The Switch-over from the D–R to the D–D Mechanism in the Photoreduction of Methylene Blue

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One of the present authors (M. K.) and his collaborators have found that some thiazine dyes undergo photoreduction in the absence of any reducing agents,[1,2] and that the primary process is an electron transfer between the triplet dye and the ground-state dye.[3,4] This finding has led to the expectation that the photoreduction of thiazine dyes may in general be classified into two types according to their primary processes. The first type begin with an electron transfer (or a hydrogen transfer) from the reductant to the dye (the D–R mechanism), whereas the second type is initiated by an electron transfer between the excited dye and the ground-state dye molecules (the D–D mechanism). However, evidence for a switch-over from one mechanism to the other has recently been presented for the first time in connection with the photoreduction of eosine by allythiourea (ATU).[5] The purpose of the present paper is to report a similar switch-over of mechanisms taking place in the photoreduction of methylene blue with such reductants as ATU and EDTA. The evidence was obtained in two ways, from an investigation of the rate formula for a run and from the effect of the dye concentration on the quantum yield of the photoreduction. In addition, an attempt was made to determine φ_{S-T}, the probabilities of a transition from the singlet-excited state to the triplet state.

Experimental

Material. — *Methylene Blue.* — Grübler's special-grade sample was recrystallized three times from *n*-butanol. $\varepsilon_{max}=6.0\times10^4$.

ATU and EDTA and the other inorganic reagents were recrystallized three times from water.

Apparatus and Procedure.—The pH of the sample solution was controlled by a phosphate buffer solution (1/50 M), and most experiments were performed at pH 7.2. The sample was degassed thoroughly, freezing and thawing being repeated six times.

The apparatus and procedure were the same as have already reported on,[3] apart from the method of following the reaction.

The reactions were carried out in an apparatus equipped with a microammeter and photocell; the light beam entered through a cut-off filter, and passed through the reaction cell and then via an interference filter ($\lambda_{max}=669$ mμ; half-width$=18$ mμ) to the photocell.

When the shift in the absorption peak was observed, a new absorption spectrum in the 600 mμ to 700 mμ region was recorded on a Hitachi spectrophotometer (EPU-2A), and the kinetics were investigated by employing Blaisdell's method. The light intensity was measured by using a thermopile (Kipp & Zonen Co.). The reactions were all carried out at 30.0°C.

Both EDTA and ATU scarcely affect the absorption spectra of methylene blue at all. Usually photobleaching occurred without a shift of the absorption peak. When air was introduced at the end of the reaction, coloration was restored in a few minutes in the methylene blue - EDTA system, whereas a longer time was required in the case of the methylene blue - ATU system, about ten minutes being necessary for an 80% recovery of the original dye.

Results and Discussion

Rate Formula for a Run.—In the case of EDTA, the relation between $\ln(e^{\alpha cd}-1)$ and time, t, (α, c and d are, respectively, the average

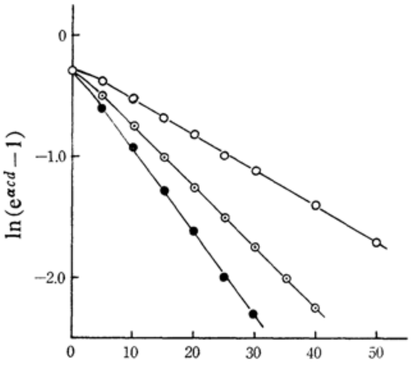

Fig. 1. Plots of $\ln(e^{\alpha cd}-1)$ against time.
pH$=7.2$, $[\mathrm{MB}]_0=9.0\times10^{-6}$ M
○ : [EDTA]$=1.4\times10^{-3}$ M
⊙ : 3.0×10^{-3} M ● : 2.0×10^{-2} M

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[1] Y. Usui, H. Obata and M. Koizumi, This Bulletin, 34, 1649 (1961).

[2] Y. Usui and M. Koizumi, ibid., 34, 1651 (1961).

[3] M. Koizumi, H. Obata and S. Hayashi, ibid., 37, 108 (1964).

[4] S. Kato, M. Morita and M. Koizumi, ibid., 37, 117 (1964).

[5] K. Ohno, Y. Usui and M. Koizumi, ibid., 38, 1022 (1965).

molar absorption coefficient, the concentration of dye, and the thickness of the cell) is satisfactorily linear for all the experiments when the concentration of EDTA is larger than 1.0×10^{-4} M and when the dye concentration is less than 10^{-5} M. As Fig. 1 shows, the linear relation holds in most cases until two-thirds or more of the dye had been bleached. This means that the rate is simply proportional to the absorption of light, for in this case the rate is given by:

$$\frac{-\mathrm{d}[\mathrm{D}]}{\mathrm{d}t}=\Phi I_{abs}=\frac{10^3 I_0\Phi}{d}(1-\mathrm{e}^{\alpha[\mathrm{D}]d}) \qquad (1)$$

where Φ is the quantum yield and I_0 is the intensity of the exciting light (expressed in moles per cm^2 per sec.), and one obtains, by integrating (1):

$$\ln(\mathrm{e}^{\alpha d[\mathrm{D}]}-1)-\ln(\mathrm{e}^{\alpha d[\mathrm{D}]_0}-1)=10^3\Phi I_0\alpha t \qquad (2)$$

where $[\mathrm{D}]_0$ is the initial concentration of dye. From the plots in Fig. 1 one can evaluate the quantum yield, Φ, since $I_0\alpha$ is obtained easily by measuring the light absorption.

