An Attempt to Determine Eosine's S*→T Transition Probability and Evidence for the Participation of a D–D Redox Mechanism

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The primary processes in the photochemical reactions of xanthene dyes have been studied by several workers[1,2] by means of the steady illumination, and the ratios of the rate constants for some elementary reactions have been evaluated. Very few attempts, however, have been made to determine exactly the rate constant of each particular elementary process, and of these attempts the flash photolytic investigations of Lindqvist[3] and Grossweiner[4,5] are the most prominent. The former was concerned with fluorescein while the latter dealt with eosine.

The decay constant of the triplet state and the transition probability of the singlet excited state to the triplet state, i. e., $\varphi_{S\to T}$ are believed to be the most fundamental. If the exact values of these two are known, many of the other rate constants can be evaluated very easily from their ratios.

One method to determine the value of $\varphi_{S\to T}$ is to make use of the kinetic data from a suitable reaction. In principle, the method consists of evaluating the quantum yield under conditions such that all the triplet state dyes react in one definite way. For example, if the photochemical reduction proceeds according to the following scheme,

$$\begin{tikzcd} \mathrm{D} \arrow[r] & \mathrm{D}^* \arrow[r] \arrow[d] & \mathrm{D}^t \arrow[r, "k_r{[\mathrm{R}]}"] \arrow[d, "k_d"] & \text{Leuco dye} \\ & \mathrm{D} & \mathrm{D} & \end{tikzcd}$$

where D^*, D^t are respectively the singlet excited state and the triplet state of the dye, and R is a reducing agent, then the quantum yield, Φ is expressed as follows

$$\Phi = \varphi_{S\to T}\frac{k_r\,[\mathrm{R}]}{k_d+k_r\,[\mathrm{R}]} \qquad (1)$$

Hence

$$\frac{1}{\Phi} = \frac{1}{\varphi_{S\to T}} + \frac{1}{\varphi_{S\to T}}\cdot\frac{k_d}{k_r[\mathrm{R}]}$$

and the plot of $1/\Phi$ against $1/[\mathrm{R}]$ gives $1/\varphi_{S\to T}$ as an intercept. For the above method to be used effectively, certain conditions must be fulfilled. 1) The reducing agent R should

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1) M. Imamura and M. Koizumi, This Bulletin, **29**, 899 (1956).

2) G. Oster and A. H. Adelman, *J. Am. Chem. Soc.*, **78**, 913 (1956).

3) L. Lindqvist, *Arkiv Kemi*, **16**, 79 (1960).

4) L. I. Grossweiner and E. F. Zweicker, *J. Chem. Phys.*, **34**, 1411 (1961).

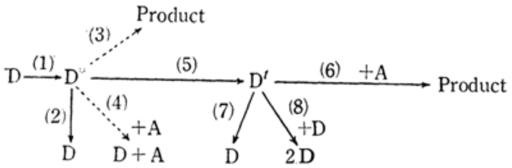
5) E. F. Zwicker and L. I. Grossweiner, *J. Phys. Chem.*, **67**, 549 (1963).

not appreciably affect the ground state or the singlet excited state of the dye. 2) Mere deactivation should not result from the attack of R on D^t. 3) The final product must be produced by a one step attack of R on D^t or else the succeeding steps must be known completely.

On the basis of the above principles, Oster obtained the values 0.092 0.020 for $\varphi_{S\to T}$ of eosine and fluorescein, respectively, at pH 7.0.[2] He used allylthiourea (ATU) as a reducing agent and investigated the photoreduction of these dyes in aqueous solution. Oster proposed the following rate formula,

$$\text{rate} = \frac{I_{ab}[A]}{\alpha+\beta[A]} \tag{2}$$

where α, β are constants, I_{ab} is the absorbed light per second per liter, and [A] is the concentration of ATU. The scheme for the reaction is



(3)

where dashed arrows indicate processes having negligible rates. The process 8 was added to take into account the fact that the rate decreases with increase of dye concentration. On the basis of the above scheme, he derived the following rate formula,

$$\text{rate} = \frac{I_{ab}k_5k_6[A]}{(k_2+k_5)(k_7+k_6[A]+k_8[D])} \tag{4}$$

which is the same as the experimental rate formula except for the term $k_8[D]$, and he estimated some of the rate constants.

In view of the importance of $\varphi_{S\to T}$, it seems desirable to repeat this experiment and to ascertain whether in fact the above conditions are fulfilled. In addition, there is a possibility that the reaction scheme is dependent on experimental conditions such as the concentration of dye as well as that of the reducing agent.

It is desirable, therefore, to examine the rate formula for a run and to study the behavior of the intermediate and of the final product before the above method is used.

