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The Dye-sensitized Photooxygenation of Hexamethyleneammonium Hexamethylenedithiocarbamate by Xanthene Dyes

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The photoelimination of hexamethyleneammonium hexamethylenedithiocarbamate (HMTC)[1] can be sensitized by xanthene dyes, such as rose bengal and eosine yellowish. In contrast to the direct photolysis results, the presence of HMTC in the dye-sensitized decomposition produces no carbon disulfide and consumes oxygen during the irradiation. The quantum yield of photoelimination in an aerated ethanol solution was measured. The quantum yield was almost unchanged on the variation of the xanthene dye concentration from 10^{-5} to 10^{-6}M. This is different from the former observation[2] that there was an apparent tendency for the quantum yield to decrease monotonously with an increase in the thiazine dye concentration. The singlet oxygen mechanism, in which the photochemical reaction is initiated by the interaction between the triplet dye and the ground-state oxygen molecules, has been inferred for the dye-sensitized photoelimination of HMTC. It has been explained in terms of the effect of 1,4-diazabicyclo [2.2.2] octane, β-carotene, and tetramethylethylene in reducing the quantum yield. The photooxygenation of HMTC by dyes seemed to be caused by attack of the singlet oxygen on the thiocarboxylion group, which has a rate constant of 10^8M^{-1}sec^{-1} in ethanol.

In the previous papers of this series,[2,3] the direct and thiazine-dye-sensitized chemistry of hexamethyleneammonium hexamethylenedithiocarbamate (HMTC) has been studied. In contrast to the direct photolysis results, the presence of HMTC in the dye-sensitized decomposition produces no carbon disulfide. It seems that the sensitization by thiazine dye takes place by means of the interaction of the triplet state of the sensitizing dye with dissolved oxygen. In this paper we will try to ascertain the role of oxygen in the dye-sensitized photoelimination of HMTC using xanthene dyes, further, we will describe how the dye-sensitization is not observed for nonionic dithiocarbamates, while it is observed for ionic dithiocarbamates such as HMTC.

Experimental

The HMTC was prepared by a method described previously,[2] Methyl dimethyldithiocarbamate[4] was obtained from Dr. Takeshi Nakai. The compound melted at 45°C and was used without further purification. The butyl ester of hexamethylenedithiocarbamic acid and 2,4-dinitrophenyl hexamethylenedithiocarbamate were prepared using the following general procedure.[5] 8 g of sodium hydroxide were dissolved in 80 m*l* of water, and the mixture was cooled to 5°C. 20 g of hexamethyleneimine and 15 g of carbon disulfide in small portions were stirred in well alternately. The sodium salt hexamethylene dithiocarbamic acid began to crystallize from the solution and was recovered as a white solid by the evaporation of the water and by drying at 110°C. 8.8 g of sodium hexamethylenedithiocarbamate were treated with 3.8 g of *n*-butyl chloride in 60 m*l* of ethanol, and then the mixture was kept at 50°C for 30 min. The sodium chloride thus precipitated was filtered off and the filtrate treated with water. The *n*-butyl ester of hexamethylenedithiocarbamic acid separated as a straw-colored liquid and was used without further purification. 44 g of sodium hexamethylenedithiocarbamate were treated with 40 g of 2,4-dinitrochlorobenzene in 300 m*l* of ethanol, and the solution was heated for 30 minutes at 50°C. The reaction mass was treated with water to dissolve the sodium chloride. The residue was crystallized from ethanol to form bright yellow needles of 2,4-dinitrophenyl hexamethylenedithiocarbamate which melted at 107.5°C.

The acetophenone, benzophenone, Michler's ketone, β-acetonaphthone, and naphthalene were purified by the methods described previously.[6]

The solvents and other reagents were of a GR grade (Tokyo Kasei Corp.), and they were used without further purification. The experimental procedure used in this study was almost the same as that described previously.[2] Degassing was carried out in the usual freeze-pump-thaw cycle at 10^{-5} mmHg. A 1-kW incandescent lamp was used as a source of actinic light for the dye-sensitization. Green light was isolated by means of an interference filter (KL-54) with a maximum in transmission at 546 nm and a transmitting glass filter which cut off light shorter than 520 nm. In most of the experiments, a heat-absorbing filter (HR 1-69) was also employed. The light intensities were measured by means of a Reinecke's salt actinometer. The concentration of oxygen in the ethanol solution was continuously measured using a dissolved-oxygen meter (Kyusuikagaku Kenkyusho D. O. Meter-TP) with a Galvanic electrode, and the output was recorded on a recorder with a 10-mV deflection. Overall, we estimate our absolute error to be within ±10%. For measuring the oxygen concentration, a glass reaction cell was used; it consisted of a cylinder 5 cm in diameter, with a total volume of 80 m*l*, and equipped with a stirrer.

Results

Participation of Oxygen. As was expected, the presence of oxygen was essential to the sensitization by xanthene dyes as well as to that by thiazine dyes,[2] as is shown in Table 1.

