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Determination of the S*–T Transition Probabilities of Some Xanthene and Thiazine Dyes on the Basis of the T-Energy Transfer. I. Experiment in Ethanol Solutions

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Intersystem crossing probability, φ_{ST}^{A} for fluorescein, eosine, erythrosine, methylene blue and thionine in ethanol (only for fluorescein, 30 vol% alkaline aqueous ethanol solution), has been determined by comparing the quantum yield of the direct (Φ) and sensitized photoreduction (Φ^s), on the basis of the following relations,

$$\Phi=\varphi_{ST}^{A}\beta \qquad \Phi^s=\varphi_{ST}^{D}\gamma\beta$$

where β is the fraction of triplet dye molecules that are reduced eventually, φ_{ST}^{A} and φ_{ST}^{D} are respectively for acceptor (dye) and donor (sensitizer) and γ is the energy transfer efficiency, which was assumed as 1. ATU was used as a reducing agent. 1,2,5,6-dibenzanthracene, triphenylene, anthracene and β-acetonaphthone were used as sensitizers. It has been confirmed that the above relations and assumption hold generally. Different sensitizers usually gave nearly the same φ_{ST}^{A} values (with the exception of thionine-anthracene. β-Acetonaphthone gave in general somewhat smaller values). The most probable φ_{ST}^{A} values obtained are; fluorescein (0.007), eosine 0.43±0.04, erythrosine 1.1±0.06, methylene blue 0.52±0.03, thionine 0.62±0.03. The values for xanthene dyes agree moderately well with the ones reported by Porter *et al.* for the aqueous solution of pH=9, fluorescein 0.05, eosine 0.71, erythrosine 1.07. Using the above φ_{ST}^{A} values, the ratio of the deactivation and genuine reaction between triplet dye and ATU has been evaluated. The ratio increases in the order, fluorescein < eosine < erythrosine, thionine < methylene blue.

One of the present authors (M. K.) with many collaborators, has long been engaged in the elucidation of the primary processes in the photochemical oxidation and reduction of some typical dyes. By means of the steady light and the flash photolytic investigations, detailed informations about many elementary processes have been obtained. But an important problem of determining the probability of S*→T transition *i. e.*, φ_{ST} still remains to be solved.

A few years ago, our group attacked this problem by Oster's method,[1] but a series of our work has revealed that the method is in general not applicable.[2–4]

Oster's method is based upon the general principle that if all the triplet dye molecules produced react with a certain substance giving a definite product, then the quantum yield of the reaction under such a condition can be taken as the value of φ_{ST}. Although the method appears simple and elegant, it often gives different φ_{ST} values depending upon the reaction adopted. For example, in the case of photoreduction, EDTA and ATU (allylthiourea) have been found to give quite different φ_{ST} values for eosine,[2] fluorescein[3] and methylene blue.[4] This fact strongly suggests that the mere deactivation of the triplet dye by the reducing agent is also occurring and that its magnitude largely depends upon the nature of the latter.

Since then our attention has been focused on the utilization of the triplet energy transfer. The principle of the method which is somewhat similar to that of Hammond,[5] is to compare the quantum yield of the direct (Φ) and sensitized photoreduction (Φ^S) under otherwise similar conditions. Denoting φ_{ST} for a sensitizer (donor) and a dye (acceptor) respectively as φ_{ST}^{D} and φ_{ST}^{A}, Φ and Φ^S will be given under favorable conditions, by

$$\Phi=\varphi_{ST}^{A}\beta^{A} \tag{1}$$

$$\Phi^{S}=\varphi_{ST}^{D}\gamma\beta^{A} \tag{2}$$

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

[2] T. Ohno, Y. Usui and M. Koizumi, This Bulletin, **38**, 1022 (1965).

[3] Y. Momose, K. Uchida and M. Koizumi, *ibid.*, **38**, 1601 (1965).

[4] N. Kosui, K. Uchida and M. Koizumi, *ibid.*, **38**, 1958 (1965).