In this paper we have attempted to determine $\varphi_{S\to T}$ for eosine in aqueous solution at pH=7.2, paying attention to the above meniioned points. Broadly speaking, we have carried out experiments similar to those of Oster, using ATU and EDTA as reducing agents, and have examined the applicability of 2 and 4. Although we could not get a satisfactory result for $\varphi_{S\to T}$, we have found strong evidence for the participation of a D-D mechanism in this system.

Experimental

Materials.—*Eosine.*—Grübler's product was used. Stock solution (1×10^{-4} M) which had been kept in the dark was diluted to 4.5×10^{-6} M—2.4×10^{-6} M for each experiment. Allylthiourea (ATU) was recrystallized from water three times. To avoid degradation of the ATU, it was stored in the ice box. Ethylenediaminetetraacetic acid disodium salt (EDTA) was prepared by dissolving Dotite 2 NA.

Disodium hydrogen phosphate ($Na_2HPO_4\cdot12H_2O$) and potassium hydrogen phosphate (KH_2PO_4) were recrystallized three times.

Procedure.—All the solutions were prepared from 1/25 M phosphate buffer at pH=7.2. Most of the solutions were degassed by use of a mercury diffusion pump, freezing and thawing (in a dry ice bath) being repeated four to six times. The degassed sample in a cell (1×1×4 cm.) was irradiated with a tungsten projection lamp (50 V. 125 W.) having a yellow glass filter cutting off <470 mμ. For solutions with initial dye concentrations in the range 2.4×10^{-6} M—10^{-5} M, the concentration of residual dye was measured colorimetrically without stopping the irradiation. With initial concentrations of dye greater than 10^{-5} M, a 7 mm. spacer was inserted into the cell, and the measurements were carried out as above.

A temperature of 25°C was chosen. To determine the quantity of light absorbed by the dye, a calibrated Kipp and Zonen thermopile having a sensitivity of 1.02×10^{-5} V./m² watt was used, and the output measured with a potentiometer.

Results

ATU.—*Rate Formula for a Run.*—Equation 4 derived from Oster's scheme 3 is not strictly of the same form as Eq. 2 and, moreover, it can not be integrated in a simple way. However, if $k_8[D]\ll k_7+k_6[A]$, then 4 is reduced to 2 and the rate is simply proportinal to the absorption of light. In this case the rate formula for a run can be derived as follows.
Putting

$$I_{ab}=I_0(1-e^{-\alpha cd})$$

where I_0 is the number of photons per cm² and α is the average molar absorbancy, one can write

$$-\frac{dC}{dt}=\Phi\frac{I_0}{d}(1-e^{-\alpha cd})1000 \tag{2}$$

Integration gives

$$\ln(e^{\alpha cd}-1)=-1000\alpha\Phi\frac{I_0}{d}t+\ln(e^{\alpha c_0 d}-1) \tag{5}$$

Hence the plot $\ln(e^{\alpha cd}-1)-t$ should give a straight line with a slope of $1000\,\alpha\Phi I_0$.

Now, as long as the concentration of ATU is in the range 5×10^{-4} M—2.0×10^{-2} M and the dye concentration is 10^{-5} M, the rate formula 5 accommodates the experimental data very satisfactorily until up to 40% of the dye has been bleached. Thus the rate is simply proportional to the absorption of light. When [ATU] becomes less, however, Eq. 5 appears to become less satisfactory and a second order rate formula in regard to dye holds better, although the initial part of the rum can still be expressed by 5. Some examples are shown in Figs. 1 and 2.

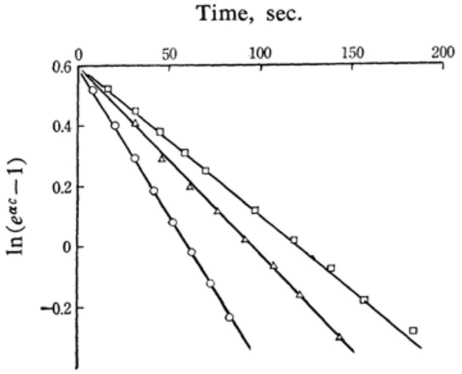


Fig. 1. Fading curves of eosine in vacuo for various concentration of ATU. At 25°C.
○ : Eosine, 10^{-5} mol./l. ATU, 2.0×10^{-2} mol./l.
△ : Eosine, 10^{-5} mol./l. ATU, 1.1×10^{-2} mol./l.
□ : Eosine, 10^{-5} mol./l. ATU, 0.8×10^{-2} mol./l.

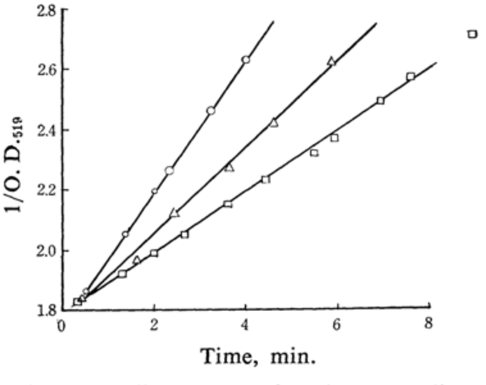


Fig. 2. Fading curves of eosine according to the second order furmula in regard to dye concentration. Dye concentration, 8×10^{-6} mol./l.
○ : ATU, 2.5×10^{-3} mol./l.
△ : ATU, 1.67×10^{-3} mol./l.
□ : ATU, 1.25×10^{-3} mol./l.

