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Photosensitized Desulfurization of Heterocyclic Thioketones and Its Accompanied Chemiluminescence[1)]

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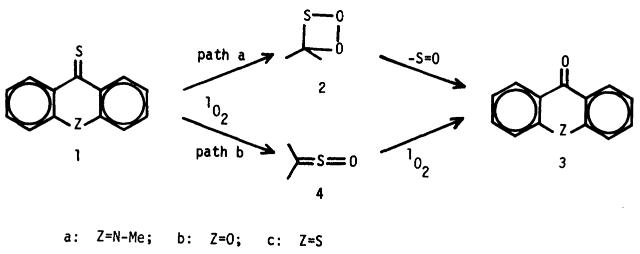
Synopsis. Photosensitized oxygenation of 10-methyl-9(10*H*)-acridinethione, 9*H*-xanthene-9-thione, and 9*H*-thioxanthene-9-thione at −78 °C gave the corresponding ketones, 10-methyl-9(10*H*)-acridinone, 9*H*-xanthen-9-one, and 9*H*-thioxanthen-9-one quantitatively in a 3—10 min-irradiation. Weak chemiluminescence was observed from the irradiated solution upon warming-up.

For photooxygenation of thiocarbonyl compounds, two alternative mechanisms have been proposed, *i.e.*, the 1,2,3-dioxathietane[2—6)] (path a) and the sulfine mechanisms[7—8)] (path b). Chemiluminescence (CL) has been expected to be accompanied with the decomposition of 1,2,3-dioxathietane (**2**)[9)] which is generated on sensitized photooxygenation of C=S compounds. The intermediate (**2**) is supposed to have a large energy enough for exciting the produced ketone (**3**) or added fluorescers to their S_1 excited states.[10)]

Since the first report by Schönberg and Mostafa,[2)] on photooxidation of thiobenzophenones and 4*H*-thiopyran-4-ones in sunlight, a number of reports on photooxidative desulfurization of C=S compounds (**1**) appeared:[2—8,11)] Sensitized photooxygenation of 4*H*-pyran-4-thiones and 4*H*-thiopyran-4-thiones by Ishibe *et al.*;[3)] of 2,2,4,4-tetramethyl-3-thioxo-1-cyclobutanone and dibenzyl thioketone by Worman *et al.*;[4)] of 9*H*-xanthene-9-thione, 9*H*-fluorene-9-thione, and alicyclic thioketones by Ramamurthy *et al.*[5)] Through the corresponding 1,2,3-dioxathietane intermediates (**2**) the reactions were supposed to proceed. Photooxygenation of sulfines (**4**)[11)] and O-alkyl thiocarboxylates[6)] was also claimed to proceed through the similar intermediates (path a).

Photooxygenation of di-*t*-butyl thioketone[7)] and 1,2-benzodithiole-3-thione[8)] was found by Tamagaki *et al.* to give the corresponding sulfines (**4**) and ketones (**3**), and hence, an alternative sulfine mechanism (path b) was proposed for the oxidation. On the other hand, Tamagaki *et al.* also reported that di-*t*-butyl sulfine was inert to singlet oxygen.[7)] Theoretical calculation of molecular orbitals suggests that the oxidation of thioketones proceeds stepwisely through the 1,2,3-dioxathietane (**2**) and its successive, radical decomposition to the ketone (**3**) and S=O.[9)] Energy liberated on the decomposition of **2** was calculated as *ca.* 92.1 kcal/mol[1,10)] which is large enough for exciting the ketones (**3**) produced or the added fluorescers to their S_1 excited state [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, resp.].

For finding out such chemiluminescent intermediates (**2**) and for clarification of the oxygenation mechanism, namely, the 1,2,3-dioxathietane or the sulfine mechanism, investigation was carried out for the sensitized photooxygenation of aromatic thioketones, **1a**, **1b**, and **1c**, which would give fluorescent ketones, **3a**, **3b**, and **3c** resp. In the present paper, photosensitized oxygenation of 10-methyl-9(10*H*)-acridinethione (**1a**),[15)] 9*H*-xanthene-9-thione (**1b**),[16)] and 9*H*-thioxanthene-9-thione (**1c**)[17)] is described to give the corresponding ketones (**3a**—**c**) in quantitative yields with 3—10 min-irradiation.