[5] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

where β^A is a fraction of the triplet dye that yields the product and γ is the efficiency of the triplet energy transfer. If φ_{ST}^D is known and if γ is unity, then the measurement of Φ^S and Φ enables us to evaluate the value of φ_{ST}^A from Eqs. (1) and (2). Of course some conditions must be fulfilled for the method to be applicable. In particular, it must be ascertained that β^A is really the same in value for the two reactions, and also that the only interaction between donor and acceptor is the triplet energy transfer.

For the aqueous solution, the selection of a suitable sensitizer is quite a big problem because very few work has yet been performed on the triplet energy transfer in the aqueous solution. Aromatic hydrocarbons of which the nature and the behavior of the triplet states have been investigated by many workers, cannot be used for the aqueous solution because of their very small solubility. There is of course no such obstacle for the ethanol solution; hence we have taken up the problem as a start, to decide φ_{ST} values of fluorescein, eosine, erythrosine (xanthene dyes), methylene blue and thionine (thiazine dyes) in ethanol by comparing the quantum yields of the direct and sensitized photoreduction. ATU was used as a reducing agent.

In the course of our work, some reliable data were published by Porter *et al.* on the φ_{ST} values of some xanthene dyes in aqueous solution.[6] The present results are somewhat similar to theirs in spite of a great difference in the method, supporting the reliability of their data as well as ours. In addition, our results give some interesting informations on the interaction between triplet dye and the reducing agent.

Experimental

Materials. Fluorescein and eosine of Gluber, G. R. grade, were recrystallized three times from ethanol. Erythrosine of Wako Junyaku, G. R. grade, was recrystallized three times from an ethanol-benzene mixture. Methylene blue and thionine of Merck, G. R. grade, were recrystallized three times respectively from *n*-butanol and ethanol.

1,2,5,6-Dibenzanthracene of Wako Junyaku, G. R. grade, was recrystallized from acetic acid and then from ethanol two times. Triphenylene of Tokyo Kasei, G. R. grade, was recrystallized three times from ethanol. β-Acetonaphthone of Tokyo Kasei, G. R. grade, was recrystallized three times from ligroin. Anthracene of high purity was kindly supplied by Professor Shimpachiro Kato of the Univeristy of Tokyo. Purity of these donors was checked by measuring the fluorescence and phosphorescence spectra.

Allylthiourea of Tokyo Kasei, G. R. grade, was recrystallized three times from water.

Ethanol of Wako Junyaku, G. R. grade, was fractionally distilled.

Degassing of the samples was performed by three times distillation to a trap immersed in liquid nitrogen under evacuation.

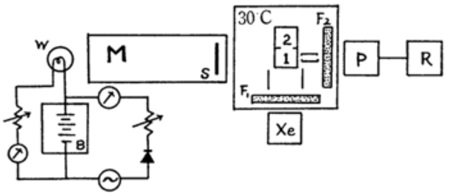

Fig. 1. Schematic diagram of the apparatus for the sensitized reaction.

B	storage battery	S	lightshuttter
F_1	Toshiba UV-D2 filter	P	photomultiplier
F_2	cut-off filter	R	recorder
M	monochromator	W	incandescent lamp

Apparatus and Procedures. Figure 1 shows a schematic diagram of the apparatus for the sensitized reaction. As a light source, an Ushio UX-L 150D Xe-lamp was used; a Toshiba UV-D2 filter was used to excite the donor selectively.

Photobleaching of dyes was measured by a monochromatic light of the wavelength at the absorption maximum which was passed through the solution in the direction perpendicular to the exciting beam. A suitable cut-off filter was inserted to remove donor's fluorescence and scattered light. To reduce the fluctuation of light intensity, special care was taken; a storage battery employed as a power supply for monitoring light (6V-5A incandescent lamp), was kept charged during the measurement.

The measurement of the light absorption was performed as follows, using a potassium ferri-oxalate actinometer. Actinometry is made at first in cell 1 and next in cell 2 with cell 1 filled with the sample solution; the difference of the two measurements then gives the quantity of light absorbed by the sample solution.

