BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 736—743 (1967)

Photoreduction of Proflavine in the Aqueous Solution. I. A Flash Photolysis Study

Kôichi Kikuchi and Masao Koizumi

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

(Received August 22, 1966)

The photoreduction of proflavine (D) in an aqueous solution at pH 4, was investigated by a flash technique. No intermediates were observed other than the triplet state (T) and the semiquinone (DH·). This, with the finding that the triplet state decays according to the second order, rules out the occurrence of such reactions as $T+D \rightarrow D^+ + D^-$, $T+T \rightarrow D^+ + D^-$. In the presence of a large quantity of allylthiourea (RH_2), the yield of leuco-proflavine (DH_2) by one flash becomes constant independent of the ATU concentration, and its value is about one half of the yield of T. This indicates that almost all the T produced reacts with ATU. The rate constants obtained are:

$T+T \rightarrow$ $k_3=0.8\text{—}1.4\times10^9\ \text{M}^{-1}\ \text{sec}^{-1}$
$T \rightarrow D$ $k_4 \lesssim 6\times10^3\ \text{sec}^{-1}$
$T+RH_2 \rightarrow DH\cdot+RH\cdot$ $k_5=4.3\times10^6\ \text{M}^{-1}\ \text{sec}^{-1}$
$DH\cdot+DH\cdot \rightarrow DH_2+D$ $k_6=7\times10^8\ \text{M}^{-1}\ \text{sec}^{-1}$
$T+O_2 \rightarrow D+O_2$ $k_7=1.5\text{—}4.7\times10^9\ \text{M}^{-1}\ \text{sec}^{-1}$
$DH\cdot+O_2 \rightarrow D+HO_2\cdot$ $k_8=1\text{—}3\times10^9\ \text{M}^{-1}\ \text{sec}^{-1}$

m-Phenylenediamine was found to produce an intermediate which decays according to the first order. Its decay constant is $1.5\times10^2\ \text{sec}^{-1}$. The rate constant for the reaction of T with *m*-phenylenediamine is $3.5\times10^6\ \text{M}^{-1}\ \text{sec}^{-1}$, about 1000 times smaller than that of the encounter-controlled process. This suggests that some of the rate constants reported by Oster should be reinvestigated.

In 1959, Oster[1] studied the kinetics of the photoreduction of proflavine by allylthiourea (ATU) in aqueous solutions and proposed a notable reaction scheme in which the triplet dye, T, is produced by $D^*+D \rightarrow T+D$, where D^* is the singlet-excited state. The chief evidence for this was the increase in the quantum yield of photoreduction with the dye concentration and the conspicuous self-quenching of the proflavine fluorescence, a concentration of less than 10^{-5} M being effective. The rate constant for the above process was of the order of $10^{12}\ \text{M}^{-1}\ \text{sec}^{-1}$, about 100 times larger than the rate constant for an encounter-controlled process. He interpreted this as being due to an energy transfer by a resonance interaction.

A little later, Melhuish[2] studied the concentration quenching of the proflavine fluorescence in greater detail. He obtained results resembling Oster's findings, but he did not observe the phenomenon of self-quenching below 10^{-5} M of the dye; this was in contradiction to Oster's findings. Using the value of 2×10^{-9} sec for the life of the singlet-excited state, Melhuish estimated the rate constant for a self-deactivation as $5\times10^{11}\ \text{M}^{-1}\ \text{sec}^{-1}$, which is, again, much larger than the diffusion-controlled rate constant. It seems, however, that he is of the opinion that this is due to the encounter distances being extraordinarily large.

Since the above fact is very remarkable, it is desirable to study it further and, in particular, to study it by a flash technique, the details of the elementary reactions constituting the overall reaction.

---

[1] F. Millich and G. Oster, *J. Am. Chem. Soc.*, **81**, 1357 (1959).

[2] G. R. Haugen and W. H. Melhuish, *Trans. Faraday Soc.*, **60**, 386 (1964).

Furthermore, since there is no apriori reason for denying such a process as $T+T \rightarrow D^+D^-$ or $T+D \rightarrow D^+ + D^-$,[3] such possibilities should be examined; if such were the case, there should be a great probability that the quantum yield of photoreduction increases with the dye concentration.

The purpose of the present paper is to study the behavior of the transient intermediates produced in an aqueous solution of proflavine at a fixed pH value of 4.0,[4] and to determine the rate constants of elementary reactions related to the overall photoreduction.

Experimental

Apparatus. The flash apparatus used was the same one as has been described in a previous paper.[3] A plastic plate was used to cut off light shorter than 350 mμ.