Scheme 1.

Each solution of the heterocyclic thioketones (**1a**—**c**) with Methylene Blue as a sensitizer in CH_2Cl_2 was irradiated under flushing O_2 gas at −78 °C for 60 min with a tungsten-halogen lamp through an optical glass filter (<510 nm cut off) cooling with a Pyrex/water filter in a Pyrex or quartz cell. Samples taken during irradiation were analysed by GLC after standing at room temperature for 30 min. The results are shown in Table 1. These results show that the present oxygenation reactions yield the corresponding ketones (**3a**—**c**) in quantitative yields[18)] in a short time-irradiation. According to Zwanenburg *et al.*,[11)] photooxygenation of aromatic sulfine compounds needs fairly long time-irradiation (2.5—6 h/5—20 mM), and hence, we speculate in spite of Tamagaki's report[8)] that the present photooxygenation proceed predominantly through path a.

For detection of the expected chemiluminescence at the spontaneous decomposition of the 1,2,3-dioxathietane (**2**), efforts were made, when the intact irradiated solution (10^{-2}—10^{-4} M) or the solutions added into several fluorescers (rubrene, DPA, and DBA at 10^{-2}—10^{-4} M) were warmed up to room temperature. Weak chemiluminescence (*ca.* 10^{-8} einstein/mol) was detected (Table 2). Since it was so weak, the emission spectra could not be measured. Although they were very weak, these were the first examples of the detection of the chemiluminescence for the supposed 1,2,3-dioxathietane. The weakness of the light emitted may result from further photochemical decomposition of **2** once produced during irradiation.[19)]

TABLE 1. PHOTOOXYGENATION OF THIOKETONES (**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.

Table 2. Relative quantum yields of chemiluminescence of **1**

Additive [A]	[A]/[**1**]	Φ_{CL}(rel)		
		1a[a)]	**1b**[a)]	**1c**[a)]
none	—	5	8	100
DBA[b)]	1—10	17	25	17
DPA[b)]	1—10	8	5	100
Rubrene	1—10	—	17	100

a) 10^{-2}—10^{-4} M. b) DBA: 9,10-Dibromoanthracene; DPA: 9,10-diphenylanthracene.

Table 3. Effect of inhibitors on photooxygenation of **1**

Inhibitors [I]	[I]/[**1**]	Φ_{CL}(rel)		
		1a[a)]	**1b**[a)]	**1c**[a)]
DABCO[b)]	25	Q[c)]	Q	Q
β-Carotene	5	Q	Q	—
TBP[b)]	25	—	N[d)]	N

a) 10^{-2}—10^{-4} M. b) DABCO: 1,4-diazabicyclo[2.2.2]octane; TBP: 2,4,6-tri-*t*-butylphenol. c) Q: Quenched. d) N: No effect.

Influence of $^1O_2$-quenchers (DABCO[20)] and β-carotene[20)]) and a radical scavenger (2,4,6-tri-*t*-butylphenol)[20)] on the oxygenation (see Table 3) suggests that the reactions proceed with $^1O_2$ non-radically.