When the concentration of EDTA is reduced to 1×10^{-4} M, the situation becomes a little different. Thus, when the original dye concentration is 5.6×10^{-6}—1.6×10^{-5} M relation 2 still holds until two-thirds of the original dye has been bleached, whereas when the dye concentration is higher, Eq. 2 ceases to be applicable and deviations become apparent when one-third of the dye has been bleached.

When ATU is the reducing agent, its concentration must be higher than $\sim 4\times 10^{-2}$ M for formula 2 to express a run down to a two-thirds bleaching of the original dye. When the concentration of ATU is decreased, although relation 2 still holds in the earlier stages down to 4.0×10^{-3} M of ATU, it becomes less applicable as the reaction proceeds, until at a concentration of $\sim 1\times 10^{-3}$ M ATU it becomes entirely unsatisfactory. Parallel with this, the plot of 1/O.D. against t becomes more linear, and when the concentration of ATU is $\sim 10^{-3}$ M the linearity of the 1/O.D. versus t plot becomes almost satisfactory. This implies that, with the decrease in ATU, the second-order reaction with regard to the dye becomes predominant. Thus, in this case:

$$\frac{1}{[\mathrm{D}]}-\frac{1}{[\mathrm{D}]_0}=kt \qquad (3)$$

or

$$\frac{1}{\mathrm{O.D}}-\frac{1}{(\mathrm{O.D})_0}=\frac{k}{\varepsilon d}t \qquad (3')$$

The above tendency is quite evident and always exists irrespective of the dye concentration, apart from the fact that the larger the dye concentration, the larger the concentration of ATU at which Eq. 2 deteriorates. Figures 2a and 2b show typical examples of the above tendency. The effect of the dye concentration on the rate formula will be discussed later.

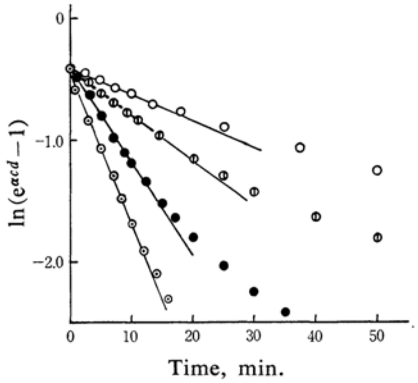


Fig. 2a. Plots of $\ln(\mathrm{e}^{\alpha cd}-1)$ against time.
pH=7.2, $[\mathrm{MB}]_0=(8.2\pm 0.2)\times 10^{-6}$ M
○: $[\mathrm{ATU}]=4.0\times 10^{-3}$ M ⦶: 8.0×10^{-3} M
●: 1.4×10^{-2} M ⊙: 4.0×10^{-2} M

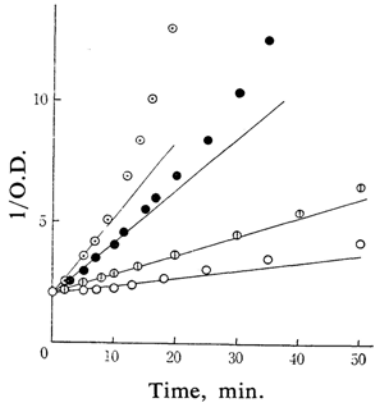
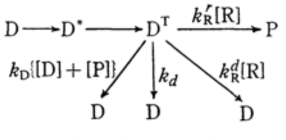


Fig. 2b. Plots of 1/O.D. against time.
pH=7.2, $[\mathrm{MB}]_0=(8.2\pm 0.2)\times 10^{-6}$ M
○: $[\mathrm{ATU}]=4.0\times 10^{-3}$ M ⦶: 8.0×10^{-3} M
●: 1.4×10^{-2} M ⊙: 4.0×10^{-2} M

An attempt to determine $\varphi_{\mathrm{S-T}}$ from the effect of the reductant concentration on Φ was made as follows. When the concentration of reductant is large enough for Eq. 2 to hold, there is scarcely any doubt that the reaction proceeds as follows:



(P denotes the photoproduct, perhaps leuco dye)

On the basis of this scheme, the following rate formula is derived:

$$-\frac{d[D]}{dt}=\frac{\varphi_{S-T}k_R{}^r[R]I_{abs}}{k_d+k_R{}^S[R]+k_D[D]_0}$$

where φ_{S-T} is the transition probability for the singlet excited state to the triplet state and $k_R{}^S$ is the sum of $k_R{}^r$ and $k_R{}^d$ (the rate constant for mere deactivation by R). Further, it is assumed that the ground-state dye and the leuco dye deactivate the triplet state at a diffusion-controlled rate.