Cells for spectrophotometry, $1\times1\times4$ cm, were used as the reaction cells. The concentration of each substance was chosen as follows; dyes 1×10^{-5}M, ATU 1×10^{-2}—5×10^{-4}M, 1,2,5,6-dibenzanthracene 5×10^{-4}M, triphenylene 1×10^{-4}M, anthracene 1.1×10^{-4}M, β-aceto naphthone 5×10^{-4}M. The reaction temperature was always 30 ± 0.5°C.

The apparatus and procedures for the direct photoreduction were similar to those described in a previous paper.[7] The quantity of light absorbed by dyes, was measured by a calibrated Kipp and Zonen thermopile having a sensitivity of 1.02×10^{-5} V/m^2 watt and a Shimadzu K-2 potentiometer.[*1]

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[6] P. G. Bowers and G. Porter, *Proc. Roy. Soc.*, **A299**, 348 (1967).

[7] M. Nemoto, Y. Usui and M. Koizumi, This Bulletin, **40**, 1035 (1967).

[*1] Some discrepancy was observed in the quantum yield of photoreduction of eosine in ethanol, as compared with the previous results.[7] This is due to the difference in the method of determining the magnitude of light absorption. In the previous paper, a relative method was employed using Imamura's Φ value on the oxydative photobleaching of eosine in the aqueous solution.[8] Reinvestigation of Φ of this reaction using the thermopile, gave about one third of the previous value.

TABLE 1. QUANTUM YIELD OF THE PHOTOREDUCTION OF DYES IN ETHANOL
dye concn., 10^{-5}M (30°C)

Concentration of ATU (M)	Fluorescein*1	Eosine	Erythrosine	Methylene blue	Thionine
5×10^{-4}				$0.4_5\times10^{-2}$	1.9×10^{-2}
1×10^{-3}				$0.7_4\times10^{-2}$	2.5×10^{-2}
2.5×10^{-3}		$2.7_6\times10^{-3}$	1.1×10^{-3}	$1.2_5\times10^{-2}$	
5×10^{-3}	$1.8_2\times10^{-4}$	3.6×10^{-3}	2.0×10^{-3}	1.3×10^{-2}	5.0×10^{-2}
7.5×10^{-3}	$1.9_8\times10^{-4}$	4.2×10^{-3}	3.0×10^{-3}	1.2×10^{-2}	5.4×10^{-2}
1×10^{-2}	2.3×10^{-4}	5.4×10^{-3}	3.7×10^{-3}	1.2×10^{-2}	5.4×10^{-2}

*1 30 vol% aq. alkaline (0.02N KOH) alcoholic solution.

Results

Dependence of the Quantum Yield of the Direct Photoreduction of Dye upon the Concentration of ATU. Quantum yields for five dyes in the ethanol solutions (except fluorescein) containing different concentrations of ATU are summarized in Table 1.

Some remarks will be added below on each dye.

As for eosine, the reaction has been investigated intensively in a previous paper.[7] Hence only the experiments using 1.0×10^{-5}M of dye were supplemented.

A detailed report on the photoreduction of erythrosine in ethanol will be published elsewhere. The feature of the reaction is essentially similar to eosine. Here only the results for 1×10^{-5}M of dye are listed in Table 1.

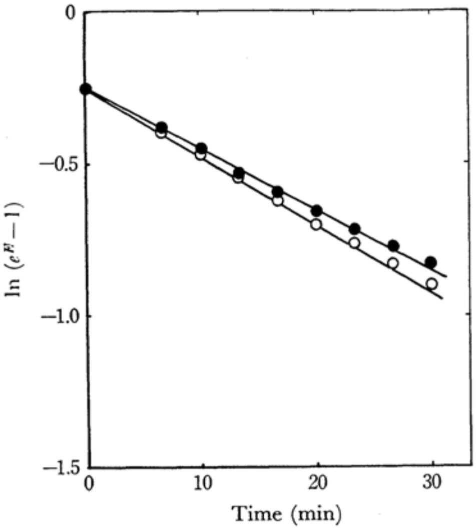

Fig. 2. Plots of $\ln(e^E-1)$ vs. t for the 30 vol % aqueous alkaline (0.02N KOH) alcoholic solution of fluorescein, 1.0×10^{-5}M.
Concentration of ATU: ● 5.0×10^{-3}M
○ 7.5×10^{-3}M