Experimental

The thioketones (**1a**—**c**) were prepared by the reaction of the corresponding ketones (**3a**—**c**) (Nakarai Chem. Co.) with P_2S_5 according to the usual procedure: *10-Methyl-9(10*H*)-acridinethione* (**1a**), mp 268—273 °C (lit,[15)] mp >260 °C); ν_{max} (KBr) 1580, 1500, 1220, 1180, 1000, and 740 cm^{-1}; δ_{ppm} (DMSO-d_6) 3.96 (s, 3H), 7.28 (m, 3H), 7.78 (m, 3H), and 8.88 (m, 2H); *m/z* 225 (M$^+$); *9*H*-xanthene-8-thione* (**1b**), mp 156—158 °C (lit,[16)] mp 155—156 °C); ν_{max} (KBr) 1590, 1450, 1320, 1100, 770, and 740 cm^{-1}; *m/z* 212 (M$^+$); *9*H*-thioxanthene-9-thione* (**1c**), mp 193—205 °C (decomp) (lit,[17)] mp 180—215 °C); ν_{max} (KBr) 1590, 1450, 1320, 1060, 740 cm^{-1}; *m/z* 228 (M$^+$).

Photosensitized Oxygenation. Each solution of the thioketones (**1a**—**c**) (*ca.* 10 mM) with Methylene Blue (*ca.* 1 mM: Nakarai Chem. Co.) in CH_2Cl_2 (distilled from CaH_2 before use) was irradiated under O_2 atmosphere at −78 °C for 60 min with a projector lamp (Silvania/Kondo tungsten-halogen lamp ELH 120 V/300 W at 100 V) through an optical glass filter (Toshiba Y-52, <510 nm cut off) and a Pyrex/water filter in a Pyrex or quartz cell (ϕ 10 mm). Aliquots were taken during irradiation and analysed by glc and tlc after standing at room temperature for 30 min. The conditions of GLC used were as follows: For **1a** and **3a**: Yanagimoto Yanaco G-80F with FID, 10% Silicone GE-SE-30 on Diasolid L (60—80 mesh) in a stainless steel column, 0.93 m × ϕ 4 mm, col. temp 250 °C, inj. temp 280 °C, carrier gas (N_2), 75.0 ml/min, internal standard, 9*H*-xanthene-9-thione. For **1b** and **3b**: Yanagimoto Yanaco G-1800F with FID, the same column as above; col. temp 250 °C, inj. temp 264 °C, carrier gas (N_2), 42.9 ml/min, internal standard, 9-benzylidene-9*H*-xanthene. For **1c** and **3c**: G-1800F, the same column as above, col. temp 250 °C, inj. temp 275 °C, carrier gas (N_2), 54.5 ml/min, internal standard, 9*H*-xanthen-9-one. The results are shown in Table 1.

Observation of the Chemiluminescence. Each irradiated cold solution as above (**1** : 10^{-2}—10^{-4} M) was poured into a quartz fluorescence cubette (1 cm) placed in front of photomultiplier tube (Hamamatsu R-105UH) and the integrated light intensity *vs.* time was recorded while the temperature of the solution rose to room temp (20 °C). The same cubette containing a fluorescer (DBA, DPA, or rubrene, 10^{-2}—10^{-4} M) was also used for the measurement. Quartz tubes were also applied for the irradiation instead of Pyrex cells in order to detect emission directly through it at ultraviolet range, with being warmed-up gradually from −78 °C. (See Table 2). The amounts of light emission are relative to CL of luminol in an aqueous solution.[24)]

References

1) Preliminary Commun.: N. Suzuki, K. Sano, N. Tani, and Y. Izawa, *Heterocycles*, **16**, 1133 (1981).

2) A. Schönberg and A. Mostafa, *J. Chem. Soc.*, **1943**, 275.

3) N. Ishibe, M. Odani, and M. Sunami, *J. Chem. Soc., Chem. Commun.*, **1971**, 118.

4) J. J. Worman, M. Shen, and P. C. Nichols, *Can. J. Chem.*, **50**, 3923 (1972).

5) R. Rajee and V. Ramamurthy, *Tetrahedron Lett.*, **1978**, 5127.

6) J. E. Gano and S. Atik, *Tetrahedron Lett.*, **1979**, 4635.

7) S. Tamagaki, R. Akatsuka, M. Nakamura, and S. Kozuka, *Tetrahedron Lett.*, **1979**, 3665.