Materials. Proflavine sulfate obtained from Tokyo Kasei was purified as follows. The precipitate obtained from the aqueous solution by adding an excess amount of ammonia, was recrystallized twice from ethanol. It was desiccated *in vacuo*. The results of the elementary analysis were as follows:

	Theoretical	Result
Carbon	74.60(%)	74.11(%)
Nitrogen	20.08	19.44
Hydrogen	5.29	5.06

ε (λ=445 mμ) is 3.93×10^4 M^{-1} cm^{-1}.

Sodium dihydrogen phosphate from Wakojunyaku, G. R. grade, was purified according to the method of the literature.[5] ATU from Tokyo Kasei, G. R. grade, was recrystallized 3—5 times from redistilled water. It was desiccated *in vacuo*.

Results

A. Intermediates in the System Involving no Reducing Agents. Several repetitions of the flash illumination cause no permanent reaction in the degassed solution of proflavine.

Absorption Spectra of the Triplet Proflavine. The transient absorption spectra are shown in Fig. 1; they may be due to the triplet state of the dye. No absorption is observed other than these. This assignment is supported by the following findings, which will be described in more detail later: 1) the second-order decay, 2) the great reactivity toward oxygen and some reducing agents, and 3) a lifetime longer than $\sim 10^{-4}$ sec.

The spectrum has two peaks, at around 350 and 560 mμ. The absorption of the original dye, extending 350—560 mμ, makes it difficult to know the exact features of the triplet state absorption in this region. The molar absorbance of the triplet dye at a given wavelength (λ), $\varepsilon_T{}^\lambda$:, can be evaluated from the following relation if no absorption of the original dye exists at λ:

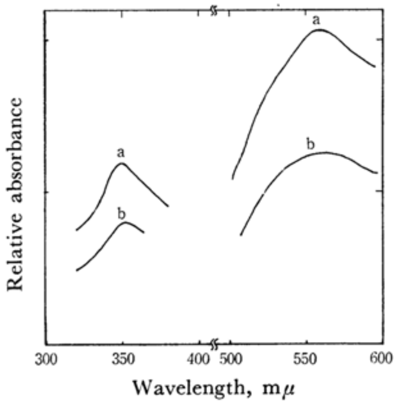

Fig. 1. Absorption spectra of transient species in the absence of any reducing agent; dye concn. 1.0×10^{-5} M.
Curves a and b are respectively for 65 μ sec and 185 μ sec after flashing (input-energy 125 J).

$$\varepsilon_T{}^\lambda = \frac{D_{t_0}{}^T(\lambda)(\varepsilon_D{}^{\lambda=445} - \varepsilon_T{}^{\lambda=445})}{D_0(\lambda=445) - D_{t_0}(\lambda=445)} \tag{1}$$

where $D_{t_0}{}^T$ (λ) is the optical density (at λ) due to the triplet state existent at time t_0, where D_0 (λ=445) and D_{t_0} (λ=445) are the optical densities at time zero and at time t_0 respectively, both at λ=445 mμ, and where ε_D and ε_T are, respectively, the molar absorbance of the original and the triplet dye at the assigned wavelength. $\varepsilon_T{}^{\lambda=445}$ is estimated to be less than 10^4 M^{-1} cm^{-1} from the decrease in the optical density immediately after the illumination. The neglect of $\varepsilon_T{}^{\lambda=445}$ yields the approximate values of $\varepsilon_T{}^\lambda$ given in Table 1. The error would not exceed 20%.

TABLE 1. THE CHANGE IN ABSORBANCE IMMEDIATELY AFTER THE FLASH

[dye]	$D_{t_0}{}^T(\lambda=350)$	$D_{t_0}{}^T(\lambda=700)$	$D_0(\lambda=445) - D_{t_0}(\lambda=445)$
2.14×10^{-6} M	0.12 ± 0.03	0.12 ± 0.01	0.24 ± 0.08
3.46×10^{-6} M	0.21 ± 0.02		0.35 ± 0.10
7.30×10^{-6} M	0.40 ± 0.10	0.36 ± 0.10	

$\varepsilon_T{}^{\lambda=350} \simeq 2 \times 10^4$ M^{-1} cm^{-1}
$\varepsilon_T{}^{\lambda=700} \simeq 2 \times 10^4$ M^{-1} cm^{-1}

Decay of the Triplet State. As is shown in Fig. 2, the triplet state decays according to the second-order rate formula. The slopes of the curves give $k_T/\varepsilon_T d$, where k_T, ε_T and d are, respectively, the second-order rate constant for $T+T \rightarrow$, the molar absorbance of the triplet state, and the thickness of the cell, 10 cm. Some results are shown in Table 2.

---

[3] T. Ohno, S. Kato and M. Koizumi, This Bulletin, **39**, 232 (1966).

[4] This is an optimum pH value according to Oster. (*Cf*. Ref. 1).

[5] H. J. Beans and S. J. Kiehl, *J. Am. Chem. Soc.*, **49**, 1878 (1927).