From the above formula, it follows that:

$$\Phi=\frac{\varphi_{S-T}k_R{}^r[R]}{k_d+k_R{}^S[R]+k_D[D]_0} \tag{4}$$

Taking the inverse of Eq. 4, one gets:

$$\frac{1}{\Phi}=\frac{1}{\varphi_{S-T}}\frac{k_R{}^S}{k_R{}^r}+\frac{1}{\varphi_{S-T}}\left\{\frac{k_d}{k_R{}^r}+\frac{k_D[D]_0}{k_R{}^r}\right\}\frac{1}{[R]} \tag{5}$$

If one assumes that $k_R{}^S=k_R{}^r$, then the value of φ_{S-T} can immediately be obtained by applying Eq. 5 to the experimental data. This was attempted first for the case of EDTA. Some of the necessary data are given in Table I, while the $1/\Phi$—$1/[R]$ plots are given in Fig. 3.

TABLE I

a) $[MB]=9.0\times10^{-6}$ M, pH=6.7

$[EDTA]\times10^3$ M	Φ	$[EDTA]\times10^3$ M	Φ
20	0.154	3.0	0.102, 0.099
10	0.144	2.0	0.080
6.0	0.127	1.6	0.067
5.0	0.133	1.4	0.061
4.0	0.116		

b) $[MB]=9.0\times10^{-6}$ M, pH=7.2

$[EDTA]\times10^3$ M	Φ	$[EDTA]\times10^3$ M	Φ
20	0.170	3.0	0.103
10	0.165	2.0	0.080
5.0	0.133	1.4	0.066

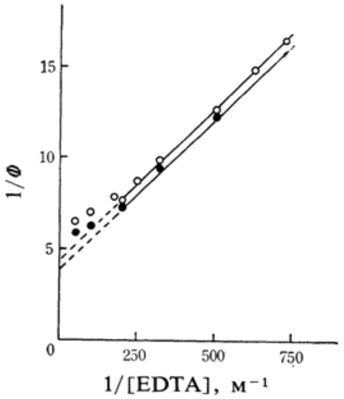


Fig. 3. Plots of $1/\Phi$ against EDTA concentration.
$[MB]_0=9.0\times10^{-6}$ M
○: pH=6.7, ●: pH=7.2

As may be seen in Fig. 3 the linearity holds satisfactorily except in the region of very high concentrations of EDTA. The values of φ_{S-T} obtained are 0.22 and 0.24, for pH=6.7 and 7.2 respectively. These values agree quite well with Oster's value of 0.21[6] at pH=7.0. Although there is some doubt concerning the assumption that $k_R{}^r=k_R{}^S$, we would like tentatively to take this value as a real value of φ_{S-T}. Besides, from the slope of the curves one gets:

$$\frac{k_d}{k_R{}^r}+\frac{k_D[D]_0}{k_R{}^r}=3.7\times10^{-3}\text{ M}$$

In the case of ATU, Eq. 2 holds when $[ATU]\gtrsim4\times10^{-3}$ M, at least in the earlier stages of bleaching; hence, as in the above case, an attempt was made to apply Eq. 2 to the results obtained under such experimental conditions. The necessary data are given in Table II, while the $1/\Phi$—$1/[R]$ plot is shown in Fig. 4.

TABLE II

$[MB]=(8.2\pm0.2)\times10^{-6}$ M, pH=7.2

$[ATU]\times10^2$ M	$\Phi\times10^3$	$[ATU]\times10^2$ M	$\Phi\times10^3$
0.40	0.96	2.0	2.92
0.48	1.15	4.0	5.0
0.80	1.60	6.0	6.9
1.0	2.10	8.0	7.4
1.4	2.81		

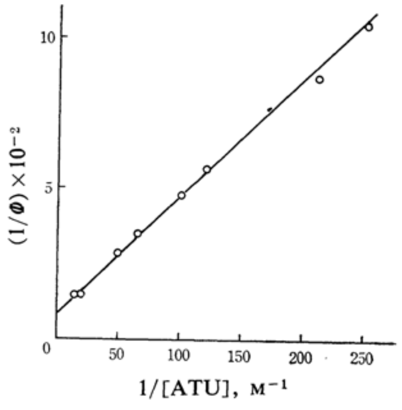


Fig. 4. Plot of $1/\Phi$ against $1/[ATU]$.
pH=7.2, $[MB]_0=(8.2\pm0.2)\times10^{-6}$ M

As can be seen from Fig. 4, the plot is linear, and from its slope and the intercept one gets $(k_d+k_D[D]_0)/\varphi_{S-T}k_R{}^r=3.9$ M and $k_R{}^S/k_R{}^r\varphi_{S-T}=80$. If one assumes that $k_R{}^S=k_R{}^r$, then one gets $\varphi_{S-T}=1.3\times10^{-2}$, which is very small compared with that for EDTA. The mere deactivation of the triplet dye by an ATU molecule seems quite plausible.

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[6] N. Wotherspoon and G. Oster, *J. Am. Chem. Soc.*, **79**, 4836 (1957).