Now if k_8[D] in the denominator of Eq. 4 is not negligible, then the rate should increase in the later stage and should be larger than that calculated from 5, whereas the actual deviation from 5 in the later stage is always in the opposite direction. This strongly suggests that Eq. 4 needs to be modified in some way. To make this point clear, the effect of various factors upon the quantum yield obtained from the initial slope of the $\ln(e^{\alpha cd}-1)-t$ plot was examined.

The Effect of the Dye Concentration.—With the concentration of ATU fixed at 5.0×10^{-3} M, 1.0×10^{-3} M and 0.50×10^{-3} M, respectively, the effect of the dye concentration on Φ was investigated. The dye concentration was varied from 2.6×10^{-6} M to 4.4×10^{-5} M. As Fig. 3 shows, the reciprocal of the quantum yield is in a linear relation to the concentration of the dye when [ATU] is 5×10^{-3} M. But when the concentration of ATU is decreased, this linearity deteriorates. Thus the deviation becomes notable at ca. 2×10^{-5} M of dye for 10^{-3} M of ATU and at an even lower dye concentration (ca. 10^{-5} M) for 0.5×10^{-3} M of ATU. The initial slopes of the curves for [ATU]$=5\times10^{-4}$M and 10^{-3} M agree quite well with that calculated from the slope for [ATU]$=5\times10^{-3}$ M by the use of Eq. 4 (see below). From the slopes in the low concentration region of dye and from the tentative value of $\varphi_{S\rightarrow T}$ (0.032, see below), k_8/k_6 was evaluated to be 1.8×10^3. Table I gives values for the quantum yield under differing conditions. The above deviation in Fig. 3, together with the rather large value of k_8/k_6 clearly implies that Eq. 5 does not hold when the concentration of dye becomes large in relation to that of ATU.

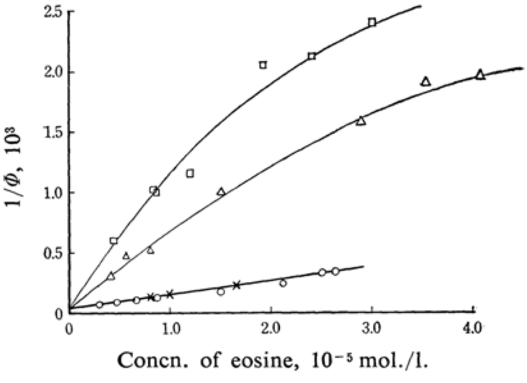


Fig. 3. Effect of eosine concentration on the quantum yield of the photobleaching by ATU.
○ : ATU, 5.0×10^{-3} mol./l.
△ : ATU, 1.0×10^{-3} mol./l.
□ : ATU, 0.5×10^{-3} mol./l.
× : ATU, 5.0×10^{-3} mol./l.
The abscissa is the sum of concentration of eosine and reaction product.

TABLE I. QUANTUM YIELDS AT VARIOUS DYE CONCENTRATIONS

Concn. of ATU $\times 10^{-3}$ M	Concn. of dye $\times 10^{-6}$ M	Φ $\times 10^{-3}$
5.0	25.4	3.1
5.0	4.2	13.0
1.0	8.0	2.5
1.0	40.0	0.52
0.5	12.0	0.77
0.5	20.0	0.51

The Effect of the Reaction Product on the Rate.—Because of the rather large value of k_8/k_6 and the ratio of the concentration of the dye to that of the reducing agent, Eq. 4 would require that as the reaction proceeds, the rate would deviate and become larger than that given by the plot $\ln(e^{\alpha cd}-1)-t$.

But contray to this expectation, the experimental data fits quite well in the initial stage and deviates in the opposite direction in the later stages. This suggest the existence of an inhibiting action due to some reaction product. To check this point, the following experiment was performed. A solution of the dye which had been irradiated until about 30% of the dye had bleached, was added to a fresh sample of dye and the rate of bleaching was measured. In Fig. 3 cross notations refer to such experiments for which the sum [Product]+[dye] was taken as abscissa. The points lie close to the line. It is inferred therefore that the term k_8[D] in 4 should be replaced by $k_8[\mathrm{D}]+k_9[\mathrm{product}]$. Assuming $k_8 \approx k_9$ and approximating $[\mathrm{product}]=[\mathrm{D}]_o-[\mathrm{D}]$, this term may be rewritten as $k_8[\mathrm{D}]_o$ where $[\mathrm{D}]_o$ is the initial concentration of the dye. The rewritten equation will be denoted as 4′.