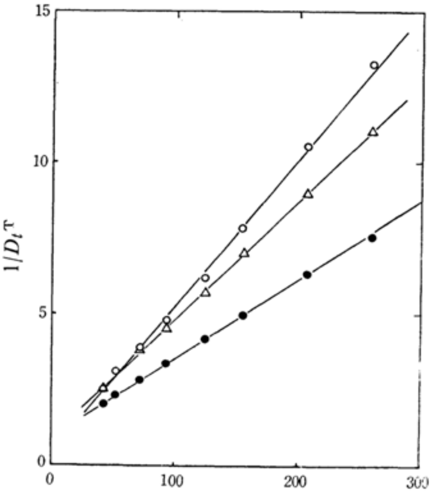

Fig. 2. Decay of the triplet dye in the phosphate buffer; dye concn. 3.2×10^{-5} M.
Wavelength: ○ 310 mμ, △ 330 mμ, ● 350 mμ

Table 2. The second-order decay constants of the triplet state

[dye] M	$2k_{\mathrm{T}}/\varepsilon_{\mathrm{T}}d$ (at 350 mμ) sec^{-1}	$2k_{\mathrm{T}}$ M^{-1} sec^{-1}
3.8×10^{-6}	2.8×10^{4}	1.4×10^{9}
6.5×10^{-6}	2.1×10^{4}	1.05×10^{9}
1.4×10^{-5}	2.1×10^{4}	1.05×10^{9}
2.9×10^{-5}	1.6×10^{4}	0.8×10^{9}
4.2×10^{-5}	1.6×10^{4}	0.8×10^{9}
6.5×10^{-5}	1.6×10^{4}	0.8×10^{9}

The decay constant seems to increase with the decrease in the dye concentration, although the increment is less than twice upon a more than tenfold decrease in the concentration. To make clear the reason for the above result, further investigation is now in progresss.

Since the second-order decay holds satisfactorily almost throughout the run in all cases, the first-order decay constant of the triplet state, k_4, can not be evaluated from the decay curve of the triplet state. Its approximate value, however, was estimated from the later part of the recovery curve of the original dye. The result is $k_4\simeq6\times10^{3}$ sec^{-1}. This is, however, perhaps an overestimation.

The Influence of the Dye Concentration on the Yield of the Triplet Dye. In order to examine whether or not the triplet state is produced according to $\mathrm{D}^*+\mathrm{D}\rightarrow\mathrm{T}+\mathrm{D}$, the effect of the dye concentration on the yield of the triplet state was investigated. The latter quantity was evaluated by extrapolate the decay curve of the triplet state to the time point immediately after the flash. The results are given in Table 3.

It is evident that the triplet yield is independent of the dye concentration when the latter is larger than $\sim1\times10^{-5}$ M. This result, however, does not show whether or not the above process is occurring (see Discussion).

Table 3. The yield of the triplet state immediately after the flash
(at a constant intensity)

[Dye] M	Triplet yield M
1.0×10^{-6}	4.5×10^{-7}
2.0×10^{-6}	7.8×10^{-7}
3.0×10^{-6}	1.7×10^{-6}
4.0×10^{-6}	2.0×10^{-6}
1.4×10^{-5}	2.0×10^{-6}
2.9×10^{-5}	2.1×10^{-6}
4.2×10^{-5}	2.5×10^{-6}
6.5×10^{-5}	2.1×10^{-6}

The Effect of the Addition of Oxygen on the Decay of the Triplet State. No new absorption spectra appear in the solution in which a very small amount of oxygen is dissolved, and the decay curve for the triplet state is scarcely changed by the repetition of the flash illumination. These findings imply that no chemical reaction is occurring. The addition of oxygen, 3×10^{-6}—5×10^{-5} M, accelerates the decay of the triplet state, and the decay curves become a superposition of the first- and the second-order processes. The later stage, however, can be expressed satisfactorily by the first order. The first-order rate constants obtained from the ln D^{T}-*vs.*-time plot in the later stage (at 530 mμ) are summarized in Table 4.

Table 4. The value of k_7
$[\mathrm{D}]=2.0\times10^{-5}$ M

$[\mathrm{O}_2]$ M	k_7 M^{-1} sec^{-1}
5.1×10^{-5}	1.4×10^{9}
2.7×10^{-5}	2.1×10^{9}
1.2×10^{-5}	3.3×10^{9}
3.2×10^{-6}	5.5×10^{9} (corrected value: 4.7×10^{9} M^{-1} sec^{-1})

The corrected value in the table was obtained by taking the second-order contribution into account. The reason why k_7 increases with the decrease in oxygen concentration is not known. It might be due to the presence of much more oxygen than the added quantity on account of the incompleteness of degassing, *etc.* At any rate, there is no doubt that the rate constant is of the diffusion-controlled order.