Dye Concentration Effects on Quantum Yields. Aerated ethanol solutions containing about 10^{-5}M xanthene

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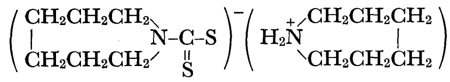
[1]


[2] T. Yamase, H. Kokado, and E. Inoue, This Bulletin, **43**, 669 (1970).

[3] T. Yamase, H. Kokado, and E. Inoue, *ibid.*, **43**, 934 (1970).

[4]


$(CH_3)_2N\text{-}\overset{\overset{\textstyle S}{\|}}{C}\text{-}S\text{-}CH_3$

[5] Ira Williams, U.S. 2187719 (1940).

[6] T. Yamase. H. Kokado, and E. Inoue, *Kogyo Kagaku Zasshi*, **72**, 162 (1969).

TABLE 1. EFFECT OF OXYGEN

Dye	$[\mathrm{HMTC}]_{\mathrm{ini}} \times 10^4$, M	$\eta^{a)}$	$\eta^{b)}$
Rose bengal	3.31	0.357	0
Erythrosine	3.30	0.251	0
Phloxine	2.86	0.142	0
Thionine[2]	5.33	0.251	0
Methylene blue[2]	5.57	0.227	0

a) Atmospheric condition.
b) Deaerated condition.

dyes and 10^{-4}M HMTC were irradiated at 546 nm. The quantum yield for HMTC elimination was then determined by colorimetric analysis using copper acetate.[7] The quantum yields obtained for different dye concentrations are tabulated in Table 2. The quantum yield was unchanged within the range of experimental uncertainty as long as all the factors were held constant. This forms a striking contrast with the case of the sensitization by thiazine dyes, where the reciprocal of the quantum yield changed linearly with the dye concentration.[2]

TABLE 2. DYE CONCENTRATION EFFECTS ON QUATUM YIELDS

Dye	$[\mathrm{HMTC}]_{\mathrm{ini}}$, M	[Dye], M	Quantum yield (η)
Erythrosine	3.7×10^{-4}	5.2×10^{-6}	0.222
		2.1×10^{-5}	0.226
		3.6×10^{-5}	0.228
		5.2×10^{-5}	0.263
Rose bengal	3.5×10^{-4}	9.2×10^{-6}	0.378
		3.7×10^{-5}	0.320
		5.5×10^{-5}	0.348
		7.4×10^{-5}	0.352
		9.2×10^{-5}	0.360

Effect of HMTC Concentration. Aerated ethanol solutions containing 10^{-5}—10^{-6}M xanthene dyes and various concentrations of HMTC were irradiated at 546 nm. The results are depicted in Fig. 1. As is represented there, a linear relation between the reciprocal of the quantum yield and that of the HMTC concentration holds for all of the dyes investigated. Apparently the efficiency of sensitization increased in the following order: eosine yellowish<phloxine<erythrosine<rose bengal. This order was the same as that of the dye-sensitized photolysis of 4-methoxy-α-naphthol[8] or sodium *N,N*-dimethyldithiocarbamate,[7] which have previously been reported by us.

Effect of the Reducing Agent, Allylthiourea. To examine if the dye-sensitized reaction is initiated by the semiquinone form of dye, allylthiourea was added as a reducing agent and the quantum yield was measured. Aerated ethanol solutions containing 9.2×10^{-6}M of rose bengal, 3.7×10^{-4}M of HMTC, and various concentrations of allylthiourea as a reducing agent were irradiated at 546 nm. Figure 2 shows the Stern-Volmer plots thus obtained. The value of the slope is of the order of 10^3M^{-1}, while it was of the order of 10M^{-1} in the case of thiazine dye. Allylthiourea did not increase, but decreased the efficiency of the sensitization. The present investigation suggests that a reducing agent is not necessary for dye-sensitization. It may be inferred that the sensitization does not take place *via* the semiquinone radical.

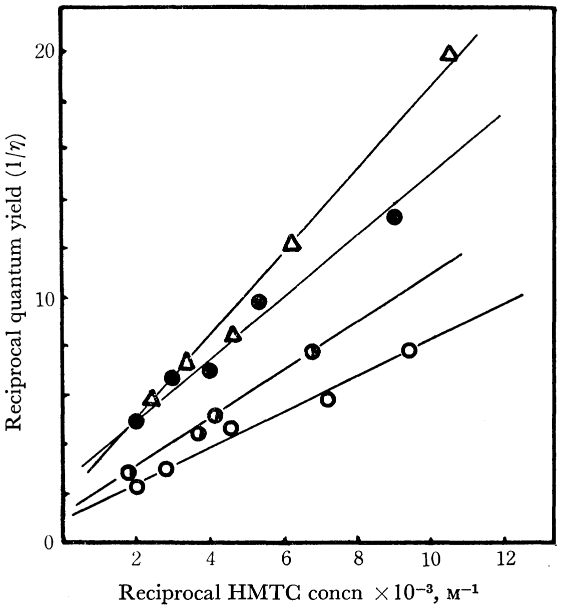


Fig. 1. Dependence of the quantum yield on the HMTC concentration.

