PHOTOSENSITIZED CHEMILUMINESCENT DESULFURIZATION OF ARENETHIONES

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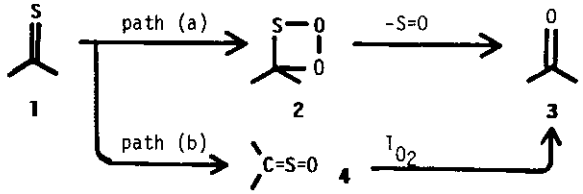
Photosensitized oxygenation of N-methylacridanethione (**1a**), xanthione (**1b**), and thioxanthione (**1c**) gave the corresponding ketones (**3**) quantitatively and weak chemiluminescence.

Since the first report on photooxidation of thiobenzophenones and 4-thiopyrones in sunlight by Schönberg and Mostafa,[1] several reports on photodesulfurization of C=S compounds (1) appeared:[2-9] Sensitized photooxygenation of 4H-pyran-4-thiones and 4H-thiopyran-4-thiones by Ishibe et al.,[3] of tetramethyl-1-cyclobutane-3-thione and dibenzylthioketone by Worman et al.,[4] and of xanthione, fluorenethione, and alicyclic thioketones by Ramamurthy et al.[5] The reactions were supposed to undergo through the corresponding thia-1,2-dioxetane intermediates (**2**). Photooxygenation of sulfines (**4**)[2] and O-alkyl thioesters[6] were also claimed to proceed through similar intermediates (path a).

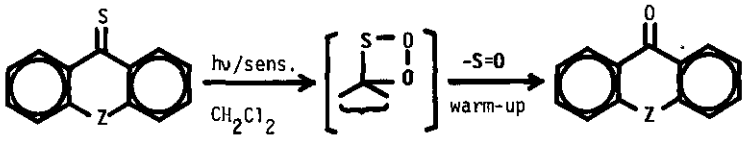
Tamagaki et al. found photooxidation of di-t-butyl thioketone[7] and 1,2-benzothiole-3-thione[8] to give the corresponding sulfines (4) and ketones (3) and hence, proposed an alternative sulfine mechanism (path b) for the oxidation.



Theoretical calculation of molecular orbitals suggests that the oxidation proceeds stepwisely through the thiadioxetane (**2**) and its successive decomposition to **3** and S=O.[9] Energy liberated on the decomposition of **2** was calculated as ca. 92.1 kcal/mol,[10,11] which is large enough for exciting 3 produced or the added fluorescers to the S_1 excited states [67.3,[12] 68.8,[13] 67.2,[14] for **3a**, **3b**, and **3c** and 66.0,[14] 64.9,[14] and 50.2 kcal/mol[14] for 9,10-diphenylanthracene (DPA), 9,10-dibromoanthracene (DBA), and rubrene, respectively].

In order to find out such chemiluminescent intermediates (**2**) and to clarify the oxygenation mechanism, i.e., the thia-1,2-dioxetane or the sulfine mechanism, we investigated sensitized photooxygenation of aromatic thioketones, **1a**, **1b**, and **1c**, which would give fluorescent ketones, **3a-c**,

respectively. In the present paper we describe photosensitized oxygenation of N-methylacridanethione (**1a**),[15] xanthione (**1b**),[16] and thioxanthione (**1c**)[17] to give the corresponding ketones (**3a-c**) in quantitative yields with 3 ∿ 10 min-irradiation.



1a-c **2** **3a-c**

a: Z = N-Me; **b**: Z = O; **c**: Z = S

Each solution of the thiones (**1a-c**)(ca. 10 mM) and methylene blue (MB)(ca. 1 mM) in CH_2Cl_2 was irradiated under flushing O_2 gas at -78°C for 60 min with a projector lamp (Sylvania tungsten-halogen lamp: ELH 120V/300W at 100V) through an optical glass filter (< 510 nm cut off) and a pyrex/water filter in a pyrex or quartz cell (ϕ 10 mm). Aliquots taken during irradiation were analysed by glc after standing at room temperature for 30 min. The results are shown in Table 1. These data show that the present reactions yield the corresponding ketones (**3a-c**) predominantly in quantitative yields[18] in a short time-irradiation (less than 10 min). According to Zwanenburg et al.,[2] photooxygenation of aromatic sulfines need fairly long time-irradiation (2.5 - 6 h/400W/10 mM), and hence, we speculate that the present photooxygenation proceeds through path (a) predominantly in spite of Tamagaki's report.[8]

Table 1. Photooxygenation of the Thiones (**1a-c**)

1	Concn. (mM)	MB (mM)	Irrad. Time (min)	Product Yield (**3**)[a] (%)
1a	10.1	1.0	3	85
1b	11.4	1.1	10	100
1c	10.9	1.2	5	100

a) Yields based on the starting materials used.

