note

Efficiency of singlet oxygen production by thiocarbonyls

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The efficiencies of singlet oxygen production by nine thioketones were measured by following the bleaching of 1,3-diphenylisobenzofuran in chloroform. The results show that the efficiencies are very high at low thioketone concentrations. The role of self-quenching in the sensitization process is discussed.

1. Introduction

Previous investigations on thioketones [1] have revealed that singlet oxygen sensitized by the thioketones themselves plays a major role in their photo-oxidation. Three routes (Fig. 1) are available for the interaction of excited triplet thioketone, which is the reactive state in these oxidations, with ground state triplet oxygen. In order to estimate the contribution of paths (b) and (c) to this process the efficiency of singlet oxygen generation (path (a)) was determined. The efficiency of singlet oxygen production by aromatic compounds and ketones has been investigated by other researchers. For the aromatic compounds the $\pi\pi^{*1}$ and $\pi\pi^{*3}$ states sensitize triplet oxygen with a high efficiency [2], whereas for ketones the $n\pi^*$ triplet is the sensitizer and the efficiency is low [3]. It is of interest to compare the effi-
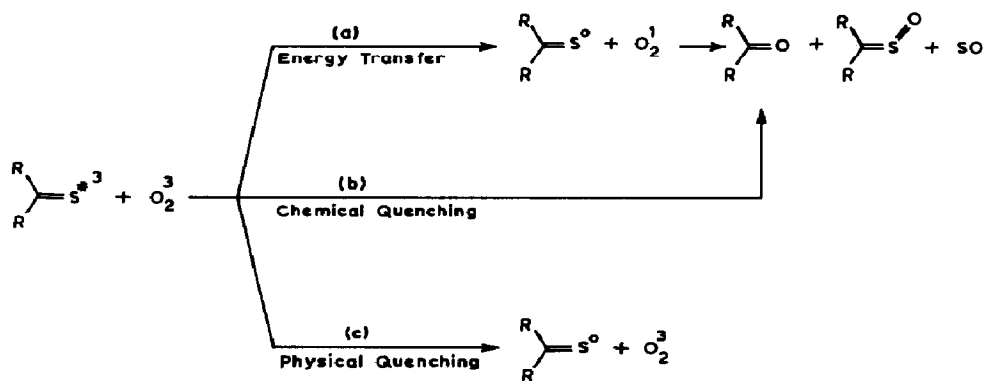

Fig. 1. Probable routes for the interaction of triplet thioketone with triplet oxygen.

ciency of singlet oxygen generation by thioketones, where the $n\pi^*$ triplet is the donor, with that of aromatic compounds and ketones. Singlet oxygen generation by dye sensitization is commonly employed; however, the insolubility of most dyes in non-polar solvents limits their use. Thioketones which exhibit absorption in the visible region and are soluble in most organic solvents appear attractive as practical sensitizers of singlet oxygen. Therefore the efficiency of singlet oxygen production was measured by following the bleaching of 1,3-diphenylisobenzofuran (DPBF) [4] and the results are discussed below.

2. Experimental details

DPBF (Aldrich Chemical Co.) was used as received. All the thioketones (Fig. 2) were synthesized and purified from the appropriate carbonyl compounds by procedures reported in the literature. Doubly distilled chloroform was used as the solvent for all the systems. A 250 W xenon arc lamp was used as the light source and the excitation wavelength was selected using a diffraction grating high radiance monochromator. The disappearance of DPBF and the thioketones was determined from their absorption spectra which were obtained using a UV–visible spectrophotometer. In a typical experiment a stock solution of DPBF was made in chloroform. Three different concentrations of the sensitizer were prepared from the stock solution. 3 ml aliquots of the sensitizer–DPBF solution were withdrawn and irradiated until about 15% of the DPBF was consumed. The amount of DPBF consumed was determined from the difference between the optical densities of the unirradiated and irradiated aliquots measured at 415 nm. The amount of thioketone degraded was determined from the optical density difference at 500 - 550 nm. The rubrene-sensitized photobleaching of DPBF (Φ = 0.91) [2] and Reinecke's salt [5] was used as an actinometer to calibrate the light intensity. The optical densities were recorded immediately after the experiment so as to minimize errors due to possible DPBF degradation or regeneration.
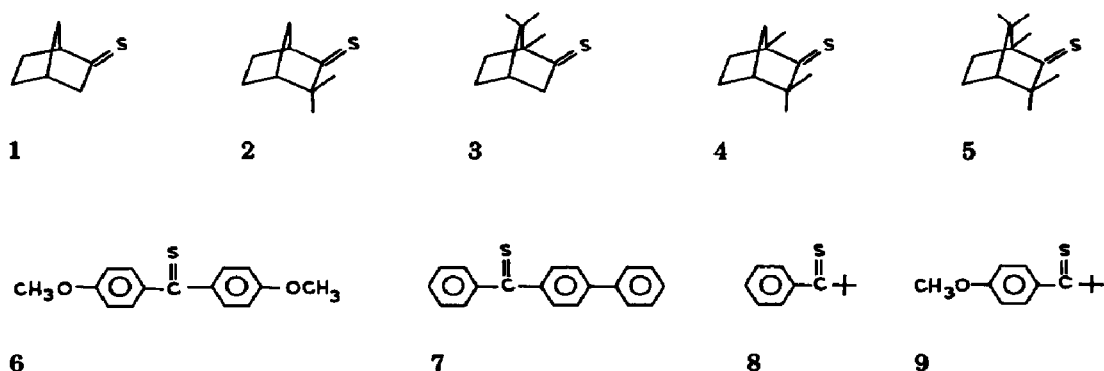