	Rose bengal (○),	Erythrosine (◐)	Phloxine (●),	Eosine yellowish (△)
Dye concn	9.2×10^{-6}M	5.2×10^{-6}M	9.2×10^{-6}M	1.8×10^{-5}M
(Slope)$^{-1}$	1.33×10^3	9.8×10^2	8.3×10^2	6.2×10^2

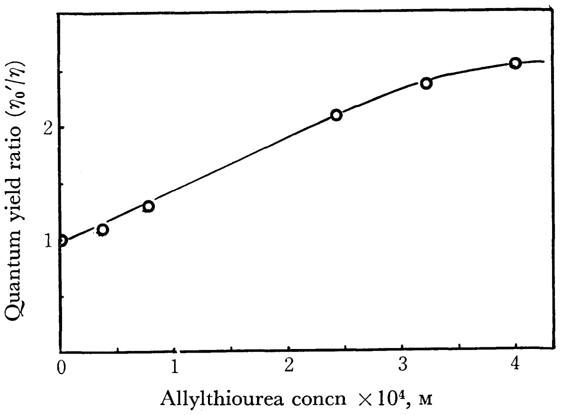


Fig. 2. Effect of allylthiourea on the quantum yield. η and η_0' indicate the quantum yields for the system with and without allylthiourea, respectively.
$[\mathrm{HMTC}]_{\mathrm{ini}} = 3.7 \times 10^{-4}$M; [Rose bengal] $= 9.2 \times 10^{-6}$M

Effects of Singlet Oxygen Quencher and Trap. The fact that HMTC did not affect the fluorescence of the xanthene dye ruled out the excited-dye singlet as the sensitizing species under our conditions. From the essentiality of oxygen and the decreasing effect of allylthiourea on the quantum yield, the dye-sensitized photoelimination of HMTC may proceed by means of the singlet oxygen ($^1\mathrm{O}_2$) formed by energy transfer from the triplet sensitizer, as was discussed in a previous paper.[2] It therefore seems interesting to find out if an actual decrease in quantum yield is observed by adding

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7) T. Yamase, H. Kokado, and E. Inoue, *ibid.*, **71**, 1587 (1968).

8) E. Inoue, H. Kokado, and T. Yamase, *ibid.*, **70**, 2337 (1967).

a $^1O_2$ quencher, such as 1,4-diazabicyclo[2.2.2.]octane (DABCO),[9] or efficient $^1O_2$ traps, such as tetramethylethylene (TME)[10] and β-carotene.[11] Aerated solutions containing 9.2×10^{-6}M of rose bengal, 2—4$\times$ 10^{-4}M of HMTC, and various concentrations of DABCO, TME, or β-carotene in ethanol solvents were irradiated at 546 nm. The results are shown in Figs. 3, 4, and 5. The resulting quantum yields were reduced; the best fit of the data to the Stern-Volmer equation gave the slope values of 5.8×10, 2.7×10^2, and 7.0×10^4M^{-1} for DABCO, TME, and β-carotene respectively. This decreasing effect on the quantum yields supports the idea of the involvement of the singlet oxygen in the dye-sensitized photoelimination of HMTC.

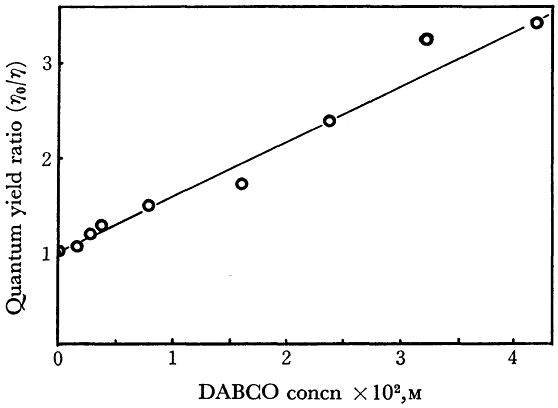

Fig. 3. Effect of DABCO on the quantum yield. η and η_0 indicate the quantum yields for the system with and without DABCO, respectively.
$\eta_0=0.435$, Slope$=5.8\times10$ M^{-1}
[HMTC]$_{\rm ini}=4.48\times10^{-4}$ M; [Rose bengal]$=9.2\times10^{-6}$ M