$$\Phi=\varphi_{\mathrm{S}\to\mathrm{T}}\times\frac{k_6[\mathrm{A}]}{k_7+k_6[\mathrm{A}]+k_8[\mathrm{D}]_o} \qquad (4')$$

The Effect of the Concentration of ATU and the Value of $\varphi_{\mathrm{S}\to\mathrm{T}}$.—The concentration of ATU was varied from 10^{-3} M to 4×10^{-2} M at some fixed dye concentrations. Figure 4 gives the plots of $1/\Phi$ against 1/[ATU], which are satisfactorily linear. This implies that Eq. 4′ holds under the present experimental conditions and this is consistent with the results shown in Fig. 3.

From 4′

$$\frac{1}{\Phi}=\frac{k_2+k_5}{k_5}\left(1+\frac{k_7+k_8[\mathrm{D}]_o}{k_6[\mathrm{A}]}\right)$$

one can evaluate $k_5/(k_2+k_5)$ from the intercept which is $\varphi_{\mathrm{S}\to\mathrm{T}}$ and $(k_7+k_8[\mathrm{D}])_o/k_6$ from the inclination. In Table II, some of the quantum yield are given, and in Table III, the values of $\varphi_{\mathrm{S}\to\mathrm{T}}$ and $(k_7+k_8[\mathrm{D}]_o)/k_6$ are tabulated. The value in parenthesis is Oster's.

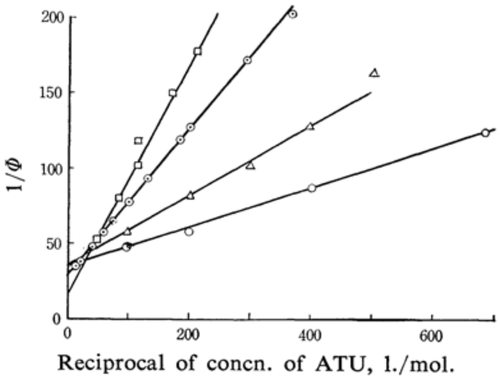


Fig. 4. Effect of ATU concentration on the quantum yield of photoreduction

○ : Eosine, 2.4×10^{-6} mol./l.
△ : Eosine, 4.0×10^{-6} mol./l.
⊙ : Eosine, 8.0×10^{-6} mol./l.
□ : Eosine, 11.6×10^{-6} mol./l.

TABLE II

Concn. of dye, M	Conc. of ATU M	Φ
1.16×10^{-5}	2.0×10^{-2}	2.2×10^{-2}
1.16×10^{-5}	8.0×10^{-3}	1.1×10^{-3}
8.0×10^{-6}	1.0×10^{-2}	1.4×10^{-3}
8.0×10^{-6}	2.5×10^{-3}	0.42×10^{-3}
4.0×10^{-6}	5.0×10^{-3}	1.4×10^{-3}
2.4×10^{-6}	1.0×10^{-3}	0.63×10^{-3}

TABLE III

Concn. of dye, M	$\varphi_{\mathrm{S}\to\mathrm{T}}$	$\frac{k_7+k_8[\mathrm{D}]_o}{k_6}$
1.16×10^{-5}	0.15	29×10^{-3}
1.0×10^{-5}	(0.092)	
8.0×10^{-6}	0.052	16×10^{-3}
4.0×10^{-6}	0.032	7.0×10^{-3}
2.4×10^{-6}	0.032	4.2×10^{-3}

The Effect of Temperature.—As can be seen in Table IV, the effect of temperature on the rate is not large.

TABLE IV

Temp., °K	Φ
289	10×10^{-3}
298	8.1×10^{-3}
308	7.9×10^{-3}
320	7.3×10^{-3}

EDTA.—*The Rate Formula for a Run.*—It is notable that a certain induction period exists in the case of EDTA. After the induction period, however, the results are satisfactorily reproduced by the plot of Eq. 5, indicating that the rate is simply proportional to the absorption of light. Some typical examples are shown in Fig. 5.

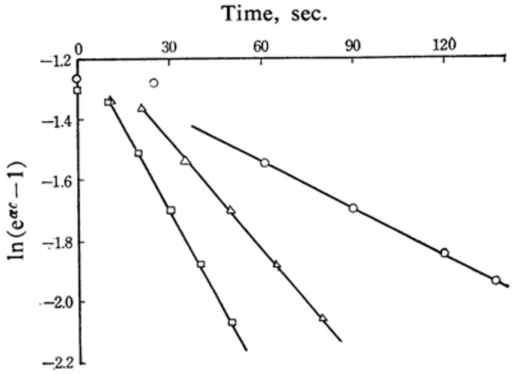
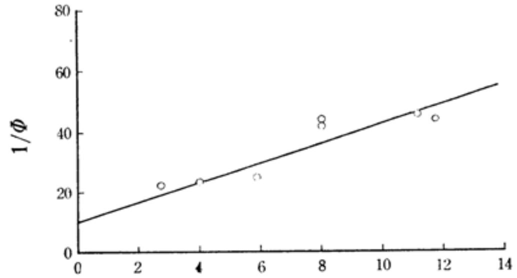


Fig. 5. Fading curves of eosine in vacuo for various concentration of EDTA. Dye concentration, 8×10^{-6} mol./l.