The Effect of the Dye Concentration on Φ.—This can be dealt with in one of two different ways, depending on the situation. The first method is used in cases in which the D–R mechanism predominates. As may be judged from Eq. 2, the mere deactivation of the triplet dye by the ground state dye causes a decrease in the quantum yield with the increase in the dye concentration. However, when the D–D mechanism begins to take part, a deviation from Eq. 2 is to be expected. The other method is used in cases in which both D–R and D–D mechanisms participate and at the same order of magnitude. In these cases, since the kinetic features of the later steps of D–D mechanism are not clear, it is desirable to discuss the experimental data from a different angle.

Judging from the applicability of Eq. 2, the D–R mechanism is considered to hold for EDTA in general, while for ATU it is dominant only when $[\mathrm{ATU}] > 1.4\times10^{-2}$ M.

EDTA.—The effect of the dye concentration was examined at two fixed concentrations of EDTA. The results are given in Table III, while the $1/\Phi$—$[\mathrm{D}]_0$ plot is given in Fig. 5.

TABLE III

a) $[\mathrm{EDTA}]=2.0\times10^{-3}$ M, pH=7.2

$[\mathrm{MB}]\times10^6$ M	$\Phi\times10^2$	$[\mathrm{MB}]\times10^6$ M	$\Phi\times10^2$
11.4	6.55	4.8	8.71
9.8	7.50	4.5	8.20
9.1	7.96	3.4	9.50
7.8	7.75	2.6	9.70

b) $[\mathrm{EDTA}]=4.0\times10^{-4}$ M, pH=7.2

$[\mathrm{MB}]\times10^6$ M	$\Phi\times10^2$	$[\mathrm{MB}]\times10^2$ M	$\Phi\times10^2$
3.2	2.23	8.6	1.75
5.6	2.01	9.5	1.70
6.6	1.90	9.9	1.58
7.2	1.85	12.7	1.41

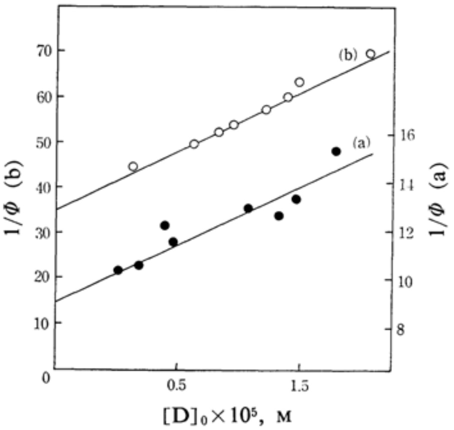

Fig. 5. Plots of $1/\Phi$ against initial dye concentration.
pH=7.2
○ : $[\mathrm{EDTA}]=4.0\times10^{-4}$ M
● : $[\mathrm{EDTA}]=2.0\times10^{-3}$ M

Although the points are subject to a rather large amount of scatter in the case of a), there does not seem to be any tendency for them to deviate from a linear plot.

From Eq. 4, one gets (R is denoted as E):

$$\frac{1}{\Phi}=\left\{\frac{1}{\varphi_{\mathrm{S-T}}}+\frac{1}{\varphi_{\mathrm{S-T}}}\frac{k_d}{k_{\mathrm{R}}{}^r}\frac{1}{[\mathrm{E}]}\right\}+\frac{1}{\varphi_{\mathrm{S-T}}}\frac{k_{\mathrm{D}}}{k_{\mathrm{R}}{}^r[\mathrm{E}]}[\mathrm{D}]_0 \qquad (6)$$

and from the intercept and the slope of the line b in Fig. 5, one gets:

$$\frac{1}{\varphi_{\mathrm{S-T}}}\left(1+\frac{k_d}{k_{\mathrm{R}}{}^r[\mathrm{E}]}\right)=9.0$$

$$\frac{1}{\varphi_{\mathrm{S-T}}}\frac{k_{\mathrm{D}}}{k_{\mathrm{R}}{}^r[\mathrm{E}]}=4.8\times10^5\ \mathrm{M}^{-1}$$

With the value of $\varphi_{\mathrm{S-T}}$ (0.24) obtained above and by putting $k_d=3.0\times10^4\ \mathrm{sec}^{-1}$,[4] one can determine $k_{\mathrm{R}}{}^r$ and k_{D} separately.

From the results in a),

$$k_{\mathrm{R}}{}^r=1.3\times10^7\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$
$$k_{\mathrm{D}}=3.0\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

while from the results in b),

$$k_{\mathrm{R}}{}^r=1.0\times10^7\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$
$$k_{\mathrm{D}}=2.5\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

It is worth noting that, when $[\mathrm{D}]_0=9.0\times10^{-6}$ M, $k_{\mathrm{R}}{}^r[\mathrm{E}]$, $k_{\mathrm{D}}[\mathrm{D}]_0$ and k_d are, respectively, 2.6×10^4, 2.7×10^4 and $3.0\times10^4\ \mathrm{sec}^{-1}$ and are of the same order of magnitude. The value of $\frac{1}{\varphi_{\mathrm{S-T}}}\left(\frac{k_d}{k_{\mathrm{R}}{}^r}+\frac{k_{\mathrm{D}}}{k_{\mathrm{R}}{}^r}[\mathrm{D}]_0\right)$ (see Eq. 5), as calculated by using the above rate constants and by putting $[\mathrm{D}]_0=9.0\times10^{-6}$ M, is 1.8×10^{-2} M, which is in good agreement with the experimental value, 1.6×10^{-2} M, obtained from the plot in Fig. 3. At $[\mathrm{EDTA}]=1.0\times10^{-4}$ M, a wider range