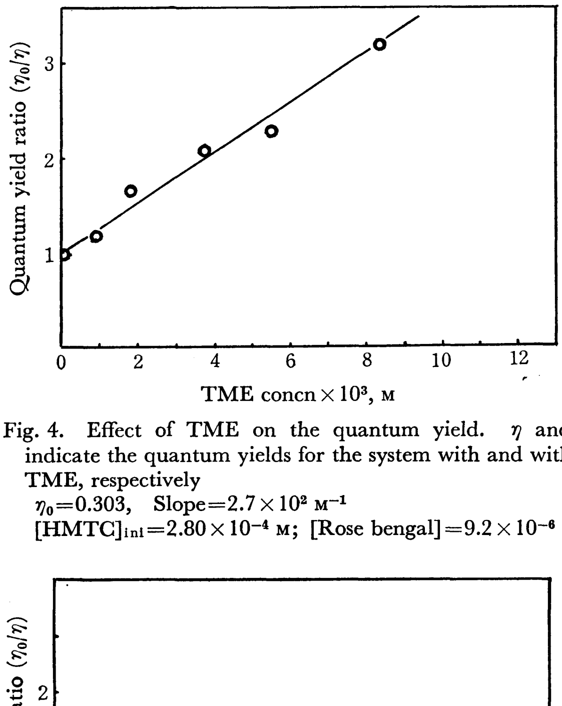

Fig. 4. Effect of TME on the quantum yield. η and η_0 indicate the quantum yields for the system with and without TME, respectively
$\eta_0=0.303$, Slope$=2.7\times10^2$ M^{-1}
[HMTC]$_{\rm ini}=2.80\times10^{-4}$ M; [Rose bengal]$=9.2\times10^{-6}$ M

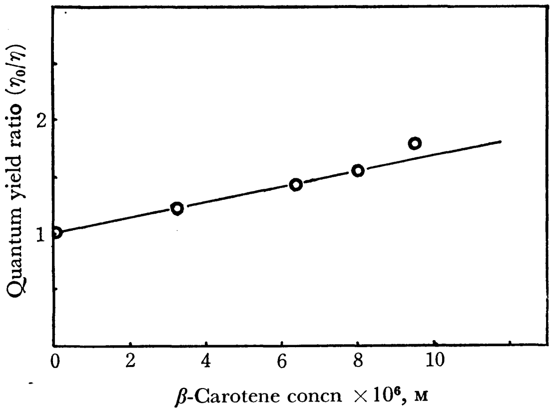

Fig. 5. Effect of β-carotene on the quantum yield. η and η_0 indicate the quantum yields for the system with and without β-carotene, respectively.
$\eta_0=0.357$, Slope$=7.0\times10^4$ M^{-1}
[HMTC]$_{\rm ini}=3.35\times10^{-4}$ M; [Rose bengal]$=9.2\times10^{-6}$ M

Consumption of Oxygen. When aerated solutions containing 9.2×10^{-6}M of rose bengal with HMTC in ethanol were irradiated at 546 nm, the dissolved oxygen contained decreased as is shown in Fig. 6. This

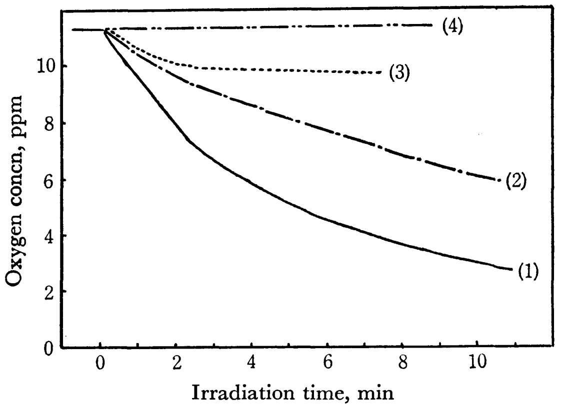

Fig. 6. Intake of oxygen during the irradiation.
(1) [HMTC]$_{\rm ini}=1.0\times10^{-3}$ M, [DABCO]$=0$
(2) [HMTC]$_{\rm ini}=1.0\times10^{-3}$ M, [DABCO]$=3.4\times10^{-2}$ M
(3) [HMTC]$_{\rm ini}=4.0\times10^{-4}$ M, [DABCO]$=0$
(4) [DABCO]$=1.0\times10^{-1}$ M, [HMTC]$_{\rm ini}=0$
[Rose bengal]$=9.2\times10^{-6}$ M

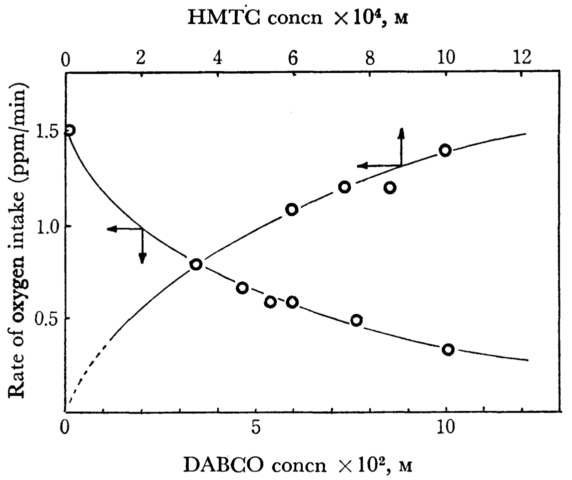

Fig. 7. Effect of DABCO or HMTC on the rate of oxygen intake.
[Rose bengal]$=9.2\times10^{-6}$ M
[HMTC]$=1.0\times10^{-3}$ M for DABCO effect

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[9] C. Ouannès and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

[10] C. S. Foote, S. Wexler, and W. Ando, *Tetrahedron Lett.*, No. **46**, 4111 (1965).

