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The Dye-sensitized Photolysis of Hexamethyleneammonium Hexamethylenedithiocarbamate by Thiazine Dyes

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Hexamethyleneammonium hexamethylenedithiocarbamate (HMTC) was photolyzed by UV light to yield carbon disulfide as the decomposition product. This photolysis could be sensitized by thiazine dyes, such as methylene blue and thionine. New methylene blue was the most effective among the sensitizers of this type examined. Bewteen the reciprocal concentration of HMTC and the reciprocal quantum yield, a linear relation was observed. The presence of oxygen was essential for the sensitization. Systems containing methylene blue appear to be more sensitive to oxygen than those containing thionine or new methylene blue. In the presence of an appropriate reducing agent such as allylthiourea, the quantum yield was decreased. The sensitization mechanism by thiazine dyes was probably different from that by benzophenone previously reported. It seems that the sensitization by thiazine dyes takes place by means of the interaction of the triplet state of the sensitizer with dissolved oxygen.

In previous papers,[1,2] the photochemical reaction of sodium *N,N*-dimethyldithiocarbamate (SMTC) was reported. Carbon disulfide was found in the decomposition products. This photolytic reaction could be sensitized by benzophenone under the light (365 nm wavelength) which was absorbed by benzophenone. The photo-sensitization was observed regardless of whether or not the solution contained dissolved oxygen. It seemed that the sensitization took place by means of energy transfer

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1) T. Yamase, H. Kokado and E. Inoue, *Kogyo Kagaku Zasshi*, **71**, 1587 (1968).

2) T. Yamase, H. Kokado and E. Inoue, *ibid.*, **72**, 162 (1969).

from the triplet state of the sensitizer to SMTC molecules.[2)]

We have found that SMTC could be efficiently sensitized by thiazine dyes such as methylene blue if the solution contained dissolved oxygen. However, we encountered difficulty in studying the sensitizing effect of these dyes for the photolysis of SMTC; for their stability is greatly reduced in the alkaline ethanol, while SMTC is stable only under alkaline conditions. This difficulty could be avoided by using HMTC as the photolyzable dithiocarbamate, because this substance is stable in neutral ethanol. This paper will describe the effects of the concentration and the reducing agent on the sensitized-photolysis by thiazine dyes. The effect of oxygen will also be discussed in connection with them.

Experimental

HMTC was prepared by adding carbon disulfide slowly to a petroleum ether solution of hexamethyleneimine cooled to about 5°C. The resultant white precipitate was then filtered off, washed with fresh petroleum ether, and dried in the air. The crystallized HMTC was a pale cream-colored powder. It was recrystallized three times from ethanol to form white needles melting at 147°C. Methylene blue, thionine, and new methylene blue (G. R. grade, Tokyo Kasei Corp.) were purified by three recrystallizations from water. Allylthiourea, triethanolamine, and ethanol were G.R. grade reagents (Tokyo Kasei Corp.). The experimental procedure used in this study was almost the same as that described previously.[1,2)] Oxygen was removed from the solution by a standard freeze-thaw cycle procedure under a vacuum of 10^{-4} mmHg. A 1 kW-tungsten lamp was used as a source of actinic light for the dye-sensitization. Transmitting glass filters which cut off light shorter than 580 and 620 nm were used for thionine or methylene blue, and for new methylene blue, respectively. In most of the experiment a filter absorbing heat (HR 1-69) was also employed. Unfortunately, convenient chemical actinometers for measuring red light are not available. We assumed, therefore, that the quantum yield under the incident red light is the same as that under a 546 nm light. The latter was easily measured using Reinecke's salt as a chemical actinometer. In this case, the concentration of dye has to be increased for it to have enough absorption at 546 nm. The dye concentration was then high enough to absorb 100% of the incident red light. The quantum yields under various dye concentrations were calculated from the dye concentration against decomposed HMTC quantity relationship at a constant illumination time.