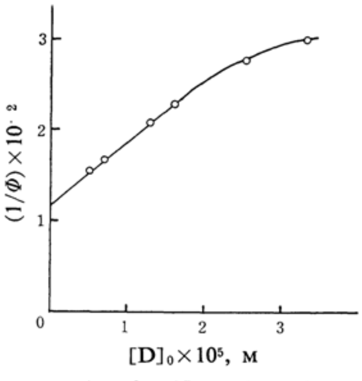

Fig. 6. Polt of $1/\Phi$ against initial dye concentration.
pH=7.2, $[\mathrm{EDTA}]=1.0\times10^{-4}$ M

of dye concentrations was chosen, i. e., from 5.6×10^{-6} to 3.3×10^{-5} M. In the case of the higher concentrations of dye, a spacer (7 mm. thick) was used to measure the optical density accurately. Equation 2 holds until one-third of the original dye has been bleached, even when the dye concentration is $\sim2.5\times10^{-5}$ M. A $1/\Phi$—$[\mathrm{D}]_0$ plot is shown in Fig. 6. It may be seen that the deviation from a linear plot begins at 2.5×10^{-5} M of dye. By extrapolating the linear part, one gets from the intercept:

$$\frac{k_{\mathrm{R}}{}^r[\mathrm{E}]+k_d}{\varphi_{\mathrm{S-T}}k_{\mathrm{R}}{}^r[\mathrm{E}]}=120$$

and from the slope:

$$\frac{k_{\mathrm{D}}}{\varphi_{\mathrm{S-T}}k_{\mathrm{R}}{}^r[\mathrm{E}]}=6.4\times10^6\ \mathrm{M}^{-1}$$

With $\varphi_{\mathrm{S-T}}=0.24$ and $k_d=3.0\times10^4\ \mathrm{sec}^{-1}$, one gets:

$$k_{\mathrm{R}}{}^r=1.1\times10^7\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$
$$k_{\mathrm{D}}=1.7\times10^9\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

From the above results, it may be concluded that as long as the concentration of EDTA is moderate, only the D–R mechanism prevails.

ATU.—Different behaviours are expected in the higher and the lower concentration regions of ATU, because the rate formula for a run is Eq. 2 in the former case and Eq. 3 in the latter case. Therefore, rather extensive studies were made by varying the concentration of ATU over a wide range.

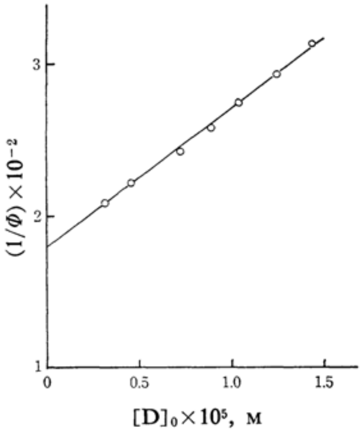

Fig. 7. Plot of $1/\Phi$ against initial dye concentration.
pH=7.2, [ATU]=4.4×10^{-2} M

TABLE IV

[ATU]=4.4×10^{-2} M, pH=7.2

[MB]×10⁶ M	Φ×10³	[MB]×10⁶ M	Φ×10³
14.4	3.21	7.1	4.15
12.5	3.4	4.6	4.51
10.3	3.65	3.2	4.8
8.8	3.9	2.6	5.80

When the concentration of ATU is 8.0×10^{-2} or 4.4×10^{-2} M, Eq. 2 fits as a rate formula. A plot of $1/\Phi$ against the original dye concentration is given in Fig. 7. Only the data for [ATU]=4.4×10^{-2} M are given in Table IV.

From the intercept and the slope of the plot shown in Fig. 8, one obtains:

$$\frac{1}{\varphi_{\mathrm{S-T}}}\left\{\frac{k_{\mathrm{R}}{}^{\mathrm{S}}}{k_{\mathrm{R}}{}^r}+\frac{k_d}{k_{\mathrm{R}}{}^r[\mathrm{A}]}\right\}=180$$

$$\frac{k_{\mathrm{D}}}{\varphi_{\mathrm{S-T}}k_{\mathrm{R}}{}^r[\mathrm{A}]}=9.0\times10^6\ \mathrm{M}^{-1}$$

Using the value of $k_{\mathrm{R}}{}^{\mathrm{S}}/k_{\mathrm{R}}{}^r\varphi_{\mathrm{S-T}}=80$, one gets $k_{\mathrm{D}}/k_{\mathrm{R}}{}^r=9.5\times10^4$, and, further, by the use of the k_d-value;

$$k_{\mathrm{R}}{}^r=1.1\times10^5\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$
$$k_{\mathrm{D}}=1.0\times10^{10}\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$$

$k_{\mathrm{R}}{}^r$ can also be obtained by applying Eq. 5 to the plot in Fig. 4 and by using the value of $k_{\mathrm{D}}/k_{\mathrm{R}}{}^r$ obtained above. The value thus obtained is $1.8\times10^5\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$, which is in good agreement with the above value. Although the values for [ATU]=8×10^{-2} M are not so accurate, the value of $k_{\mathrm{R}}{}^r$ obtained is of the order of 10^5.