[11] C. S. Foote and R. W. Denny, *J. Amer. Chem. Soc.*, **90**, 6233 (1968).

Table 3. Attempt at sensitization in other dithiocarbamates

Substrate	Substrate concn, M	Sensitizer	Sensitizer concn, M	Quantum yield
Methyl dimethyldithiocarbamate	3.0—12.0×10^{-5}	Dye[a]	$\sim10^{-5}$ [b]	0[16]
Butyl hexamethylenedithiocarbamate	1.0—10.0×10^{-5}	Dye[a]	$\sim10^{-5}$ [b]	0[16]
2,4-dinitrophenyl hexamethylene-dithiocarbamate	1.0—5.0×10^{-5}	Dye[a]	$\sim10^{-5}$ [b]	0[16]
Tetramethylthiuram monosulfide[14]	1.0—5.0×10^{-5}	Dye[a]	$\sim10^{-5}$ [b]	0[16]
Tetramethylthiuram disulfide (TMTD)[15]	1.0—10.0×10^{-5}	Dye[a]	$\sim10^{-5}$ [b]	0[16,17]
	2.1×10^{-4}	Acetophenone	8.0×10^{-2}	0.053[17]
	2.0×10^{-4}	Benzophenone	8.0×10^{-2}	0.043[17]
	3.5×10^{-4}	Michler's ketone	1—2×10^{-4}	0[17]
	2.5×10^{-4}	β-Acetonaphthone	8.0×10^{-3}	0[17]
	3.0×10^{-4}	Naphthalene	6.2×10^{-3}	0[17]

a) Rose bengal or methylene blue.

b) The initial dye concentrations in all of the experiments were 4.0×10^{-5}M and 2.0×10^{-5}M for rose bengal and methylene blue respectively.

shows that the photooxygenation of HMTC took place. Furthermore, DABCO was found to be apparently unreactive toward $^1O_2$, yet to retard the oxidation of HMTC. This is identical with what Wilson had said regarding the effect of DABCO on the rubrene photooxygenation.[9] If the rate of oxygen consumption corresponds to the slope of the linear portion of the curve during the initial stage of the reaction in Fig. 6, the effect of the DABCO or HMTC concentration on the rate of oxygen consumption is also determinable. The results are given in Fig. 7.

Attempts at Dye-sensitization in Other Dithiocarbamates. Unfortunately, we encountered difficulty in identifying the photoproducts. Instead of the direct way of identification, therefore, we attempted to examine the sensitization in the variation of the dithiocarbamates. Esters of dithiocarbamic acid or thiuram sulfide show two strong ultraviolet bands in the 275—290 nm (N conjugation) and 245—260 nm (S conjugation) regions, both with log ε about 4, and another weaker absorption in the 325—360 nm region (log ε about 1.8), as well as HMTC, which represents a true ionic salt.[12] These dithiocarbamates were photolyzed by UV light.[13] In the course of the study we examined whether or not dye-sensitization takes place in these dithiocarbamates. Some representative results of sensitized photolysis in an aerated solution are presented in Table 3. No detectable dye-sensitized reaction occurred, though tetramethylthiuram disulfide (TMTD) was photo-sensitized by a few aromatic ketones possessing a high triplet energy. Furthermore, ethanolic solutions of these dithiocarbamates containing excess hydrogen peroxide were not oxidized by adding dilute aqueous sodium hypochloride.

Discussion

An attempt to check further the singlet-oxygen mechanism for the photooxidations by the action of H_2O_2 mixed with NaOCl, which is known to produce singlet oxygen, failed because HMTC was completely eliminated when NaOCl was injected into a HMTC ethanol solution in the dark. However, all the data presented here on the dye-sensitized photooxidation of HMTC are entirely consistent with a mechanism *via* the singlet oxygen. Because of the spin conservation, only a triplet-triplet transfer (Eq. 1) or a triplet-triplet annihilation (Eq. 2) can be responsible for the excitation of oxygen. Here, $^1D_0$, $^1D_1$, $^3D_1$, and $^3O_2$ represent the singlet ground state, the first excited singlet state, the lowest triplet state of the photosensitizing dye, D, and the ground state of oxygen respectively:

$$ {}^1D_1 + {}^3O_2 \longrightarrow {}^3D_1 + {}^1O_2 \tag{1} $$

$$ {}^3D_1 + {}^3O_2 \longrightarrow {}^1D_0 + {}^1O_2 \tag{2} $$

In dyes, the singlet-triplet splitting is very small.[18] Unfortunately, no literature on the energies of the triplet states of thiazine dyes is available except for thionine.[19] However, if the singlet-triplet splitting (ΔE_{ST}) is smaller than 10 kcal, as is the case with eosine and other xanthene derivatives, then the triplet-triplet transfer can not be responsible for the excitation of oxygen even to the lowest $^1\Delta_g$ state. This can be achieved only by the triplet-triplet annihilation (Reaction 2), in which the whole of the triplet energy of the sensitizer is available. This hypothesis is supported by the conclusion of Stevens and Algar[20] that the singlet oxygen is produced solely by energy transfer from the sensitizer triplet state, even when transfer from excited singlet state is spin-al-

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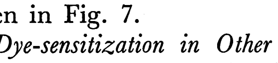
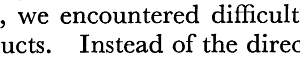
[12] M. J. Janssen, *Rec. Trav. Chim. Pays-Bas*, **76**, 827 (1957).

[13] For esters of dithiocarbamic acid, see: M. Okawara, T. Nakai, K. Morishita, and E. Imoto, *Kogyo Kagaku Zasshi*, **67**, 130, (1964). For thiuram sulfide, T. Yamase, H. Kokado, and E. Inoue, unpublished results.

[14] 

$(CH_3)_2N\text{-}\underset{\overset{\|}{S}}{C}\text{-}S\text{-}\underset{\overset{\|}{S}}{C}\text{-}N(CH_3)_2$

[15] 

$(CH_3)_2N\text{-}\underset{\overset{\|}{S}}{C}\text{-}S\text{-}S\text{-}\underset{\overset{\|}{S}}{C}\text{-}N(CH_3)_2$

[16] The quantities of dithiocarbamate listed in Table 3 were determined by measuring the optical densities of undiluted or diluted samples of irradiated and nonirradiated solutions, if possible, in regions where the dithiocarbamate had a UV absorption which was not interfered with by the dye absorption.

[17] An excess of cupric acetate was added to the TMTD solutions and then, after they had stood at room temperature for at least half an hour (in case the reaction was not complete), tbe quantity of TMTD was determined by almost the same method as that employed for HMTC.

[18] L. S. Forster and D. Dudley, *J. Phys. Chem.*, **66**, 838 (1962).

[19] H. E. A. Kramer and M. Hafner, *Z. Naturforsch.*, **24b**, 452 (1969).

[20] B. Stevens and B. E. Algar, *J. Phys. Chem.*, **73**, 1711 (1969).

lowed and exothermic. The reaction scheme which can explain the experimental data consists of the following steps:

$^1D_0 + h\nu \xrightarrow{I_{abs}} {}^1D_1$ Absorption (3)

$^1D_1 \xrightarrow{k_1} {}^1D_0$ Fluorescence and internal conversion (4)

$^1D_1 \xrightarrow{k_2} {}^3D_1$ Intersystem crossing to the triplet state (5)

$^3D_1 \xrightarrow{k_3} {}^1D_0$ Intersystem crossing to the ground state (6)

$^3D_1 + {}^3O_2 \xrightarrow{k_4} {}^1D_0 + {}^1O_2$ Formation of the singlet oxygen (7)

$^3D_1 + \text{Red} \xrightarrow{k_5} \text{D}\cdot + \text{Red}\cdot$ Radical formation (8)

$^1O_2 \xrightarrow{k_6} {}^3O_2$ Deactivation of the singlet oxygen (9)

$^1O_2 + \text{H} \xrightarrow{k_H} \text{H-O}_2$? Product formation (10)

$^1O_2 + \text{Q} \xrightarrow{k_Q} \begin{array}{l}\text{Q} + {}^3O_2 \\ \text{Q-O}_2\end{array}$ Quenching or trapping of the singlet oxygen (11)

where Red, Red·, D·, H, and Q are, respectively, the reducing agent, the radical of Red, the semiquinone radical of D, HMTC, and the singlet-oxygen quenches or trap. If any reducing agent is rigorously excluded, the quantum yield (η) for HMTC photoelimination is given by:

$$\eta = \frac{k_2}{k_1+k_2} \cdot \frac{k_4[O_2]}{k_3+k_4[O_2]} \cdot \frac{k_H[H]}{k_6+k_Q[Q]+k_H[H]} \tag{12}$$

Under [Q]=0, the quantum yield (η_0) is given by:

$$\eta_0 = \alpha \cdot \beta \cdot \frac{k_H[H]}{k_6+k_H[H]} \tag{13}$$

where

$$\alpha = \frac{k_2}{k_1+k_2}, \quad \beta = \frac{k_4[O_2]}{k_3+k_4[O_2]} \tag{14}$$