B. Intermediates in the System Involving a Reducing Agent. The transient spectra for the system containing 2.0×10^{-2} M of ATU are shown in Fig. 3. The absorption spectra with two peaks, at 355 and 550 mμ, resemble those for

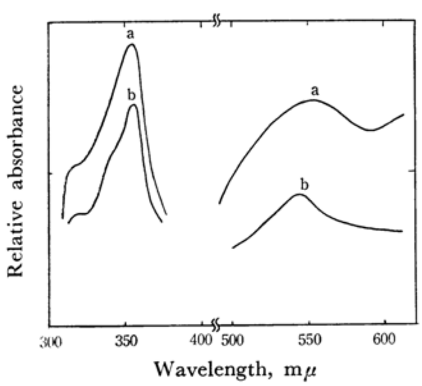

Fig. 3. Absorption spectra of transient species in the presence of ATU; dye concn. 3.2×10^{-5} M, ATU concn. 2.0×10^{-2} M.
Curves a and b are respectively for 93 μsec and 185 μsec after flashing.

the triplet state, but they are not quite the same. The behavior described below strongly supports the view that these spectra are due to the semiquinone. However, an unfortunate resemblance in the spectra of the two species makes accurate studies very difficult.

The Effect of the Concentration of ATU on the Transient Absorption Spectra. Since the absorption of the original dye does not exist in the 310—350 mμ region (the value of ε_D at 370 mμ and at 390 mμ are, respectively, 3×10^3 and 8×10^3 M^{-1} cm^{-1}), and since both the triplet state and the semiquinone have their absorptions in this region, the time dependence of the optical density in this region was investigated at several wavelengths. Some results are shown in Figs. 4 and 5.

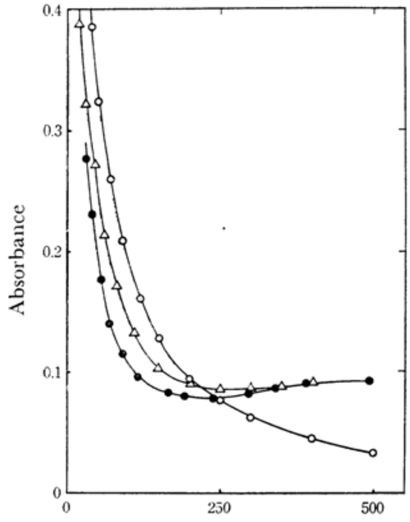

Fig. 4. Change of the absorbance at 310 mμ; dye concn. 3.2×10^{-5} M.
ATU concn.: ○ 0 M　△ 2.0×10^{-3} M
● 1.0×10^{-2} M

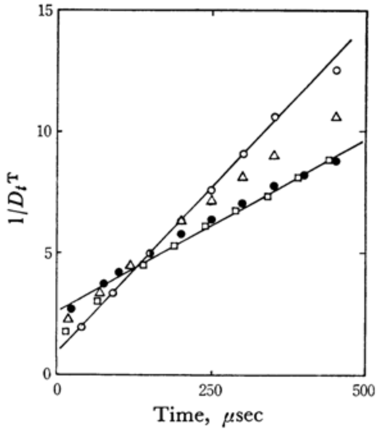

Fig. 5. Change of the absorbance at 350 mμ; dye concn. 3.2×10^{-5} M.
ATU concn.: ○ 0 M　△ 2.0×10^{-3} M
□ 5.0×10^{-3} M　● 1.0×10^{-2} M

It is notable that, at 310 mμ, the shape of the curve is profoundly affected by the addition of ATU. When the concentration of ATU is low, the shape of the transient spectra immediately after the flash is quite similar to that in the absence of ATU, with only a slight decrease in the absorbance. This indicates that ATU attacks the triplet state. In fact, the decay at 310 mμ in the early stage proceeds faster with the increase in the ATU concentration. However, in the later stage, the absorbance increases until it reaches a certain constant value, indicating the formation of a final product which has its absorption at this wavelength.

Identification of the Final Product. Since leuco proflavine has an absorption peak at 295 mμ, the above-mentioned increase in absorbance at 310 mμ is to be ascribed to leuco proflavine. Further, no shift of the peak of the dye absorption upon repeated flash illuminations perhaps negates the possibility of the production of a compound other than leuco proflavine.

The molar absorbance of leuco proflavine, at 310 mμ, can easily be evaluated by combining the increase in absorbance at 310 mμ, where no absorption of proflavine exists, and the decrease in the absorbance of proflavine at a proper wavelength. The result is $\varepsilon_{DH}{}^{\lambda=310}=1.35\times10^4\ M^{-1}\ cm^{-1}$.

The Effect of the Concentration of ATU on the Yield of Leuco Dye. As may be seen from Table 5, the yield of leuco proflavine becomes practically constant when $[RH_2]>5\times10^{-3}$ M.