To examine the dye concentration effect more extensively, the concentration of dye was varied over a wider range at a fixed ATU

TABLE V

[ATU]=4.0×10^{-2} M, pH=7.2

[MB]×10⁵ M	Φ×10³	[MB]×10⁵ M	Φ×10³
0.32	4.70	2.36	2.82
0.56	4.30	2.40	2.82
0.66	4.16	3.30	2.56
1.03	3.65	3.46	2.54
1.37	3.35		

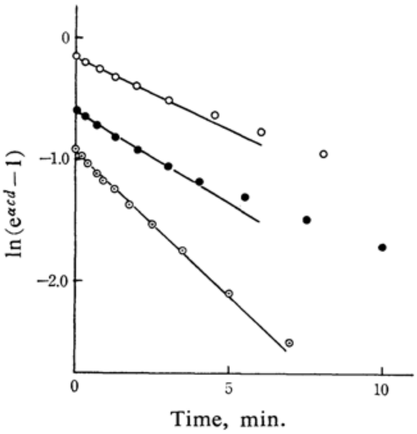

Fig. 8a. Plots of $\ln(e^{\alpha cd}-1)$ against time.
pH=7.2, [ATU]=4.0×10^{-2} M
○ : $[\mathrm{MB}]_0=3.46\times10^{-5}$ M
● : 2.36×10^{-5} M ⊙ : 5.6×10^{-6} M

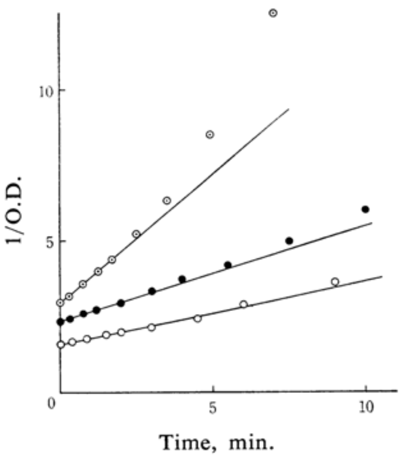

Fig. 8b. Plots of 1/O.D. against time.
pH=7.2, [ATU]=4.0×10^{-2} M
○ : $[\text{MB}]_0=3.46\times10^{-5}$ M
● : 2.36×10^{-5} M ⊙ : 5.6×10^{-6} M

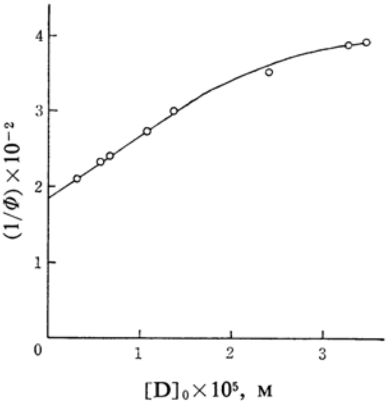

Fig. 9. Plot of $1/\Phi$ against initial dye concentration.
pH=7.2, [ATU]=4.0×10^{-2} M

concentration (4.0×10^{-2} M). The results are given in Table V. Figures 8a and 8b show that with the increase in the dye concentration, the applicability of Eq. 2 gets worse, while that of 3 gets better.

Figuare 9, which gives the $1/\Phi$—$[\text{D}]_0$ plot, shows that deviation becomes appreciable at 2×10^{-5} M of dye. From the intercept and the slope of the straight part,

$$\frac{1}{\varphi_{\text{S-T}}}\left\{\frac{k_{\text{R}}{}^{\text{S}}}{k_{\text{R}}{}^{r}}+\frac{k_d}{k_{\text{R}}{}^{r}[\text{A}]}\right\}=185$$

$$\frac{k_{\text{D}}}{\varphi_{\text{S-T}}k_{\text{R}}{}^{r}[\text{A}]}=8.5\times10^{6}\ \text{M}^{-1}$$

With the use of $\varphi_{\text{S-T}}=0.24$ and $k_{\text{R}}{}^{\text{S}}/k_{\text{R}}{}^{r}=20$, one gets:

$$k_{\text{R}}{}^{r}=1.1\times10^{5}\ \text{M}^{-1}\ \text{sec}^{-1}$$

and $$k_{\text{D}}=9.0\times10^{9}\ \text{M}^{-1}\ \text{sec}^{-1}$$

When the concentration of ATU is low, Eq. 3′ instead of Eq. 2 becomes applicable, as Fig. 10 shows. At the same time, a slight shift in the main absorption peak of the dye becomes apparent. The kinetics were investigated, therefore, by employing Blaisdell's method.