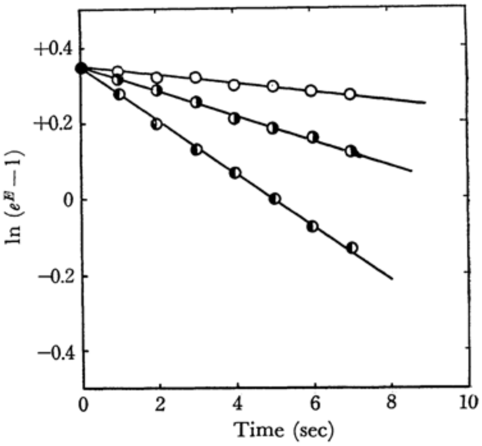

Fig. 3. Plots of $\ln(e^E-1)$ vs. t for thionine, 1.0×10^{-5}M.
Concentration of ATU: ○ 5.0×10^{-4}M
◑ 1.0×10^{-3}M
◐ 5.0×10^{-3}M

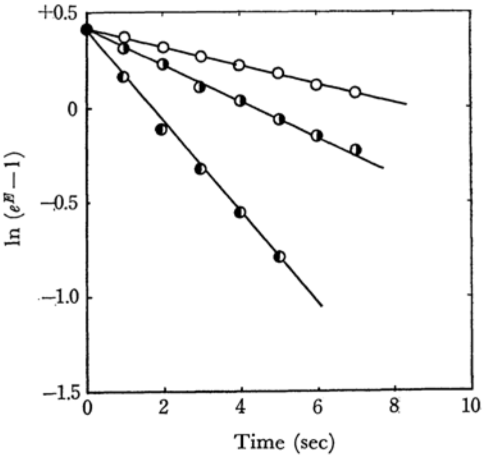

Fig. 4. Plots of $\ln(e^E-1)$ vs. t for methylene blue, 1.0×10^{-5}M.
Concentration of ATU: ○ 5.0×10^{-4}M
◑ 1.0×10^{-3}M
◐ 5.0×10^{-3}M

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[8] M. Imamura, *J. Inst. Polytech. Osaka City Univ.*, Vol. 5, Ser. C, 85 (1956).

TABLE 2. SOME CHARACTERISTICS OF THE TRIPLET STATES OF THE SENSITIZERS AND DYES

	Triplet level (cm^{-1})	Decay constant, $1/\tau$[e] (sec^{-1})	φ_{ST}^{D}
1,2,5,6-Dibenzanthracene	18300[a]	4×10^3	0.89[g]
Triphenylene	23310[b]	2.6×10^4	0.95[g]
Anthracene	14700[a]	7×10^2	0.70[h]
β-Acetonaphthone	20746[b]	1.8×10^4	0.84[h]
Fluorescein		~50[f]	
Eosine	14900[c]	3.0×10^3	
Erythrosine	15400	6.4×10^3	
Methylene blue	—[d]	1.8×10^3	
Thionine	—[d]	1.5×10^3	

a) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, **1954**, 1589.
b) W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).
c) From the phosphorescence spectrum in EPA at 77°K.
d) Phosphorescence spectrum not observed in EPA at 77°K.
e) From the decay of T–T absorption at room temperature in ethanol.
f) The value for the aqueous solution. L. Lindqvist, *Arkiv Kemi.*, **16**, 79 (1960).
g) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
h) T. Medinger and F. W. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).

As for fluorescein, it is well-known that its ethanol solution has no distinct absorption in the visible region perhaps because of the isomerization into lactonic form.[9] 30 vol% aqueous alkaline (0.02N KOH) alcoholic solution was successful for the present purpose. Figure 2 shows the $\ln(e^E - 1)$ *vs.* t plots for the two experiments (E is the optical density).