The comparison of Table 5 with Table 3 leads to the conclusion that almost all the triplet reacts with ATU, provided leuco proflavine is produced by the dismutation of the semiquinone (see below). (Since $T+RH_2\rightarrow DH\cdot+RH\cdot$ and $2DH\cdot\rightarrow D+DH_2$, [Yield of DH_2] : [T which reacted with RH_2] $=1:2$.)

TABLE 5. THE YIELD OF LEUCO PROFLAVINE $[D]=3.2\times10^{-5}$ M

$[RH_2]$ M	Yield of DH_2 M
2.0×10^{-3}	1.0×10^{-6}
5.2×10^{-3}	$1.2_3\times10^{-6}$
1.0×10^{-2}	$1.1_5\times10^{-6}$
1.0×10^{-2}	$1.2_4\times10^{-6}$
2.0×10^{-2}	$1.2_4\times10^{-6}$

The Rate Constant of Dismutation of the Semiquinone. The success of the following analysis verifies that leuco proflavine is formed by the dismutation of the semiquinone. This mechanism gives the following rate formula:

$$\frac{d[DH_2]}{dt} = k_6[DH\cdot]^2 \tag{2}$$

Putting the total yield of the triplet state by one flash as $[T]_0$, the concentration of the semiquinone $[DH\cdot]$ at a certain time is written:

$$[DH\cdot] = [T]_0 - 2[DH_2] \tag{3}$$

since $2DH\cdot \rightarrow D+DH_2$ and since the entire triplet state reacts with ATU when the latter concentration is high.

When we substitute Eq. (3) into Eq. (2) and integrate,

$$\frac{1}{2([T]_0-2[DH_2])} = k_6t + \text{constant}. \tag{4}$$

Since ε_{DH} at $\lambda=310$ mμ is negligible,

$$D^{\lambda=310} = \varepsilon_{DH_2}{}^{\lambda=310}[DH_2]d$$

and Eq. (4) can be rewritten:

$$\frac{\varepsilon_{DH_2}d}{2([T]_0\varepsilon_{DH_2}d-2D)} = k_6t + \text{constant}$$

Putting:

$$D_{t=\infty} = \frac{\varepsilon_{DH_2}[T]_0d}{2}$$

one obtains:

$$\frac{\varepsilon_{DH_2}d}{4(D_{t=\infty}-D)} = k_6t + \text{constant}$$

or:

$$\frac{4k_6}{\varepsilon_{DH_2}d}(t-t_0) = \frac{1}{D_{t=\infty}-D} - \frac{1}{D_{t=\infty}-D_{t_0}} \tag{5}$$

An example of the plots of $1/(D_{t=\infty}-D)$ *vs.* the time is given in Fig. 6.

The results of the analysis are givein in Table 6.

The later stage of the decay at 350 mμ, where only the absorbance of the semiquinone is prominent, can also be dealt with in a similar manner. Some examples of the decay curves are shown in Fig. 5; the slopes are $k_6/(\varepsilon_{DH\cdot}{}^{\lambda=350}d)$. The value of the latter quantity is 6.5×10^3 M^{-1} sec^{-1}. Using the k_6-value listed in Table 6, $\varepsilon_{DH\cdot}{}^{\lambda=350}$ can be evaluated thus,

$$\varepsilon_{DH\cdot}{}^{\lambda=350\ m\mu} = 1\times10^4\ M^{-1}\,cm^{-1}$$

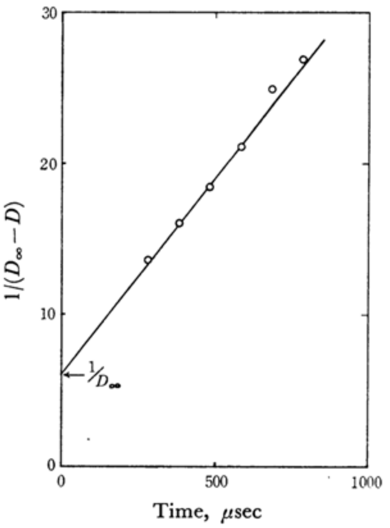

Fig. 6. Change of the absorbance at 310 mμ as interpreted to be due to the formation of leucoproflavine; dye concn. 3.2×10^{-5} M, ATU concn. 1.0×10^{-2} M (input-energy 120J).