Results and Discussion

Photolysis Rate. Typical examples of the degree of photolysis *versus* time relationships under different experimental conditions are shown in Fig. 1. The logarithm of the surviving HMTC concentration changed linearly with the time. Sensitization showed no induction period and proceeded at a considerable speed. Almost no fading of dye was observed, even if the initial HMTC concentration was changed ($2-6\times10^{-4}$M). The slope in Fig. 1 was unchanged within the range of experimental uncertainty, as long as all the other factors were held constant.

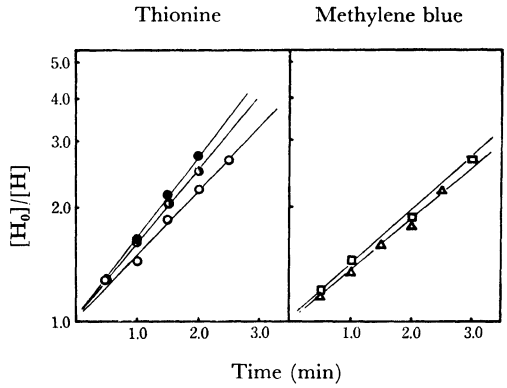


Fig. 1. Photolysis of HMTC as a function of illumination time.
Thionine conc. $=8.0\times10^{-5}$M; methylene blue conc. $=4.0\times10^{-5}$M; initial HMTC conc. ($[H_0]$) $\times10^4=3.69$. (○), 7.51 (●), 2.64 (◐), 3.75 (△), 2.64 (□)

Effect of Dye Concentration. The effects of the concentrations of thiazine dyes are shown in Fig. 2. The reciprocal of the quantum yield changed linearly with the dye concentration.

	Thionine	Methylenene blue	New methylene blue
Intercept	4.3	6.0	3.4
$(\text{Slope})^{-1}$	3.9×10^4	3.4×10^4	1.9×10^4

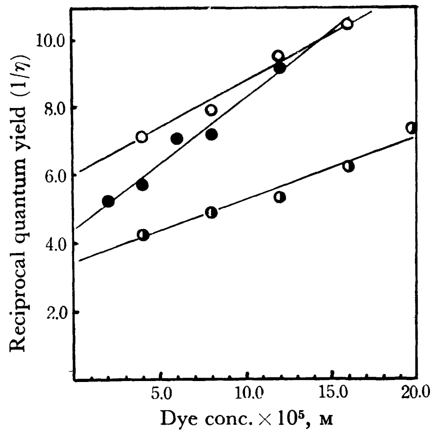
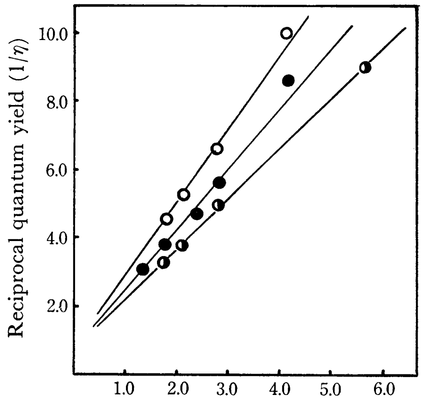


Fig. 2. Dependence of the quantum yield on the dye concentration.
HMTC conc. $=3.7$—3.8×10^{-4}M; methylene blue (○), thionine (●), new methylene blue (◐)

Effect of HMTC Concentration. The results of photolysis at different HMTC concentrations are

	Thionine	Methylene blue	New methylene blue
$(\text{Slope})^{-1}$	5.9×10^2	4.5×10^2	7.0×10^2

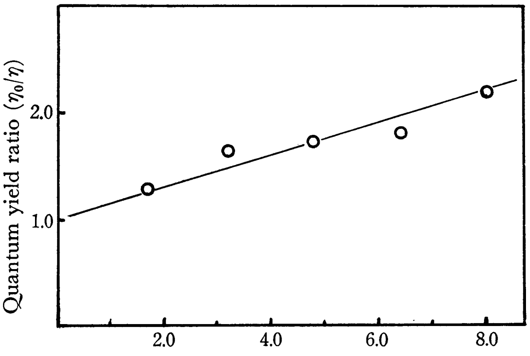


Reciprocal HMTC conc. $\times10^{-3}$, M^{-1}

Fig. 3. Dependence of the quantum yield on the HMTC concentration.
Dye conc. $=4.0\times10^{-5}$M; methylene blue (○), thionine (●), new methylene blue (◑)

represented in Fig. 3. Figure 3 shows that 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 increases in the following order: methylene blue$<$thionine$<$new methylene blue.