The photoreduction of thiazine dyes by ATU in ethanol have not yet been investigated in detail. But the general feature of the reaction is believed to be similar to that of xanthene dyes. $\ln(e^E - 1)$ *vs.* t plots for thionine and methylene blue are given in Figs. 3 and 4. They are satisfactorily linear, and it may be said that the reaction proceeds *via* D-R mechanism. No shift of the absorption maximum has been observed during the reaction, and upon introduction of air into the bleached solution, 100% recovery of the dye occurred.

Sensitized Photoreduction of Dye. In Table 2 some characteristics of the triplet states of the sensitizers and the dyes used in the present investigation, are tabulated.

The sensitizers were chosen from the following viewpoints; 1) high triplet levels compared with those of the dyes, 2) the φ_{ST} value is known and is close to unity, 3) rather small decay constant. In addition, it is desirable that a sensitizers' absorption band is located in the region where there is no appreciable absorption by dyes. For the sensitizers used in the present investigation, there was scarcely any fear of the appreciable superposition of the direct photochemical reaction over the sensitized one. From the values of τ listed in Table 2, 10^{-5}M of dye is expected to be sufficient for the energy transfer to occur as a diffusion controlled process. This was really proved in most cases by the zero order rate law as described below. It was checked by the flash experiments that the decays of the triplet sensitizers are not affected by the addition of 1×10^{-2}M of ATU. Some examples are shown in Fig. 5. The plots of optical density against

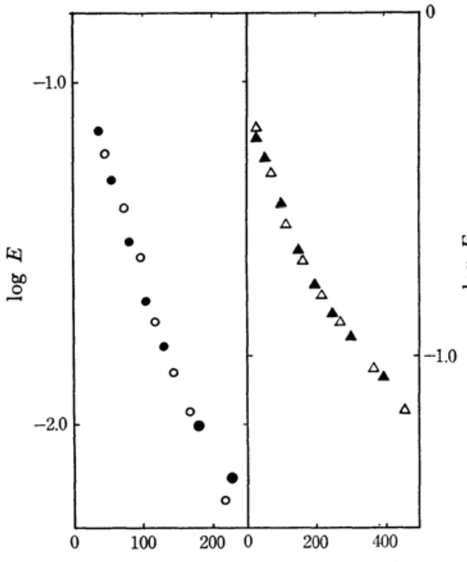

Fig. 5. Effect of the addition of ATU on the donor's triplet decay.
Triphenylene ○ [ATU]=0
● [ATU]=1.0×10^{-2}M
1,2,5,6-Dibenzanthracene
△ [ATU]=0
▲ [ATU]=1.0×10^{-2}M

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[9] T. Nash, *J. Am. Chem. Soc.*, **62**, 1574 (1958); V. Zanker and W. Peter, *Berichte*, **91**, 572 (1958).

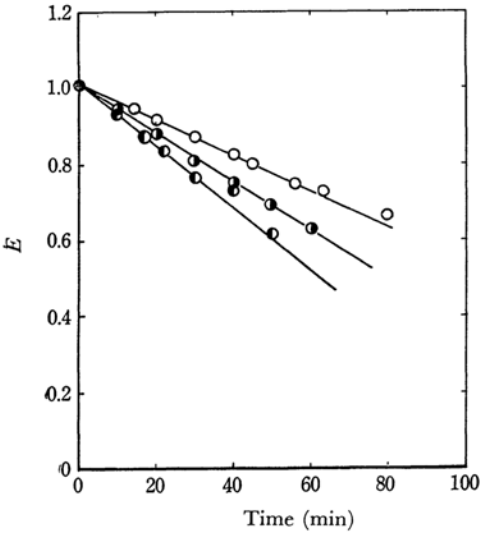


Fig. 6. An example of the plots of E *vs.* t for the sensitized reaction.
[Erythrosine] = 1.0×10^{-5}M
[1,2,5,6-Dibenzanthracene] = 5.0×10^{-4}M
Concentration of ATU: ○ 5.0×10^{-3}M
◑ 7.5×10^{-3}M
◐ 1.0×10^{-2}M

time are always satisfactorily linear for 10^{-5}M of dye. Some examples are shown in Fig. 6.