TABLE 6. THE RATE CONSTANT OF THE DISMUTATION OF THE SEMIQUINONE

$[RH_2]$ M	$k_6/\varepsilon_{DH_2}{}^{\lambda=310\ m\mu}$ sec^{-1}	k_6 M^{-1} sec^{-1}
2.0×10^{-3}	7.3×10^3	
5.2×10^{-3}	4.3×10^3	
1.0×10^{-2}	4.7×10^3	
1.0×10^{-2}	6.2×10^3	
2.0×10^{-2}	3.6×10^3	
	Average 5×10^3	7×10^8

The Rate Constant for $T+RH_2\rightarrow DH\cdot+RH\cdot$. This can be estimated from the decrease in absorbance at 310 mμ and at 350 mμ in the early stage. In the latter case, $\varepsilon_{DH\cdot}{}^{\lambda=350}$ has an appreciable value and the contribution of the semiquinone to the absorbance was estimated from the extrapolation of the later stage of the run. The values obtained are, respectively, 4.1×10^6 M^{-1} sec^{-1} and 4.4×10^6 M^{-1} sec^{-1}. The average is 4.3×10^6 M^{-1} sec^{-1}.

The Rate Constant for $DH\cdot+O_2\rightarrow D+HO_2$. When $[D]=3.2\times10^{-5}$ M and $[RH_2]=1.0\times10^{-2}$ M, the yield of leuco proflavine is 1.2×10^{-6} M for the degassed solution and 3×10^{-7} M for the solution containing 0.72×10^{-5} M of oxygen. Thus the ratio of the latter to the former is about 0.25. From the rate constant for the reactions of the triplet state with oxygen and with ATU, about half of the produced triplet state can be expected to react with oxygen under the above conditions; hence, the above ratio indicates that the original dye is restored by the reaction of the semiquinone with oxygen. Most plausibly the reaction is $DH\cdot + O_2 \rightarrow D + HO_2$.

Since the influence of oxygen on the decay of the $DH\cdot$ semiquinone was difficult to study, the rate constant for the above reaction, k_8, was estimated in the following way. In general, semiquinone is considered to decay by:

$$DH\cdot + DH\cdot \rightarrow D + DH_2$$

and:

$$DH\cdot + O_2 \rightarrow D + HO_2,$$

but at high concentrations of oxygen, the latter process will predominate and $[DH\cdot]$ decreases according to the first-order formula:

$$[DH\cdot] = [DH\cdot]_0 \exp(-k_8[O_2]t) \qquad (6)$$

where the time origin is set at the time immediately after the flash. When we put Eq. (6) in Eq. (2) and integrate:

$$[DH_2]_{t=\infty} = \frac{k_6[DH\cdot]_0{}^2}{2k_8[O_2]} \qquad (7)$$

Assuming that:

$$[DH\cdot]_0 \simeq \frac{k_5[RH_2]}{k_5[RH_2] + k_7[O_2]} \cdot [T]_0$$

where $[T]_0$ is the total yield of the triplet by one flash, Eq. (7) is rewritten as:

$$[DH_2]_{t=\infty} \simeq \frac{k_6}{2k_8[O_2]}\left(\frac{k_5[RH_2]}{k_5[RH_2]+k_7[O_2]}\right)^2 \cdot [T]_0{}^2$$

In the degassed solution,

$$[DH_2]^0{}_{t=\infty} \simeq \frac{[DH\cdot]}{2} = \frac{[T]_0}{2}$$

as has been shown already. Therefore, the ratio of the yields of leuco proflavine in the presence and in the absence of oxygen is given by the following formula:

$$[DH_2]_{t=\infty} \simeq \frac{2k_6([DH_2]^0{}_{t=\infty})^2}{k_8[O_2]}\left(\frac{k_5[RH_2]}{k_5[RH_2]+k_8[O_2]}\right)^2 \qquad (8)$$

Thus, $k_8[O_2]$ can be determined from the experimental values of $[DH_2]^0{}_{t=\infty}$, $[DH_2]_{t=\infty}$, k_6 and $k_5[RH_2]/(k_5[RH_2]+k_8[O_2])$. When $[D]=3.2\times10^{-5}$ M and $[RH_2]=1.0\times10^{-2}$ M, it turns out that $[DH_2]^0{}_{t=\infty}=1.2\times10^{-6}$ M and $[DH_2]_{t=\infty}=3\times10^{-7}$ M for [added O_2]$=0.72\times10^{-5}$ M. Further,

$$\frac{k_5[RH_2]}{k_5[RH_2] + k_8[O_2]} = 0.7$$

and

$$k_6 = 7\times10^8\ \mathrm{M^{-1}\,sec^{-1}}$$

Hence:

$$k_8[O_2] \simeq 3.5\times10^3\ \mathrm{sec^{-1}} \qquad (9)$$

The concentration of oxygen during the decay of the semiquinone is different from that of the added oxygen, because, during the settlement of the synchroscope, it decreases to a large extent as a result of the reaction with the semiquinone. Therefore, the average concentration of oxygen to be used in Eq. (13) was estimated from the increase in $[DH_2]_{t=\infty}$ when the sample was repeatedly illuminated. The value for k_8 thus obtained was 1.8—$2.7\times10^9\ \mathrm{M^{-1}\,sec^{-1}}$.