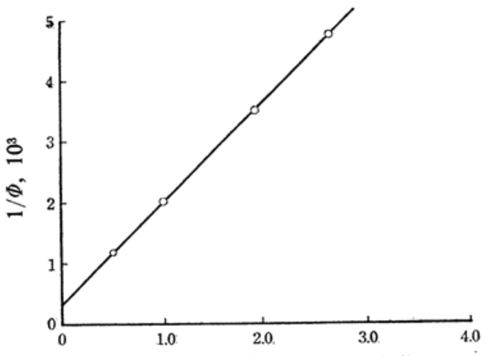
Concn. of EDTA, ○: 2.0×10^{-3} mol./l.
△: 3.3×10^{-3} mol./l.
□: 5.0×10^{-3} mol./l.

The Effect of the Dye Concentration.—Figures 6a and 6b give the plot of $1/\Phi$ aginst the dye concentration. Although the data in Fig. 6a show a fair amount of scatter, it is evident that the effect of the dye concentration is much less than in the case of ATU. In Fig. 6b, where a lower concentration of EDTA was used, the linearity is excellent. This result is in sharp contrast with that in the case of ATU for which the deviation from linearity is notable at $[\mathrm{ATU}]=0.5\times10^{-3}$ M and 10^{-3} M. From the slope and the intercept of the plot in b and from the value (0.080) of $\varphi_{\mathrm{S}\rightarrow\mathrm{T}}$, k_8/k_6 was calculated to be 1.3×10^3. The result from 6a is $k_8/k_6=1.1\times10^3$, which is in agreements with the above value.



Concn. of eosine, 10^{-6} mol./l.

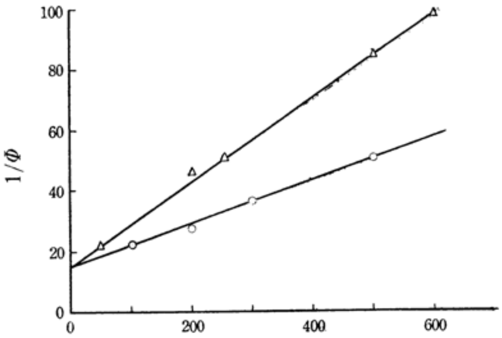
Fig. 6a. Effect of eosine concentration on the quantum yield of photoreduction.
Concn. of EDTA, 5.0×10^{-3} mol./l.



Concn. of eosine, 10^{-5} mol./l.

Fig. 6b. Effect of eosine concentration on the quantum yield of photoreduction.
Concn. of EDTA, 10^{-4} mol./l.

The Effect of the Concentration of EDTA.—The concentration of EDTA was varied from 6.7×10^{-3} M to 2×10^{-2} M at two fixed dye concentrations, 8.0×10^{-6} M and 5.5×10^{-6} M. As Fig. 7 shows, the plots are satisfactorily linear and in this case, the two intercepts are exactly the same. Table V gives the quantum yilds under various conditions and Table VI gives $\varphi_{\mathrm{S}\rightarrow\mathrm{T}}$ and the value of $(k_7+k_8[\mathrm{D}]_\mathrm{o})/k_6$.



Reciprocal of concn. of EDTA, l./mol.

Fig. 7. Effect of EDTA concentration on the quantum yield of photoreduction.
○: Eosine, 5.5×10^{-6} mol./l.
△: Eosine, 8.0×10^{-6} mol./l.

TABLE V

Concn. of dye, M	Concn. of EDTA, M	Φ
8.0×10^{-6}	1.0×10^{-2}	1.0×10^{-2}
8.0×10^{-6}	5.0×10^{-3}	0.41×10^{-2}
8.0×10^{-6}	2.0×10^{-3}	0.12×10^{-2}
5.5×10^{-6}	3.3×10^{-3}	0.11×10^{-2}

TABLE VI

Concn. of dye, M	$\varphi_{\mathrm{S}\rightarrow\mathrm{T}}$	$\dfrac{k_7+k_8[\mathrm{D}]_\mathrm{o}}{k_6}$
8.0×10^{-6}	0.080	$72\ \times10^{-3}$
5.5×10^{-6}	0.080	5.8×10^{-3}

Supplementary Experiments and Discussion

As will be described later, the finding, that for ATU the linearity between $1/\Phi$ and $[\mathrm{D}]_\mathrm{o}$ does not hold when $[\mathrm{D}]_\mathrm{o}$ exceeds a certain value, leads to the conclusion that a switch-over of the mechanism is taking place in this case. But in most cases Eq. 4′ holds or approximately holds and in such cases, the values of $\varphi_{S\to T}$ can be obtained by formally applying this equation to the experimental data. The rate constants of some elementary reactions can also be estimated in a simple manner. Therefore, we will first discuss these data before entering on a critical discussion of the procedure.