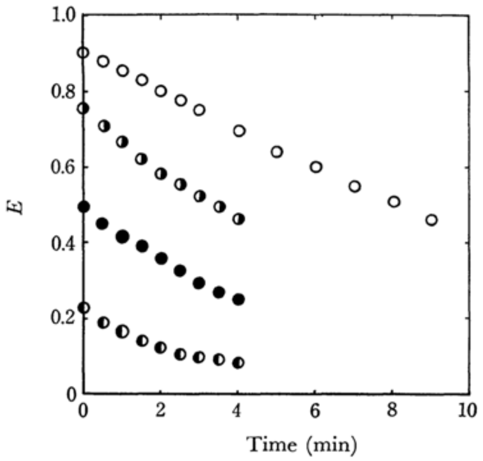


Fig. 7. Effect of dye concentration on sensitized reaction.
[1,2,5,6-Dibenzanthracene] = 5.0×10^{-4}M
[ATU] = 1.0×10^{-2}M
Concentration of eosine: ○ 9.3×10^{-6}M
◑ 7.7×10^{-6}M
● 5.3×10^{-6}M
◐ 2.4×10^{-6}M

Since the rate is expressed by the following formula,

$$-\frac{dA}{dt} = I_{ab}\varphi_{ST}^{D}\gamma\beta^{A} \tag{3}$$

the results in Fig. 6 ensures that all the factors on the right hand side are kept constant during the reaction. On the contrary, when the concentration of dye was smaller, the rate gradually decreased which undoubtedly is due to the decrease of the energy transfer efficiency, γ. Some examples for such a case are shown in Fig. 7. In all cases there was no sign that the sensitized reaction proceeds rather in a different way than in the direct reaction.

Table 3 gives the quantum yields of the sensitized photoreduction of xanthene dyes at various ATU

TABLE 3. QUANTUM YIELDS FOR THE SENSITIZED PHOTOREDUCTION OF XANTHENE DYES AT DIFFERENT ATU CONCENTRATIONS

	[ATU]M/donor	1,2,5,6-Dibenzanthracene	Triphenylene	β-Acetonaphthone
Fluorescein	1.0×10^{-2}	5.0×10^{-3}		2.9×10^{-2}
	7.5×10^{-3}	3.7×10^{-3}		2.6×10^{-2}
	5.0×10^{-3}	3.3×10^{-3}		1.8×10^{-2}
Eosine	1.0×10^{-2}	9.9×10^{-3}	1.3×10^{-2}	$1.3_8\times10^{-2}$
		1.0×10^{-2}	1.3×10^{-2}	
			1.2×10^{-2}	
			1.1×10^{-2}	
	7.5×10^{-3}	8.9×10^{-3}	0.9×10^{-2}	1.1×10^{-2}
		9.7×10^{-3}	1.0×10^{-2}	
		8.6×10^{-3}	$0.9_8\times10^{-2}$	
	5.0×10^{-3}	8.4×10^{-3}	$0.8_5\times10^{-2}$	9.0×10^{-3}
		6.9×10^{-3}	$0.7_2\times10^{-2}$	
		6.9×10^{-3}		
	2.5×10^{-3}			7.5×10^{-3}
Erythrosine	1.0×10^{-2}	2.8×10^{-3}	3.2×10^{-3}	3.2×10^{-3}
				$3.1_4\times10^{-3}$
	7.5×10^{-3}	$2.4_6\times10^{-3}$	2.5×10^{-3}	2.6×10^{-3}
	5.0×10^{-3}	$1.8_3\times10^{-3}$	1.7×10^{-3}	$1.8_7\times10^{-3}$