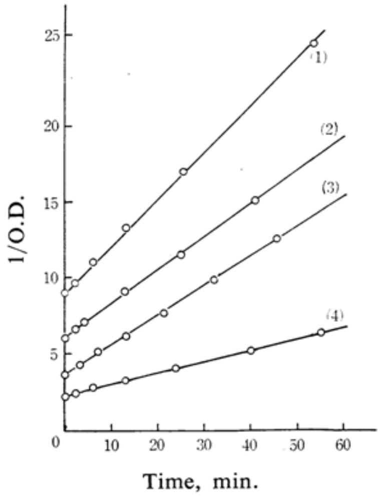

Fig. 10. Plot of 1/O.D. against time.
pH=7.2, [ATU]=8.0×10^{-4} M,
(1) : $[\text{MB}]_0=1.8\times10^{-6}$ M, (2) : 2.9×10^{-6} M
(3) : 4.7×10^{-6} M (4) : 7.9×10^{-6} M

TABLE VI

a) [ATU]=8.0×10^{-4} M, pH=7.2

$[\text{BM}]\times10^6$ M	$\Phi\times10^4$	$\Phi_{\text{D-R}}\times10^4$	$\Phi_{\text{D-D}}\times10^4$
9.6	6.03	1.50	4.53
7.9	6.70	1.73	4.97
6.1	7.51	2.07	5.44
5.2	7.63	2.33	5.30
4.7	8.20	2.43	5.77
3.9	7.51	2.71	4.80
3.5	7.13	2.87	4.26
2.9	6.42	3.20	3.22
2.2	5.88	3.55	2.33
1.9	6.10	3.77	2.33

b) [ATU]=2.0×10^{-3} M, pH=7.2

$[\text{MB}]\times10^6$ M	$\Phi\times10^4$	$\Phi_{\text{D-R}}\times10^4$	$\Phi_{\text{D-D}}\times10^4$
21.5	3.03	1.93	1.10
17.6	3.70	2.22	1.48
15.3	4.47	2.57	1.90
13.4	4.90	2.85	2.05
10.8	5.77	3.44	2.33
10.5	5.96	3.48	2.48
9.3	6.89	3.79	3.10
8.6	7.60	4.02	3.58
7.1	7.67	4.32	3.35
6.2	7.87	5.04	2.83
5.6	7.74	5.32	2.42
5.2	7.90	5.65	2.25
2.8	9.25	7.84	1.41
1.27	11.2	10.6	0.6

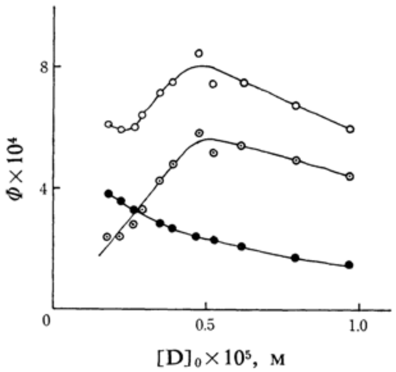

Fig. 11. Plots of Φ, Φ_{D-R} and Φ_{D-D} against initial dye concentration.
pH=7.2, [ATU]=8.0×10⁻⁴ M
○ : Φ ● : Φ_{D-R} ⊙ : Φ_{D-D}

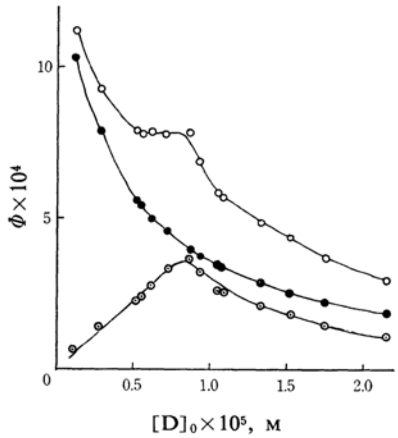

Fig. 12. Plots of Φ, Φ_{D-R} and Φ_{D-D} against initial dye concentration.
pH=7.2, [ATU]=2.0×10⁻³ M
○ : Φ ● : Φ_{D-R} ⊙ : Φ_{D-D}

Under such conditions, there is scarcely any doubt that, in addition to a D–R mechanism, a D–D mechanism plays a large part in the reaction. Hence, the total quantum yield should consist of two parts, Φ_{D-R} and Φ_{D-D}, which are, respectively, the quantum yields due to the D–R and the D–D mechanisms. One can estimate Φ_{D-R} by inserting the values of the rate constants obtained above and the concentrations of ATU and dye into Eq. 4. Φ_{D-D}, then, is obtained as the difference between Φ and Φ_{D-R}. The results are shown in Table VI and in Fig. 11 and 12, which show that the curves for Φ_{D-D} are quite similar in the two series of experiments.

Thus, Φ_{D-D} increases with the dye concentration until it reaches its maximum at $[D]_0\approx(5-8)\times10^{-6}$ M, where $\Phi_{D-D}=(4-6)\times10^{-4}$, and then decreases again.