From 4′, the intercept and the inclination of the plots in Fig. 3 and Fig. 6 should be expressed by $\frac{1}{\varphi_{S\to T}}\times\left\{1+\frac{k_7}{k_6[R]}\right\}$ and $\frac{1}{\varphi_{S\to T}}\times\frac{k_8}{k_6[R]}$, respectively. By utilizing the tentative values of $\varphi_{S\to T}$, one can evaluate the ratio k_8/k_6 from the inclination. The result, as already stated, is 1.8×10^3 M for ATU and 1.3×10^3 M for EDTA. Furthermore, it is possible to evaluate k_6 by putting[4] $k_7=4.2\times10^2$ in the expression for the intercept. But this procedure is not so reliable, firstly because the value of the intercept is subject to a large error and secondly because this error profoundly affects the value of k_6. Hence the following conventional procedure was adopted. The average value of k_8 from several determinations for both EDTA and ATU was taken as 5.5×10^8 ($\pm1.0\times10^8$) and the value of k_6 was calculated from the value of k_8/k_6. This results in a value of $k_6=3.1\times10^5$ for ATU, and 4.1×10^5 in the case of EDTA.

To check these results, the value of k_6 is recalculated from the inclination of the plot $1/\Phi-1/[R]$ by inserting the above values of k_8 and k_7 into the expression $(k_7+k_8[D]_o)/k_6$. The results are as follows.

Reducing agent	Concn. of dye $\times10^{-6}$ M	The value of k_6
ATU	2.4	3.8×10^5
ATU	4.0	3.4×10^5
EDTA	5.5	5.4×10^5
EDTA	8.0	4.1×10^5

In spite of the crudeness of the method, there is no doubt that k_6 and k_8 are of the order of 10^5 and 10^8 respectively, and it seems that the choice of reducing agent makes little difference in these values. But judging from the data given in Table II and Table V, the quantum yield for EDTA is several times larger than that for ATU under otherwise similar conditions. The following data refer to such results. It appears from the above argument that this difference is closely connected with the value of $\varphi_{S\to T}$.

TABLE VII

$[\mathrm{Dye}]\times10^6$	4	8	12	16
Φ_{EDTA}/Φ_{ATU}	3.1	3.3	3.6	3.8

Next, we will discuss the various conditions necessary for obtaining a reliable value of $\varphi_{S\to T}$ (see the introduction). The first point, which concerns the possibility of the singlet excited state being attacked by R, need not be considered, because neither ATU nor EDTA quenches the fluorescence of eosine appreciably,[2] and also because the $1/\Phi-1/[R]$ plots, given in Fig. 4 and Fig. 7, do not show any deviation in the high concentration region of ATU or EDTA.

To investigate the second point which concerns the behavior of the intermediate, a few supplementary experiments were carried out. In the air-saturated solution, the reaction was found to be completely interrupted in the case of EDTA, but with ATU, for example at 2×10^{-2} M, the reaction proceeds with a quantum yield of 0.005, which is about a quarter of that in the degassed solution under otherwise similar conditions. Such a difference is due, without doubt, to different behaviors of the intermediates in the two cases. In view of the fact that semiquinone produced in ethanol solution is very sensitive to a minute amount of oxygen,[1] the same effect would be expected also in aqueous solution. Therefore, there is a great possibility that semiquinone in a free state is formed in the case of EDTA but not in the case of ATU.* The induction period, which was observed in the case of EDTA, might therefore be due to a small quantity of residual oxygen.

Although the formation of semiquinone in a free state is improbable in the case of ATU, the following experiment strongly suggests the formation of some sort of intermediate with absorption near 360 mμ. Thus when the reaction cell was illuminated from the back with Hg 365 mμ during the reaction, the rate was found to increase by about 20%.

In both cases the behavior of the final product also appears to be quite different. In the case of EDTA, the product had an absorption maximum near 290 mμ and is most probably a leuco dye. But it was found that when the solution was kept in the dark, the oxidized form was regained very slowly. Figure 8 shows that this reversion proceeds as a first order reaction in respect to the photobleached product. This might be due to the formation of a complex composed of molecules of the leuco dye and the oxidized product of EDTA closely held together. The introduction of air increased the rate by about 10%. It is regrettable that in the case of ATU, a spectroscopic investigation could not be carried out due to

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* In case of fluorescein, this was really verified by comparing the quantity of semiquinone produced in the two cases. See next paper.

the existing absorption of ATU up to ~290mu. But it was confirmed that the final product is quite stable. All the observations on the intermediate and the final product, although they are still preliminary in nature, suggest that the reaction in question is not so simple and differs from case to case.