Effect of Reducing Agent, Allylthiourea. The fact that the fluorescence of thionine (or methylene blue) was not quenched by HMTC in ethanol suggests that the excited singlet state of dye does not participate in the sensitization. If the sensitization occurs from the semiquinone radicals which are formed from the excited triplet state of the sensitizer, the efficiency of sensitization will be increased by adding a weak reducing agent, such as triethanolamine or allylthiourea.[3,4] Figure 4 shows the effect of allylthiourea on the sensitization by methylene blue. Allylthiourea did not increase the efficiency of the sensitization. Allylthiourea was regarded rather a quencher for the chemically-active state of the dye. 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, while in the dye-sensitized photopolymerization,[3,4] this type of process is quite common.



Allylthiourea conc. $\times10^2$, M

Fig. 4. Effect of allythiourea on the quantum yield. initial HMTC conc. $=3.96\times10^{-4}$M; methylene blue conc. $=4.0\times10^{-5}$M; η and η_0 indicate the quantum yields for the system with and without allylthiourea, respectively

Effect of Oxygen. Some representative results of photolysis in a deaerated solution are presented here. Table 1 gives the results for 4.0×10^{-5}M thiazine dye. Table 1 also includes the results obtained in solutions into which oxygen or nitrogen containing a small amount of oxygen had been bubbled in. Remarkable sensitization did not take place in the deaerated systems. This finding indicates the presence of a mechanism different from the photolysis by UV light or sensitized-photolysis by benzophenone, which was almost unaffected by oxygen, as has been reported previously.[1,2] It may be inferred that sensitization by thiazine dyes takes place not by energy transfer from the excited triplet state of the dye to HMTC, as has been proposed in connection with the sensitization of benzophenone,[2] but *via* the interaction of triplet state of dyes with oxygen. Methylene blue appeared to be more sensitive to oxygen than was thionine or new methylene blue. This is identical with what Chaberek has said regarding the effects of thionine and methylene blue on the dye-sensitized photopolymerization.[4]

Sensitization Mechanism. On the basis of the above results, the mechanism of the main reactions may be represented by the following scheme:

Rate

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^* \qquad aI \tag{1}$$

$$\mathrm{D}^* \xrightarrow{k_1} \mathrm{D} \qquad k_1[\mathrm{D}^*] \tag{2}$$

$$\mathrm{D}^* + \mathrm{D} \xrightarrow{k_2} 2\mathrm{D} \qquad k_2[\mathrm{D}^*][\mathrm{D}] \tag{3}$$

$$\mathrm{D}^* + \mathrm{O}_2 \xrightarrow{k_3} \mathrm{X} \qquad k_3[\mathrm{D}^*][\mathrm{O}_2] \tag{4}$$

$$\mathrm{X} + \mathrm{HMTC} \xrightarrow{k_4} \text{Decomposed HMTC} \qquad k_4[\mathrm{X}][\mathrm{H}] \tag{5}$$

$$\mathrm{X} \xrightarrow{k_5} ?\ (\mathrm{D}+\mathrm{O}_2) \qquad k_5[\mathrm{X}] \tag{6}$$

where a is the efficiency of the conversion of initially-excited singlets to the triplet states (D*)

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3) G. Delzenne, W. Dewinter, S. Toppet and G. Smets, *J. Polym. Sci., Part A*, **2**, 1069 (1964).