TABLE 4. QUANTUM YIELDS FOR THE SENSITIZED PHOTOREDUCTION OF THIAZINE DYES AT DIFFERENT ATU CONCENTRATIONS

	[ATU]M/donor	1,2,5,6-Dibenzanthracene	Anthracene	β-Acetonaphthone
Methylene blue	7.5×10^{-3}	2.1×10^{-2}	$2.2_4\times10^{-2}$	$2.0_9\times10^{-2}$
	5.0×10^{-3}	2.0×10^{-2}	$1.9_4\times10^{-2}$	$1.6_8\times10^{-2}$
	2.5×10^{-3}	$1.9_8\times10^{-2}$		
	1.0×10^{-3}		$1.1_8\times10^{-2}$	
	5.0×10^{-4}	0.8×10^{-2}		
Thionine	1.0×10^{-2}	7.2×10^{-2}	8.8×10^{-2}	
	7.5×10^{-3}	7.2×10^{-2}	8.7×10^{-2}	
	5.0×10^{-3}	7.2×10^{-2}	8.5×10^{-2} (10.0×10^{-2})	9.0×10^{-2}
	1.0×10^{-3}	3.8×10^{-2}	4.5×10^{-2} (6.2×10^{-2})	5.3×10^{-2}
	5.0×10^{-4}	$2.9_4\times10^{-2}$	3.7×10^{-2} (3.7×10^{-2})	4.4×10^{-2}

TABLE 5. φ_{ST}^{A} VALUES OF FIVE DYES OBTAINED BY USING DIFFERENT SENSITIZERS AND AT DIFFERENT ATU CONCENTRATIONS

	[ATU]M/donor	1,2,5,6-Dibenzanthracene	Triphenylene	β-Acetonaphthone
Fluorescein	1×10^{-2}	(0.04)		0.006_5
	7.5×10^{-3}	(0.047)		0.006_4
	5×10^{-3}	(0.04_8)		0.008_3
	average	$0.004_5\pm0.005$		$0.007_0\pm0.001$
Eosine	1×10^{-2}	0.48	0.39	0.33
		0.46	0.39	
			0.40	
			0.43	0.31
	7.5×10^{-3}	0.42	0.42	
		0.39	0.39	
		0.41	0.40	
	5.0×10^{-3}	0.3_8	0.41	
		0.4_6	0.46	
		0.4_6		
	2.5×10^{-3}			0.31
	average	0.43 ± 0.04	0.42 ± 0.04	0.31 ± 0.02
Erythrosine	1×10^{-2}	1.1	1.1	0.9_5
				0.98
	7.5×10^{-3}	1.0	1.2	0.9_8
	5×10^{-3}	0.9	1.1_4	0.9_0
	average	1.06 ± 0.01	$1.1_5\pm0.06$	0.92 ± 0.06
Methylene blue	1.0×10^{-2}			
	7.5×10^{-3}	0.51	0.47	0.41
	5.0×10^{-3}	0.57	0.57	0.54
	2.5×10^{-3}	0.56		
	1.0×10^{-3}		0.53	
	5.0×10^{-4}	0.48		
	average	0.52	0.52	0.48
Thionine	1.0×10^{-2}	0.66		0.52
	7.5×10^{-3}	0.66		0.52
	5.0×10^{-3}	0.62	0.39(0.35)	0.59
	1.0×10^{-3}	0.59	0.33(0.34)	0.49
	5.0×10^{-4}	0.58	0.30(0.30)	0.44
	average	0.62	0.34	0.51

concentrations.

In the case of fluorescein, only 1,2,5,6-dibenzanthracene and β-acetonaphthone could be used for the reason of solubility. Moreover, in the case of the former sensitizer, its absorption declined when the solution containing 1×10^{-2}M of ATU was illuminated. The reason is unknown. Such a phenomenon was not observed when the solvent was a pure ethanol.

Table 4 summarizes the similar data for thiazine dyes.

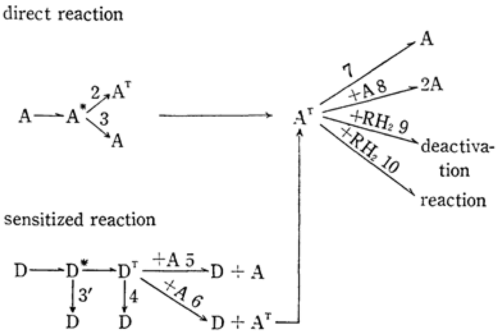
Table 5 gives the $\varphi_{\mathrm{ST}}^{\mathrm{A}}$ values for five kinds of dye evaluated by applying Eqs. (1) and (2) respectively to Φ's and Φ^{S}'s obtained under otherwise similar conditions.