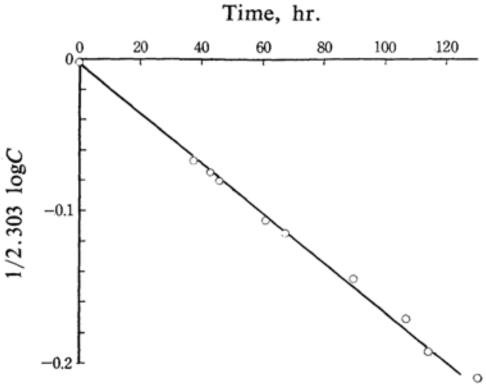

Fig. 8. Reversion curve of eosine according to the first order formula in respect to the photobleached product after eosine was completely photobleached.

As far as the behaviors of the intermediates and final products are concerned, one can not say that the formal procedure of evaluating $\varphi_{S\to T}$ is amply justified. We are at present planning more systematic flash experiments to elucidate the detailed mechanism of the reaction.

Next to be discussed is the switch-over of the mechanism. As has already been clarified by investigations in our laboratory,[6] the photoreduction of methylene blue can proceed by a D-D redox mechanism or a D-R redox mechanism; thus according to the concentration of dye and the type of reducing agent, the primary step of the photoreduction of methylene blue is a) $D^t+D \to$ semi-reduced dye + semi-oxidized dye (D-D redox mechanism) or b) $D^t+R \to$ semi-reduced dye + semi-oxidized R (D-R redox mechanism).

Now with the xanthene dyes, photoreduction in the degassed solution does not occur in the absence of a reducing agent.[5] Yet, it was confirmed in the present experiment that deactivation of D^t by the ground state dye occurs, as Oster proposed,[2] and further, it was established that deactivation by leuco dye also occurs, the rate constants for both deactivation processes being close to that controlled by diffusion. This makes us suspect that, with some suitable reducing agents, the photoreduction of this dye may also proceed via a D-D mechanism. This suspicion is further strengthened if one considers Lindqvist's discovery that half-reduced and half-oxidized flurorescein is produced by flash illumination, without addition of any reducing or oxidizing agents.[3]

Now the present results strongly suggest that such a switch-over of the mechanism really exists, in the case of ATU, but not in the case of EDTA, under the present experimental conditions. Thus the findings that the plot of $1/\Phi$—$[D]_o$ begins to deviate at a concentration of 2.4×10^{-5} M of dye when $[ATU]=10^{-3}$, and at 1.2×10^{-5} M dye at 0.5×10^{-3} M ATU, seems to be understandable only on this basis. If the photoreduction in the small concentration region of ATU occurs exclusively by a D-D mechanism, then the rate formula would presumably be given by

$$-\frac{d[D]}{dt}=\frac{\varphi_{S\to T}I_{ab}k_8'[D]}{k_7+k_8[D]_o+k_6[A]}\times\frac{k_r'[A]}{k_d'+k_r^{s\prime}[A]} \tag{6}$$

where k_8' is the rate constants for $D^t+D\to D^++D^-$ redox intermediate, and k_d', k_r' are respectively the rate constants for monomolecular deactivation of this intermediate and the rate constants of the reaction with ATU, and $k_r^{s\prime}$ is the sum of the rate constants for the reaction and deactivation with ATU. According to the following analysis it seems unnecessary to take into account the deactivation of the redox-intermediate by the ground state dye. In the usual condition, $k_8[D]_o\gg k_7$ and $k_8[D]>k_6[A]$, hence one can put approximately

$$\Phi^o{}_{D-D}=\frac{k_r'[A]}{k_d'+k_r^{s\prime}[A]}\times\frac{k_8'}{k_8}\varphi_{S\to T}$$

In the general case where the D-R and D-D mechanisms occur simultaneously, Φ is given by

$$\Phi=\Phi_{D-R}+\Phi_{D-D}=\varphi_{S\to T}\times\frac{k_6[A]}{k_7+k_6[A]+k_8[D]_o}+\varphi_{S\to T}\frac{k_8'[D]}{k_7+k_6[A]+k_8[D]_o}\times\frac{k_r'[A]}{k_d'+k_r^{s\prime}[A]} \tag{7}$$

Since k_6 k_8 are respectively $\sim10^5$ and $\sim10^8$, the second term cannot be neglected at $[D]_o\gg10^{-5}$ M and at $[ATU]\sim10^{-3}$ M unless $\Phi_{D-D}{}^o$ is very small, and this view interprets the results given in Fig. 3. Thus the deviation can safely be attributed to the contribution of a D-D process in the entire reaction. Further information about the D-D process can be obtained as follows, although the analysis is still provisional in nature.