Fig. 2. Structures of the thioketones investigated.

Since the thioketones themselves react with singlet oxygen, the concentration of both thioketone and DPBF was chosen such that more than 99% of the singlet oxygen produced in the solution was captured by DPBF alone. This could be achieved as the rates of singlet oxygen quenching by thioketones had been determined earlier [6]. Table 1 gives the details of the experimental conditions.
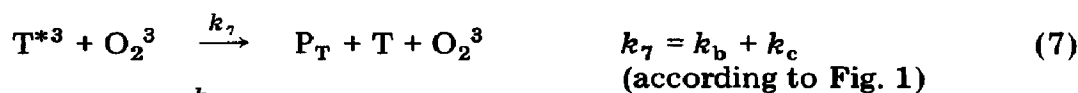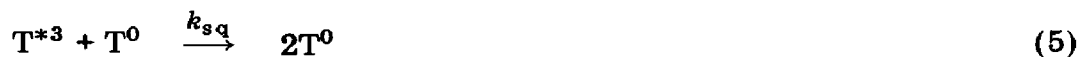
TABLE 1

Experimental conditions for the measurement of the quantum yield of oxidation of 1,3-diphenylisobenzofuran

Thioketone	$\lambda_{excitation}$ (± 10 nm)	$\lambda_{monitor}$ (nm)	Thioketone concentration (M)	DPBF concentration (M)
1 - 5	500	415; 500	0.04 - 0.08	0.005
6; 7	550	415; 550	0.01 - 0.02	0.007
8	550	415; 550	0.05 - 0.07	0.006
9	550	415; 550	0.01 - 0.03	0.006

3. Results

The simplest mechanistic scheme required to interpret the data is

$$T \xrightarrow{h\nu} T^{*1} \tag{1}$$

$$T^{*1} \xrightarrow{k_2} T^{*3} \qquad\qquad k_2 = k_{ISC} \tag{2}$$

$$T^{*1} \xrightarrow{k_3} T^0 \qquad\qquad k_3 = k_F + k_{IC} \tag{3}$$

$$T^{*3} \xrightarrow{k_4} T^0 \qquad\qquad k_4 = k_P + k_{ISC} \tag{4}$$

$$T^{*3} + T^0 \xrightarrow{k_{sq}} 2T^0 \tag{5}$$

$$T^{*3} + O_2{}^3 \xrightarrow{k_{ET}} T^0 + O_2{}^1 \tag{6}$$

$$T^{*3} + O_2{}^3 \xrightarrow{k_7} P_T + T + O_2{}^3 \qquad k_7 = k_b + k_c \tag{7}$$

(according to Fig. 1)

$$O_2{}^1 + T^0 \xrightarrow{k_q} P_T \tag{8}$$

$$O_2{}^1 + DPBF \xrightarrow{k_{ox}} P_D \tag{9}$$

$$O_2{}^1 \xrightarrow{k_{10}} O_2{}^3 \tag{10}$$

The energy difference between S_1 and T_1 $(n\pi^*)$ (about 5 - 10 kcal mol^{-1}) and the reported high intersystem crossing efficiency (about 1) [7] rule out the possiblity of energy transfer from the S_1 state of the thioketones to ground state oxygen. The quantum yield of singlet oxygen generation from the thioketone triplet is given by

$$\Phi_{O_2^1} = \frac{k_{ET}[O_2]}{k_{ET}[O_2] + k_7[O_2] + k_{sq}[T^0] + k_4} \tag{11}$$

and the quantum yield of the oxidation of DPBF is given by

$$\Phi_{ox} = \frac{k_{ox}[DPBF]}{k_{ox}[DPBF] + k_q[T^0] + k_{10}} \Phi_{O_2^1} \tag{12}$$

Under conditions where all the singlet oxygen produced is captured by DPBF, the quantum yield of oxidation reduces to the quantum yield of singlet oxygen production. A useful form of eqn. (11) is given by

$$\Phi_{ox}^{-1} = \Phi_{O_2^1}^{-1} = \frac{k_{ET}[O_2] + k_7[O_2] + k_4}{k_{ET}[O_2]} + \frac{k_{sq}[T^0]}{k_{ET}[O_2]} \tag{13}$$

A plot of Φ_{ox}^{-1} against the thioketone concentration should therefore be linear with a slope of $k_{sq}/k_{ET}[O_2]$, and the intercept will give the inverse of the limiting quantum yield in the absence of self-quenching (process (5)).