Efforts were made for detection of the expected chemiluminescence at the simultaneous decomposition of the thia-1,2-dioxetane (**2**), when warming-up the intact irradiated solution (10^{-2}-10^{-4} M), or the solutions added into some fluorescers (rubrene, DPA, and DBA at 10^{-2}-10^{-5}M)[19] to room temp. Weak chemiluminescence (ca. 10^{-8} einstein/mol) was detected, when DBA or DPA was added to the cold irradiated solutions. So weak it was, the emission spectra could not be measured. These were the first examples of the detection of the chemiluminescence, though weak they were, for the supposed thia-1,2-dioxetane.[20]

The detection of chemiluminescence supports the dioxetane mechanism (path a) for the oxygenation of the thiones. The weakness of the emission could be explained that most **2** once produced may decompose photochemically during irradiation, as known for the ordinary 1,2-dioxetanes.[21]

Influence of $^1O_2$-quenchers (DABCO[22] and β-carotene[22]) and a radical scavenger (2,4,6-tri-t-butylphenol)[22] (see Table 2) suggests that the oxygenation undergoes with singlet oxygen non-radically.

Table 2. Effect of Inhibitors on Photooxygenation of the Thiones (**1a-c**).

Inhibitor (In)	[In]/[**1**]	**1a**	**1b**	**1c**
DABCO	25	Q[a]	Q	Q
β-Carotene	5	Q	Q	--
2,4,6-tri-t-butylphenol	25	--	N[b]	N

a) Q: quenched. b) N: not effected.

Acknowledgement. We thank Professor T. Goto, Nagoya University for the measurements of MS and CL and the Ministry of Education, Science, and Culture of Japan for the financial support (Grant-in-Aid).

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10. Heat of decomposition (ΔH) of **2** to a C=O and a S=O compounds was calculated as follows[11] assuming that the ring strain of **2** is not much different from that of ordinary 1,2-dioxetanes (26 kcal/mol)[25]; C-C-O-O ⟶ C=O + C=O; C-S-O-O ⟶ C=O + S=O: a) 1 C-C ∿∿ 1 C-S (ΔHa), b) 1 C-O ∿∿ 1 S-O (ΔHb), c) 1 C=O ∿∿ 1 S=O (ΔHc), where ΔHa = 82.6[23] - 65[23] = +17.6; ΔHb = 85.5[23] - 83[24] = +2.5; and ΔHc = 179[22] - 151[24] = +28: therefore, ΔH' = -(ΔHa + ΔHb) + ΔHc = +7.9 (kcal/mol); and ΔH + ΔH (dioxetane)[25] - ΔH' = -(ca. 100 - 7.9) = ca. -92.1 (kcal/mol).
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14. Calculated from λ_{max} of the fluorescence spectra measured in CH_2Cl_2 at room temp. (19°C).

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18. No other organic products than **3** were detected by tlc and glc.

19. The photooxygenated solution (diluted to ca. 10^{-4} M) in a pyrex vial was put in front of photomultiplier tube (Hamamatsu R-105UH) and the integrated light intensity vs time was recorded while the temp. of the solution rose to r. t. (20°C).

Table 3. Relative Quantum Yields of Chemiluminescence

1[a]	Φ_{CL} (rel.) without FL	DBA[b]	DPA[b]	Rubrene[b]
1a	5	17	8	---
1b	8	25	5	17
1c	100	150	100	100

a) $10^{-2} \sim 10^{-4}$ M. b) $10^{-2} \sim 10^{-4}$ M.

20. For the other hetero 1,2-dioxetanes, see ref. 11.

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Received, 25th March, 1981