By dividing Eq. (13) by Eq. (12), we obtain the Stern-Volmer expression:

$$\frac{\eta_0}{\eta} = 1 + \frac{k_Q[Q]}{k_6+k_H[H]} \tag{15}$$

and a plot of η_0/η *vs.* [Q] should result in a straight line with a slope of $k_Q/(k_6+k_H[H])$. Such a plot is found to be linear for a quencher and two traps, as is shown in Figs. 3, 4, and 5. The value of k_H can be calculated as $1.5\times10^8\text{M}^{-1}\text{sec}^{-1}$ from the $k_Q/(k_6+k_H[H])$ ($7.0\times10^4\text{M}^{-1}$) obtained from Fig. 5, since k_6 and k_Q are 10^4sec^{-1} and $5.0\times10^9\text{M}^{-1}\text{sec}^{-1}$ respectively.[11,12] Using $k_H=1.5\times10^8\text{M}^{-1}\text{sec}^{-1}$, the k_Q values for DABCO and TME were calculated to be 5.3×10^6 and $1.6\times10^7\text{M}^{-1}\text{sec}^{-1}$ respectively. The data obtained by the indirect kinetic approach are summarized in Table 4.[22]

Table 4. Rate constants for the process

Quencher or trap	$[\text{HMTC}]_{\text{ini}}$ $\times 10^4$, M	k_Q/k_6 $+k_H[H]$ $\times$ M	$k_Q \times$ M sec	$k_H \times$ M sec
DABCO	4.48	5.8×10	5.3×10^6	
TME	2.80	2.7×10^2	1.6×10^7	1.5×10^8
β-carotene	3.35	7.0×10^4	5.0×10^9 [11]	

The rate of the oxygen consumption ($-\text{d}[^3O_2]/\text{d}t$) is given by:

$$-\frac{\text{d}[^3O_2]}{\text{d}t} = k_4[^3D_1][^3O_2] - k_{QD}[^1O_2][\text{DO}] - k_6[^1O_2] \tag{16}$$

where k_{QD} refers to the rate constant for DABCO (DO). Assuming the steady concentrations for $^1O_2$ and $^3D_1$,

$$[^1O_2] = \frac{k_4[^3O_2][^3D_1]}{k_6+k_H[H]+k_{QD}[\text{DO}]} \tag{17}$$

$$k_4[^3O_2][^3D_1] \approx \alpha I \tag{18}$$

since $k_4[^3O_2] \gg k_3$.[26] The substitution of Eqs. (17) and (18) into (16) gives the rate of oxygen consumption:

$$-\frac{\text{d}[^3O_2]}{\text{d}t} = \alpha I \cdot \frac{k_H[H]}{k_6+k_H[H]+k_{QD}[\text{DO}]} \tag{19}$$

Eq. (19) can be rewritten as:

$$1/-\frac{\text{d}[^3O_2]}{\text{d}t} = \frac{1}{\alpha \cdot I}\left(1+\frac{k_6}{k_H[H]}+\frac{k_{QD}}{k_H[H]}[\text{DO}]\right) \tag{20}$$

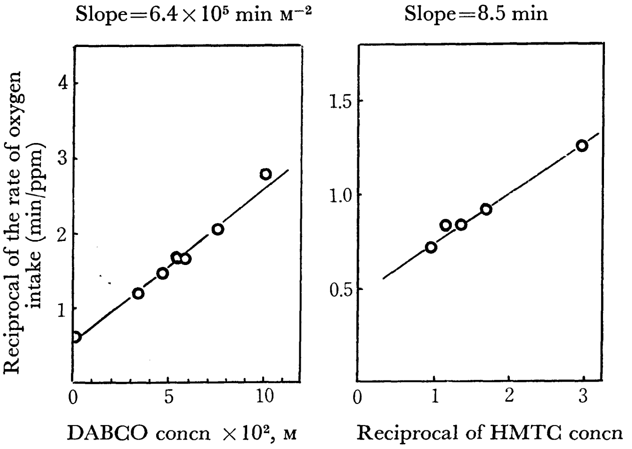


Fig. 8. Relationship between the rate of oxygen intake and DABCO or HMTC concentration.
[Rose bengal]$=9.2\times10^{-6}$ M

The best fit of the data in Fig. 7 to this equation gives $k_{QD}/\alpha I \cdot k_H[H] = 6.4\times10^5$ min M^{-2} for the plot of $1/(-\text{d}[^3O_2]/\text{d}t)$ *vs.* [DO], with the [H] and αI constants, as shown in Fig. 8. Experimentally, the values of I and [H] were determined to be 4—5×10^{-5} Einstein/l min and 1.0×10^{-3}M respectively. If k_{QD} is taken to be

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[21] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

[22] In the gas phase, k_Q for DABCO has recently been found to equal $1.2\pm0.1\times10^7\text{M}^{-1}\text{sec}^{-1}$,[23] so the present value of k_Q $=5.3\times10^6\text{M}^{-1}\text{sec}^{-1}$ seems reasonable. The value of k_Q obtained for TME is less than $10^8\text{M}^{-1}\text{sec}^{-1}$,[24] but greater than $10^5\text{M}^{-1}\text{sec}^{-1}$,[25] though these values were obtained in the gas phase.