4) S. Chaberek and R. J. Allen, *J. Phys. Chem.*, **69**, 647 (1965).

TABLE 1

Sensitizer	$[H]_{\mathrm{ini}} \times 10^4$	$\eta^{a)}$	$\eta'^{b)}$	$\eta''^{c)}$	$\eta'''^{d)}$
Thionine	5.33	0.251	0	0.128	—
Methylene blue	5.57	0.227	0	0	0.310
New methylene blue	4.86	0.263	0	0.056	—
Benzophenone	3.78	0.160	0.130	—	—

a) atmospheric condition
b) deaerated condition
c) saturated with nitrogen to contain little oxygen
d) saturated with oxygen

and where I is the rate of red-light absorption by dye (D) in Einsteins/min. Reaction (2) represents the thermal deactivation of D* to the ground state. Reaction (3) denotes the quenching of D* by the dye of the ground state. Reaction (4) is the interaction between D* and oxygen (O_2) to form an unknown substance, X, which then reacts with HMTC as is shown by Reaction (5). Reaction (6) presents the thermal deactivation of X. According to this scheme, and assuming the steady-state condition, the quantum yield can be expressed by Eq. (7):

$$\eta = a\{k_3[O_2]/(k_1+k_2[D]+k_3[O_2])\}\{k_4[H]/(k_5+k_4[H])\} \tag{7}$$

or by

$$1/\eta = (1/ab)(1+k_5/k_4[H]) \tag{8}$$

$$b = k_3[O_2]/(k_1+k_2[D] + k_3[O_2]) \tag{9}$$

$$1/\eta = (1/ac)\{1+(k_1+k_2[D])/k_3[O_2]\} \tag{10}$$

$$c = k_4[H]/(k_5+k_4[H]) \tag{11}$$

The good fit of the data to Eqs. (8) and (10) is shown in Figs. 3 and 2. To introduce the illumination time into the rate equation, let us consider the following rate equation:

$$-\mathrm{d}t/\mathrm{d}[H] = (1/abI)(1+k_5/k_4[H]) \tag{12}$$

If $k_5/k_4[H]$ is sufficiently large, as is shown in the slope of Fig. 3, Eq. (12) becomes:

$$\log([H]_0/[H]) = (k_4/k_5)abIt \tag{13}$$

where H_0 is the initial concentration of HMTC. Figure 1 shows that a linear relation between log $([H_0]/[H])$ and t holds experimentally. However, the greater concentration of HMTC will allow the plots to deviate from the relationship of Eq. (13). The presence of oxygen is essential to the sensitization by thiazine dyes, as is shown in Table 1. This finding contrasts with what we had earlier found, that oxygen was not necessary for the sensitization by benzophenone or for the direct photolysis. It is well-known that singlet oxygen can be generated from exogenous photo-sensitizers such as methylene blue in the photooxygenation.[5] The sensitized photolysis of HMTC by thiazine dyes may proceed by means of the singlet oxygen formed by energy transfer from the triplet sensitizer. One conceivable mechanism involves the (a) reaction;

$$^1O_2 + \mathrm{HMTC} \rightarrow {}^3O_2 + {}^3\mathrm{HMTDC} \tag{a}$$

This is tenable only if the triplet energy of HMTC is below or near that of singlet oxygen (the $^1\Delta_g$ state is at 22.5 kcal). Unfortunately, the triplet energy is not known, but such a low energy would be unreasonable. The following reaction, (b) is, thus:

$$^1O_2 + \mathrm{HMTC} \rightarrow \text{Decomposed HMTC} \tag{b}$$

This is the only mechanism which is consistent with our present knowledge, though the mechanism is not yet understood in detail. It should be noted that, in the reactions of amines with singlet oxygen, tertiary aliphatic amines are known to yield no reactive products, but rather act as inhibitors of the oxidation of known reactive acceptors of singlet oxygen.[6] Further studies are necessary to examine the above possibility.

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

6) C. Quannes and T. Wilson, *ibid.*, **90**, 6527 (1968).