From the results shown in Fig. 3, one can easily estimate the dye concentration at which

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6) S. Kato, M. Morita and M. Koizumi, This Bulletin, 37, 117 (1964); M. Koizumi, H. Obata and S. Hayashi, ibid., 37, 108 (1964).

Φ_{D-D}/Φ_{D-R} attains a value of 0.3 (chosen conventially) for a given concentration of ATU. The results are given in Table VIII.

TABLE VIII

ATU	Initial slope	$[D]_0$ for $\Phi_{D-D}/\Phi_{D-R}=0.3$
5.0×10^{-3} M	1.4×10^{7}	—
1.0×10^{-3}	6.6×10^{7}	3.5×10^{-5}
0.5×10^{-3}	14.5×10^{8}	1.7×10^{-5}

Now Φ_{D-D}/Φ_{D-R} is expressed as follows,

$$\frac{\Phi_{D-D}}{\Phi_{D-R}}=\frac{k'_8[D]}{[A]k_6}\quad\frac{k_r'[A]}{k_d'+k_r^{s\prime}[A]}\tag{8}$$

By substituting the values of [D], [A], $k_6(=3.8\times10^5)$ and $\Phi_{D-D}/\Phi_{D-R}(=0.3)$ into Eq. 8, one can calculate the value of $k_8'\times k_r'/k_d'+k_r^{s\prime}[A]$, which is 3.3×10^9 for ATU 10^{-3} M (9−a) and 7×10^9 for ATU$=5\times10^{-4}$(9−b)

From the ratio of the above two values,

$$\frac{k_d'+k_r^{s\prime}\times5\times10^{-4}}{k_d'+k_r^{s\prime}\times10\times10^{-4}}\approx\frac{1}{2}$$

Hence

$$k_r^{s\prime}\times5\times10^{-4}\gg k_d'$$

This implies that most of the intermediates produced from D^t and D attacked by ATU molecules. The values of $k_8'\times k_r'/k_r^{s\prime}$, evaluated from (9−a) and (9−b), are respectively 3.3×10^6 and 3.5×10^6. If this is compared with the value of k_8', the value of k_8' lies in the range 10^8—3.3×10^6 and the corresponding value of $k_r'/k_r^{s\prime}$ in the range 1/100—1.

From the above analysis there is scarcely any doubt that in the case of ATU the reaction proceeds via a D-D mechanism, whereas in the case of EDTA no such reaction occurs. The reason for the different behavior is unknown at present, but we have already found a similar result in the photoreduction of methylene blue.6) It is to be noted that the data in Table VIII are consistent with the result that the rate formula for a run obeys Eq. 5 quite well as long as the concentration of ATU is in the range 10^{-3}—2×10^{-2} M and the dye concentration is $\sim10^{-5}$ M.

Finally a brief comment will be given on the value of $\varphi_{S\to T}$. As Fig. 4 and Table III show, the value of $\varphi_{S\to T}$ for ATU appears to depend on the concentration of dye and to increase regularly with it. An interpretation which occurred to us at first was to consider that the higher the dye concentration the greater becomes the contribution of the D-D process, resulting in an apparent increase in the $\varphi_{S\to T}$ value. But the quantitative investigation given above, as well as the values of k_8 and k_6, completely reject this idea. Although the reason is still unknown, it seems worth metioning that Oster's value at $[D]_0=10^{-5}$ M agrees quite well with ours if one takes the dependence of $\varphi_{S\to T}$ on [D] into consideration. The value $\varphi_{S\to T}=0.032$ for the lowest concentration of dye is close to the value (0.023) that Parker obtained from the phosphorescence experiment using ethanol as solvent7) and to our own value (0.046) using the same solvent. On the other hand, the value for EDTA (0.080) is about three times larger than the above value for ATU. Since the features of the reaction in the case of EDTA are rather simple, one is tempted to consider the value 0.080 more reliable. But this is not conclusive. The smaller value for ATU might be due to the fact that mere deactivation of D^t is produced much more so by ATU than by EDTA. At present we have no information at all on how the two reducing agents attack D^t. Further experiments employing more suitable reducing agents will be necessary to solve this question and to obtain a more reliable $\varphi_{S\to T}$ value.

Summary

Using ATU and EDTA as a reducing agent, an attempt was made to determine the transition probability of the singlet excited state to the triplet state. The values obtained are 0.032 for ATU and 0.080 for EDTA. The cause of this difference is not known at present.

Deactivation of the triplet state by a leuco dye as well as by the ground state dye was confirmed. In the case of ATU, it was established that a D-D mechanism operates when the concentration of ATU islow and the con centration of dye is high. This conclusion was supported by the fact that at a constant low concentration of ATU the $1/\Phi$—$[D]_0$ plot deviates from linearity, when the dye concentration becomes high.

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7) C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, 57, 1894 (1961).