The quantum yields of the thioketone-sensitized photobleaching of DPBF were determined for three different concentrations of thioketone at a fixed DPBF concentration. The plots of Φ_{ox}^{-1} against the thioketone concentration were approximately linear as shown in Figs. 3 and 4. Table 2 gives the experimental data. Our results show that the degradation of thioketone as monitored by the optical density difference at 500 or 550 nm was negligible, *i.e.* the direct reaction of triplet oxygen with triplet thioketone
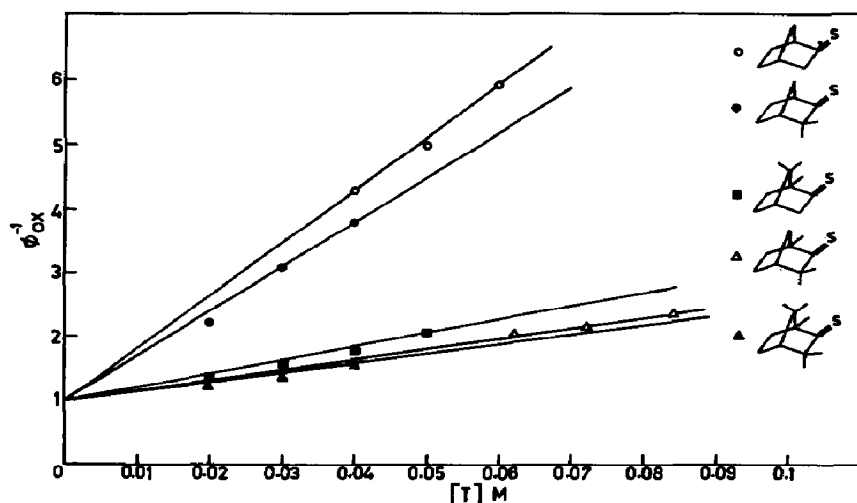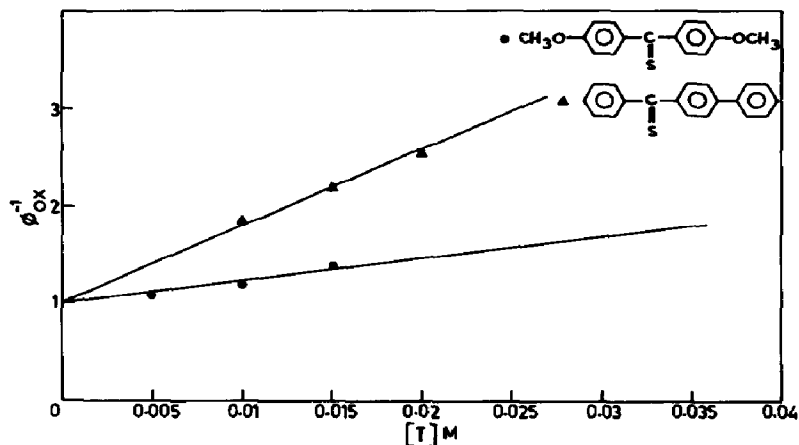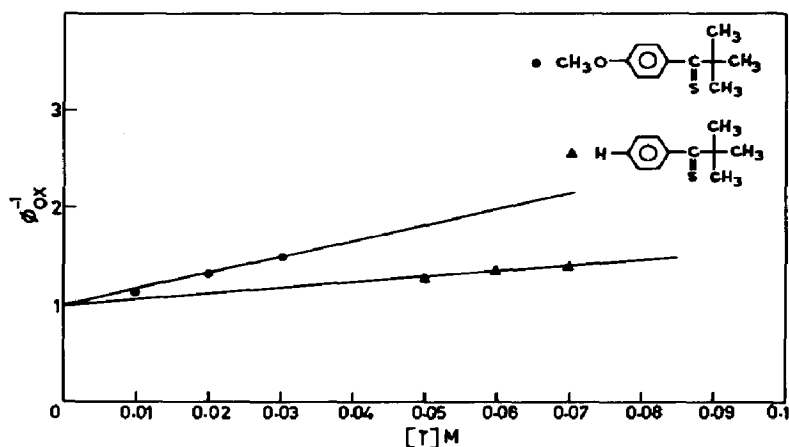

Fig. 3. Quantum yields of oxidation of DPBF by singlet oxygen sensitized by dialkyl thioketones. The data are plotted according to eqn. (13).