8) S. Tamagaki and K. Hotta, *J. Chem. Soc., Chem. Commun.*, **1980**, 598.

9) L. Carlsen, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 188.

10) Heat of decomposition (ΔH) of **2** to a C=O and a S=O compounds was calculated as follows[1)] assuming that the ring strain of **2** is not much different from that of ordinary 1,2-dioxetanes (26 kcal/mol);[23)] $\mathrm{\overline{C{-}C{-}O{-}O}} \rightarrow \mathrm{C{=}O + C{=}O}$; $\mathrm{\overline{C{-}S{-}O{-}O}} \rightarrow \mathrm{C{=}O + S{=}O}$: a) 1 C–C$\rightsquigarrow$1 C–S ($\Delta H$a), b) 1 C–O$\rightsquigarrow$1 S–O ($\Delta H$b), c) 1 C=O$\rightsquigarrow$1 S=O ($\Delta H$c), where $\Delta H\mathrm{a}=82.6^{21)}-65^{21)}=+17.6$; $\Delta H\mathrm{b}=85.5^{21)}-83^{22)}=+2.5$; and $\Delta H\mathrm{c}=179^{21)}-151^{22)}=+28$: therefore, $\Delta H'=-(\Delta H\mathrm{a}+\Delta H\mathrm{b})+\Delta H\mathrm{c}=+7.9$ (kcal/mol); and $\Delta H=\Delta H$ (dioxetane)[23)] $-\Delta H'=-$(*ca.* 100—7.9)=*ca.* −92.1 (kcal/mol).

11) B. Zwanenburg, A. Wagenaar, and J. Strating, *Tetrahedron Lett.*, **1970**, 4683.

12) E. H. White, N. Suzuki, and W. H. Hendrickson, *Chem. Lett.*, **1979**, 1491.

13) S. L. Murov, "Handbook of Photochemistry," Dekker, New York, N. Y. (1973).

14) Calculated from λ_{max} of the fluorescence spectra measured in CH_2Cl_2 at room temp. (19 °C).

15) J. Jaeken, M. A. de Ramaix, Ger. Patent, 1146751, Apr. 4 (1963); *Chem. Abstr.*, **59**, 15422 (1963).

16) E. G. Davis and S. Smiles, *J. Chem. Soc.*, **1910**, 1296.

17) A. Schönberg and M. M. Sidky, *J. Am. Chem. Soc.*, **81**, 2259 (1959); R. Meyer, *Chem. Ber.*, **33**, 2570 (1900).

18) No other organic products than **3** were detected by TLC and GLC.

19) *Photolyses of 1,2-dioxetanes*: P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223 (1970); T. Wilson and A. P. Schaap, *ibid.*, **93**, 4126 (1971); N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnaham, and T. J. Katz, *ibid.*, **95**, 2035 (1973); N. J. Turro, H.-C. Steinmetzer, and A. Yekta, *ibid.*, **95**, 6468 (1973). Prolonged irradiation of the ordinary 1,2-dioxetanes resulted in the similar decomposition even by the light of >510 nm (See also Ref. 12). This might be caused by the reabsorption of the CL as suggested by one of the referees.

20) M. E. Landis and D. C. Madoux, *J. Am. Chem. Soc.*, **101**, 5106 (1979).

21) J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," Benjamin, New York, N. Y. (1964).

22) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y. (1966), p. 824.

23) L. J. Bollyky, *J. Am. Chem. Soc.*, **92**, 3230 (1970); P. Lechtken and G. Höhne, *Angew. Chem., Int. Ed. Engl.*, **12**, 772 (1973); T. Wilson, D. E. Golan, M. S. Harris, and A. L. Baumstark, *J. Am. Chem. Soc.*, **98**, 1086 (1976); W. Adam, *Adv. Heterocycl. Chem.*, **21**, 437 (1977).

24) J. Lee and H. H. Seliger, *Photochem. Photobiol.*, **4**, 1015 (1965); **15**, 227 (1972).