Although the above method of evaluation is not very reliable, there is scarcely any doubt that the value of K_8 is of the order of $10^9\ \mathrm{M^{-1}\,sec^{-1}}$.

Reaction between the Triplet State and m-Phenylenediamine. It is interesting to investigate the reaction of the triplet state with *m*-phenylenediamine (MPD), because Oster has established that this substance suppresses the photoreduction very efficiently. The log*D*-*vs.*-time plot at 350 mμ for a system containing MPD is shown in Fig. 7. It is evident that the later stage obeys the first-order rate formula.

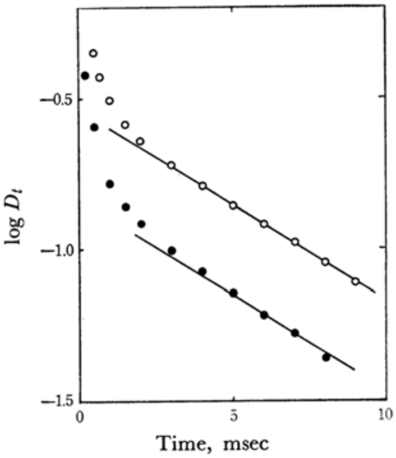

Fig. 7. Change of the absorbance at 350 mμ for the solution containing MPD; dye concn. 1.6×10^{-5} M.
MPD concn.; ○ 5×10^{-4} M, ● 5×10^{-5} M

Since no permanent reaction occurs, it can be concluded that a certain intermediate, X, is produced, and that X regenerates D and MPD according to:

$$X \xrightarrow{k_{10}} D + MPD$$

The rate constant, k_{10}, is $1.5\times10^2\ \mathrm{sec^{-1}}$.

It is most plausible to consider that X is formed by the reaction:

$$T + MPD \xrightarrow{k_9} X$$

The rate constant, k_9 (including the simple deactivation of the triplet state,) is estimated from the early stages of the curves in Fig. 7 by properly correcting the absorbance due to X, which is estimated by the extrapolation of the later part. The result is:

$$k_9 \simeq 3.5\times10^6\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

Discussion

The present results have shown that the elementary reactions which follow the formation of the triplet state are mostly the usual ones. Thus, the reaction of the triplet state with AUT is like other dyes, $T+RH_2 \rightarrow DH\cdot + RH\cdot$. The $2DH\cdot \rightarrow D+DH_2$ process is also an ordinary dismutation. The interaction of two triplet molecules, as well as that of the triplet state with the ground-state dye, in contrast to xanthene and thiazine dyes,[3] does not produce any new transient species; only the mere deactivation of the triplet state occurs. Thus, such reactions as $T+T\rightarrow D^+ + D^-$, $T+D\rightarrow D^+ + D^-$ do not occur. The decay of the triplet state chiefly proceeds as in the second-order, but the nature of the interaction between two triplet dye molecules which ultimately results in the mere deactivation is still quite unknown.

Next, the possibility of the $D^* + D \rightarrow D + T$ process will be briefly discussed with reference to the results in Table 3. If the production of the triplet state occurs only according to the following scheme:

$$
\begin{array}{ll}
(0) & D \xrightarrow{h\nu} D^* \\
(1) & D^* \xrightarrow{k_1} D \\
(2) & D^* + D \xrightarrow{k_2} D + T \\
(3) & T + T \xrightarrow{k_3}
\end{array}
$$

then;

$$\frac{\mathrm{d[T]}}{\mathrm{d}t} = I_{abs}\,\frac{k_2[\mathrm{D}]}{k_1+k_2[\mathrm{D}]} - k_3[\mathrm{T}]^2 \qquad (10)$$

In evaluating the total yield of the triplet state immediately after the flash, the second term on the right side may be neglected and a good approximation still achieved. That the yield of the triplet state tends to a constant value with the increase in the dye concentration, can be interpreted in the following way if the a) condition, $k_2[\mathrm{D}]\gg k_1$ holds. Thus, in this case Eq. (10) is reduced to:

$$\frac{\mathrm{d[T]}}{\mathrm{d}t} = I^0(t)\,(1-\mathrm{e}^{-2.303\,\varepsilon_\mathrm{D}[\mathrm{D}]d})$$

where $I_0(t)$ is the flash intensity at time t, and the value of d is estimated to be about 1 cm. Integration gives:

$$\ln\,(\mathrm{e}^{2.3\,\varepsilon_\mathrm{D}[\mathrm{D}]d}-1) = \ln\,(\mathrm{e}^{2.3\,\varepsilon_\mathrm{D}[\mathrm{D}]_0 d}-1) - \varepsilon_\mathrm{D} d\int I_0(t)\mathrm{d}t \qquad (11)$$