Fig. 4. Quantum yields of oxidation of DPBF by singlet oxygen sensitized by (a) diaryl thioketones and (b) arylalkyl thioketones. The data are plotted according to eqn. (13).

(Fig. 1, path (b)) contributed very little to the photo-oxidation process under our experimental conditions.

4. Discussion

The efficiencies of singlet oxygen generation are unity at zero thioketone concentration, as given by the intercepts in Figs. 3 and 4, and decrease with increasing thioketone concentration for all the thioketones investigated (Table 2). The rate of decrease is dependent on the ratio k_{sq}/k_{ET} of the rate of self-quenching to the rate of energy transfer. As is evident from the measured intercepts, the physical and chemical quenching of excited thioketone by oxygen and the decay of the triplet do not compete effectively with the energy transfer step which is expected to be at least 10%

TABLE 2

Quantum yields of singlet oxygen generation by thioketones

Thioketone	$\Phi_{O_2^1}$ [a] (±0.1)	$\Phi_{O_2^1}(0.01 \text{ M})$ [b] (±0.05)	k_q [c] (M^{-1} s^{-1} ± 10%)	k_{sq}/k_{ET} [d]
1	1.00	0.56	1.8×10^5	0.114
2	1.00	0.59	1.0×10^5	0.097
3	1.00	0.83	8.1×10^4	0.030
4	1.00	0.87	5.1×10^5	0.024
5	1.00	0.91	5.8×10^4	0.022
6	1.00	0.83	9.6×10^6	0.036
7	1.00	0.56	3.1×10^6	0.111
8	1.00	0.94	4.3×10^5	0.009
9	1.00	0.86	9.2×10^5	0.023

[a] The quantum yield of singlet oxygen production at zero thioketone concentration (Figs. 3 and 4).
[b] The quantum yield of singlet oxygen production at a thioketone concentration of 0.01 M (displayed for comparison).
[c] From ref. 6.
[d] Obtained from the slopes of Figs. 3 and 4.

of the diffusion-limited value[†]. Therefore, of the thioketones investigated, the only process that reduces the efficiency is self-quenching [9]. Examination of Table 2 reveals that k_{sq}/k_{ET} varies with the thioketones, suggesting that k_{sq} or k_{ET} or both are dependent on the nature of the thioketone, *i.e.* are governed by steric and electronic factors. Since earlier attempts to detect the influence of steric and electronic parameters on the rate of energy transfer were unsuccessful [10], we believe that the self-quenching rate probably varies with the nature of the thioketone. A drop in the self-quenching rate from northiocamphor (thioketone 1) to other members of the series (thioketones 2 - 5) may be the result of steric hindrance produced by methyl groups during the interaction between two thiocarbonyl chromophores. It would therefore be of interest to measure the absolute rates of energy transfer to oxygen[†] and the self-quenching for a series of related thioketones to gain insight into the mechanism of these processes.

The efficiency of singlet oxygen production by aromatic compounds and ketones has been investigated elsewhere [2, 3]. For aromatic compounds the $\pi\pi^{*1}$ and $\pi\pi^{*3}$ states are expected to sensitize oxygen production and hence in many cases the efficiency is greater than unity. In some of

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[†] An encounter complex between triplet oxygen and a triplet thioketone can have singlet, triplet or quintet multiplicity. The quintet encounter complex can only decay to the starting materials. The singlet complex can generate singlet oxygen, whereas in the absence of effective spin–orbit coupling the triplet complex can produce only the ground state thioketone and triplet oxygen. Hence the expected value of k_{ET} is 10% of the diffusion-limited value. However, thioketones are reported to have very high spin–orbit coupling parameters, and if this is reflected in the encounter complex k_{ET} may reach the diffusion-limited value [8].

the ketones investigated efficiencies of less than unity were reported (benzophenone, 0.4; 2-acetonaphthone, 0.5). For thioketones $n\pi^{*3}$ alone is expected to be the donor because of the high quantum yield of intersystem crossing [7]. It is interesting to note that $n\pi^{*3}$ thioketone is a better singlet oxygen producer than $n\pi^{*3}$ carbonyl. The inefficient production of singlet oxygen in the case of ketones has been attributed to the generation of ground state oxygen and ketone by intersystem crossing within the singlet encounter complex[†]. If this is the case, thioketones which are reported to possess high spin–orbit coupling should favour the above process and thus be poor singlet oxygen producers, which is contrary to the observed results. Therefore much more experimental work is needed to understand the mechanism of singlet oxygen production by $n\pi^*$ and $\pi\pi^*$ triplets.

5. Conclusion

We have shown that thioketones which have a high efficiency of singlet oxygen production, absorb in the visible region and are soluble in non-polar solvents can be used as singlet oxygen sensitizers. However, their use is limited by their reactivity with singlet oxygen.

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[†]See footnote on p. 298.