[23] E. A. Ogryzlo and C. W. Tang, *J. Amer. Chem. Soc.*, **92**, 5034 (1970).

[24] S. J. Arnold, M. Kubo, and E. A. Ogryzlo, "Oxidation of Organic Compounds," Advances in Chemistry Series, No. **77**, American Chemical Society, Washington, D. C., 1968, p. 133.

[25] W. S. Gleason, A. D. Broadbent, E. Whittle, and J. N. Pitts, Jr, *J. Amer. Chem. Soc.*, **92**, 2068 (1970).

[26] R. M. Danziger, K. H. Bar-Eli, and K. Weiss, *J. Phy. Chem.*, **71**, 2633 (1967).

$5.3\times10^6\text{M}^{-1}\,\text{sec}^{-1}$, as is shown in Table 4, then k_H can be calculated to be about 1—$2\times10^8\text{M}^{-1}\,\text{sec}^{-1}$ from the value of the slope with 6.4×10^5 min M^{-2}, since α and k_6 are about unity[27] and $10^4\,\text{sec}^{-1}$ [11] respectively. The value of k_H calculated here is in good agreement with that obtained by the plot of η_0/η *vs.* [Q]. As a further check, plots of $1/(-d[^3O_2]/dt)$ *vs.* $1/[H]$ were carried out for the data in Fig. 7; they gave a straight line, as is shown in Fig. 8. Then, k_H can be calculated to be about $5\times10^7\text{M}^{-1}\,\text{sec}^{-1}$ from the value of the slope with $k_6/\alpha I\cdot k_H=8.5$ min. The values of k_H obtained by different methods are in satisfactory agreement if one allows for the difference in reaction conditions and the errors included in the measurements. The best value of k_H is, therefore, probably around $10^8\text{M}^{-1}\,\text{sec}^{-1}$. These results illustrate the sensitivity of HMTC as a photometric detector of oxidation *via* $^1O_2$.

Considering the findings, shown in Table 3, that dye-sensitization did not take place for each dithiocarbamate representing a true nonionic structure, it may be suggested that the thiocarboxyl-ion group $(-C\langle^{S}_{S}\ominus)$ plays the important role in the dye-sensitized photooxygenation of HMTC. In connection with the involvement of the singlet oxygen, it was inferred that the singlet oxygen attacked the thiocarboxyl-ion group of HMTC with a rate constant of $10^8\text{M}^{-1}\,\text{sec}^{-1}$ in ethanol.[28]

Returning now to the dye reactions, the effects of the dye concentration and of allylthiourea delineated the differences between xanthene dyes and thiazine dyes (Table 2, Fig. 2).[2] As one conceivable mechanism to explain the differences, the D-D mechanism (Eq. 8′) may be mentioned:

$$^3D_1 + {}^1D_0 \xrightarrow{k_5'} D^+\text{-}D^- \tag{8′}$$

The occurrence of a D-D mechanism, in which the photochemical reaction is initiated by the interaction of the triplet-dye and the ground-state-dye molecules, is established for the ethanol solution of xanthene or thiazine dye.[29] When the rate constant of the D-D mechanism is represented by k_5', Eq. (15) can be rewritten to:

$$\eta_0'/\eta = 1 + \frac{k_5}{k_3+k_4[O_2]+k_5'[D]}[\text{Red}] \tag{21}$$

with a η_0'=quantum yield under [Red]=0. Fig. 2 and a previous paper show that the concentration of allylthiourea, which reduces η to one-half of its original value, is of the order of 10^{-4}M for rose bengal and of 10^{-2}M for methylene blue. In connection with the fact that, on the quantum yield, there is a remarkable effect of the thiazine-dye concentration in comparison with the case of the xanthene dye, for rose bengal, k_5' must be smaller than that for methylene blue provided that k_3, k_4, and k_5 are of similar magnitudes for the two dyes. The above estimation suggests that the D-D mechanism easily occurs for the thiazine dye, resulting in a decrease in the rate of T-T annihilation. Further studies are necessary to examine the above possibility, however.

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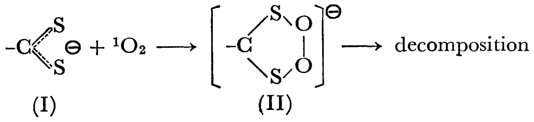
[27] K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964).

[28] As one conceivable reaction, if the singlet oxygen is to cycloadd to a isolated thiocarboxyl anion group (I), one possible product is an intermediate endoperoxide (II):



though we can not construct a state correlation diagram for this reaction because of the lack of thermochemical data.

[29] M. Koizumi, *Nippon Kagaku Zasshi*, **90**, 1 (1969).