If the b) condition, $\mathrm{e}^{2.3\,\varepsilon_\mathrm{D}[\mathrm{D}]d}\gg1$, holds, then Eq. (11) leads to:

$$\varepsilon_\mathrm{D}[\mathrm{D}]d = \varepsilon_\mathrm{D}[\mathrm{D}]_0 d - \text{constant.}$$

Hence,

$$[\mathrm{T}] = [\mathrm{D}]_0 - [\mathrm{D}] = \text{constant.}$$

The results in Table 3 imply that both conditions, a) and b), should hold when the dye concentration is $\sim10^{-5}$ M. There is scarcely any doubt for the holding of the b) condition. The a) condition requires that $k_2/k_1 > 10^5\ \mathrm{M}^{-1}$, which seems to be moderately consistent with Oster's value, $3.6\times10^4\ \mathrm{M}^{-1}$.

However, it is obvious that the interpretation can be given equally well on the basis of the following scheme:

$$
\begin{array}{ll}
(0) & D \xrightarrow{h\nu} D^* \\
(1') & D^* \xrightarrow{k_1'} D \\
(2') & D^* \xrightarrow{k_2'} T
\end{array}
$$

Then:

$$\frac{\mathrm{d[T]}}{\mathrm{d}t} = I_{abs}\,\frac{k_2'}{k_1'+k_2'}$$

for which the a) condition is not necessary. Thus, the constant triplet yield in the high concentration region of dye shown in Table 3 does not show whether process (2) or (2′) is occurring.

The elementary reactions established in the present investigation, along with the ε-values determined, are summarized in Table 7.

TABLE 7.

	Scheme	
(0)	$D \xrightarrow{h\nu} D^*$	
(1)	$D^* \rightarrow D$	
(2)	$D^* + D \rightarrow D + T$	
(3)	$T + T \rightarrow$	$k_3 = 0.8$—$1.4\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(4)	$T \rightarrow D$	$k_4 \lesssim 6\times10^3\ \mathrm{sec}^{-1}$
(5)	$T + RH_2 \rightarrow DH\cdot + RH\cdot$	$k_5 = 4.3\times10^6\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(6)	$DH\cdot + DH\cdot \rightarrow DH_2 + D$	$k_6 = 7\times10^8\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(7)	$T + O_2 \rightarrow D + O_2$	$k_7 = 1.5$—$4.7\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(8)	$DH\cdot + O_2 \rightarrow D + HO_2\cdot$	$k_8 = 1$—$3\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(9)	$T + MPD \rightarrow X$ (Including $T + MPD \rightarrow D + MPD$)	$k_9 \simeq 3.5\times10^6\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$
(10)	$X \rightarrow D + MPD$	$k_{10} = 1.5\times10^2\ \mathrm{sec}^{-1}$
	$\varepsilon_{DH_2}{}^{\lambda=310\ \mathrm{m}\mu} = 1.3_5\times10^4\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$	
	$\varepsilon_{DH\cdot}{}^{\lambda=350\ \mathrm{m}\mu} = 1\times10^4\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$	
	$\varepsilon_{T}{}^{\lambda=350\ \mathrm{m}\mu} = 2\times10^4\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$	
	$\varepsilon_{T}{}^{\lambda=700\ \mathrm{m}\mu} = 2\times10^4\ \mathrm{M}^{-1}\,\mathrm{cm}^{-1}$	

Some of the rate constants listed above may be compared with those of Oster's values given below:

$$k_4 = 2.5\times10^2\ \mathrm{sec}^{-1}$$

$$k_5 = 1.0\times10^6\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$$

$$k_9 = 6.6\times10^9\ \mathrm{M}^{-1}\ \mathrm{sec}^{-1}$$

The k_5 values are not very much apart, but the k_4 and k_9 values are different in order of magnitude, although our k_4 and k_9 values are not very accurate.

It should be noted that Oster's k_9 value is a theoretical value for the encounter-determining rate constant, while ours is a value determined experimentally. Since Oster's k_4 and k_5 were evaluated using the k_9 value, the above approximate agreement of the k_5 values seems to be accidental. It might be related to the fact that he evaluated his k_5 value using the results of experiments on rather low ATU concentrations. The reason why he used the data pertaining to low ATU concentrations is that he considered a different type of reaction to occur simultaneously in the presence of a large quantity of ATU. According to the present investigation, however, the reaction seems to be simple under such conditions. Thus, our results indicate not only that the triplet state is a sole reactive species, but also that the entire triplet state almost completely reacts with ATU (when its concentration is higher than 5×10^{-3} M), thus producing the semiquinone.

In view of these facts, it seems desirable to reinvestigate the steady-light reaction. This will be reported elsewhere. Apart from the above points, however, the present results seem to be consistent with Oster's scheme.

The authors wish to express thier thanks to Professor Shunji Kato and Professor Michio Okuda for their kind advice. They also wish to thank Dr. Akira Kira for his help during the course of these experiments.