The results can be interpreted by assuming the analogous scheme proposed for the photoreduction in the absence of any reducing agent :4)

$$\begin{tikzcd}
D^{T} \arrow[rrr, "{k_D^r[D]}"] \arrow[d, "k_d"'] \arrow[dr, "{k_R^d[A]}"] \arrow[drr, "{k_D\{[D]+[P]\}}"] & & & D^{+} \arrow[r, dotted, no head] \arrow[d, "k_d'"'] \arrow[dr, "{k_D'\{[D]+[P]\}}"] & D^{-} \arrow[r, "{k_R'[A]}"] & {} \\
D & D & D & D & D &
\end{tikzcd}$$

From this scheme, one gets:

$$\Phi_{D-D}=\frac{\varphi_{S-T}k_D{}^r[D]k_R{}'[A]}{\{k_R{}^S[A]+k_d+k_D[D]_0\}\{k_R{}'[A]+k_D{}'[D]_0+k_d{}'\}} \qquad (7)$$

At very low concentrations of D, Φ at the initial stage is approximated by:

$$\Phi_{D-D}\frac{\varphi_{S-T}k_D{}^r[D]_0k_R{}'[A]}{\{{}_R{}^S[A]+k_d\}\{k_R{}'[A]+k_d{}'\}}$$

which increases with $[D]_0$, while at high concentrations of D,

$$\Phi_{D-D}\frac{\varphi_{S-T}k_D{}^rk_R{}'[A]}{k_Dk_D{}'[D]_0}$$

which decreases with $[D]_0$.

If the second factor in the denominator in Eq. 7 is missing, then Φ_{D-D} should increase monotonously with $[D]_0$, without showing any maximum. Thus, in order to interpret the present results, it is necessary to take into account the deactivation of the redox intermediate, $D^+\cdots D^-$, by the ground state dye and (perhaps) by the leuco dye produced.

Conclusions

It may be concluded from the present results that a switch-over in mechanism really does take place in the photoreduction of methylene blue by EDTA and ATU. This was verified consistently from the rate formula for a run and from the dye concentration effect on the quantum yield. The rate constants of the elementary reactions obtained in the present paper are summarized in the following table:

	φ_{S-T}	$k_R{}^r/k_R{}^S$	$k_R{}^r$ M⁻¹sec⁻¹	k_D M⁻¹sec⁻¹
EDTA	(0.23)	(1)	1.2×10⁷	2.4×10⁹
ATU	(0.23)	(0.052)	1.1×10⁵	9.5×10⁹

These values were obtained by assuming that

$$k_d=3.0\times10^4\ \mathrm{sec}^{-1}$$

It is seen from the above table that EDTA is a hundred times more efficient as a reducing agent than is ATU. The reason for the rather large difference in the values of k_D for the two reducing agents is unknown.

As to the switch-over of the mechanism, it does not take place very easily in the case of EDTA; thus, even when the concentration of EDTA is $\sim 1\times10^{-4}$ M, the D–D mechanism only operates to a slight extent when the dye concentration is as high as 2.5×10^{-5} M. On the other hand, in the case of ATU, the D–D mechanism becomes appreciable even with 4×10^{-2} M of reductant and 2.5×10^{-5} M of dye. When the concentration of ATU is $\sim 1\times10^{-3}$ M, the D–D mechanism operates to a large extent.

From these results it may be inferred that the proportion of leuco dye formed by the D–D mechanism is only one hundredth, or less, of that from the entire reaction between D^T and D. This is consistent with a small value of Φ_{D-D}.

Moreover, the rate of the reaction proceeding by the D–D mechanism is greatly reduced at higher concentrations of dye. Hence, it is rather difficult to study the D–D reaction separately. This is consistent with the scheme, proposed in the previous paper, in which the D–D intermediate or $D^+\cdots D^-$ is deactivated by the ground state dye as well as by the leuco dye.[3)] Were this not the case, Φ_{D-D} would have reached a constant limiting value when the dye concentration was increased.

Another notable finding in the present paper is that, at a lower concentration of dye, Φ_{D-D} increases with the dye concentration. This is naturally to be expected from the scheme, but it was not observed in the photoreduction of toluidine blue and methylene blue in the absence of a reducing agent. This is perhaps due to the fact that the minimum dye concentration then used was 0.7×10^{-5} M, while in the present investigation a concentration as low as 0.2×10^{-5} M was employed.

Although the occurence of a switch-over in the mechanism of the photoreduction of methylene blue has now been proved, it is not so clear-cut as in the case of eosine.[5)] This seems rather strange at first sight, because eosine, in contrast to thiazine dyes, does not bleach photochemically in the absence of a reducing agent. However, the reason is that, in the case of eosine, only the reverse reaction of $D^-\cdots D^+$ follows its formation on account of the absence of a simultaneous reaction, such as demethylation, to make the forword reduction feasible. On the other hand, there appear to be at least two reasons why eosine shows this change of mechanism more clearly than thiazine dyes. First, the triplet state of eosine has a longer life than thiazine dyes, so it has a greater chance to be attacked by the ground state dye. Second, its redox intermediate seems to be more easily attacked by ATU and less effectively attacked by the ground state dye than in the case of thiazine dyes.

Summarizing the results obtained so far on xanthene dyes and thiazine dyes, one may state, that as far as the primary processes of the D–D and the D–R mechanisms are concerned, there seems to be no essential difference between xanthene dyes and thiazine dyes.

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