$\varphi_{\mathrm{ST}}^{\mathrm{A}}$ values of each dye obtained by using different sensitizers, agree fairly well except the ones for fluorescein and for the thionine-anthracene system. The reason for the very low $\varphi_{\mathrm{ST}}^{\mathrm{A}}$ value for the latter system is unknown. The value for fluorescein is somewhat doubtful on account of the scanty data. A survey of the data in Table 5 may indicate that the $\varphi_{\mathrm{ST}}^{\mathrm{A}}$ values in the case of β-acetonaphthone are laways somewhat smaller. The value of $\varphi_{\mathrm{ST}}^{\mathrm{D}}$ of this compound might not be correct. Apart from these points, the results are very satisfactory. It is judged that the conditions for the method to be applicable, are amply satisfied.

Discussion

In view of the results obtained, the method seems to be generally applicable. But in order to make it more confident, two further confirmations will be added below.

Firstly, according to the following reaction schemes,[2–4)]



γ and β^{A} are written in general as,

$$\gamma=\frac{k_6[\mathrm{A}]}{k_4+(k_5+k_6)[\mathrm{A}]} \tag{4}$$

$$\beta^{\mathrm{A}}=\frac{k_{10}[\mathrm{RH}_2]}{k_7+k_8[\mathrm{A}]+k_9[\mathrm{RH}_2]+k_{10}[\mathrm{RH}_2]} \tag{5}$$

Hence the plots $1/\Phi^{\mathrm{S}}$ *vs.* $1/[\mathrm{RH}_2]$ as well as $1/\Phi$ *vs.* $1/[\mathrm{RH}_2]$ for the same dye concentration, should give, irrespective of a sensitizer, the same value of intercept/slope, which corresponds to $(k_9+k_{10})/(k_7+k_8[\mathrm{A}])$. The comparison is made in Table 6, which shows that the above requirement is well satisfied. This assures that the steps succeeding the formation of triplet dye are quite the same in all the systems.

Secondly, the rate constant of the triplet energy transfer was estimated as follows. Under the condition $k_7>k_8$ [A], the inverse Φ^{S} is written as follows,

$$\frac{1}{\Phi^{\mathrm{S}}}=\frac{1}{\varphi_{\mathrm{ST}}^{\mathrm{D}}}\left(\frac{k_9+k_{10}}{k_{10}}+\frac{k_7}{k_{10}[\mathrm{RH}_2]}\right)\times\left(\frac{k_5+k_6}{k_6}+\frac{k_4}{k_6[\mathrm{A}]}\right)$$

TABLE 6

Donor	$(k_9+k_{10})/(k_7+k_8[\mathrm{A}])$				
	Fluorescein	Eosine	Erythrosine	Methylene blue	Thionine
None	~200	45—95	42	~500	1050
1,2,5,6-Dibenzanthracene	100	82	45	~750	~1000
Triphenylene		73	33		
β-Acetonaphtone	100	80	35	~750	~1000
Anthracene				~750	~1000

TABLE 7. RATIO OF THE DEACTIVATION AND TRUE REACTION BETWEEN TRIPLET DYE AND ATU (k_9/k_{10})

Donor/Acceptor	Fluorescein	Eosine	Erythrosine	Methylene blue	Thionine
1,2,5,6-Dibenzanthracene	9	28	97	30	9
Triphenylene	—	24	81	—	—
β-Acetonaphthone	14	19	72	—	—
Anthracene	—	—	—	23	7
None	2	7	51	23	8

Thus the plot $1/\Phi^S$ *vs.* $1/[A]$ gives $k_4/(k_5+k_6)$ as the ratio, intercept/slope. The plots were drawn by using such data as given in Fig. 7. The method is of course very rough, but the values of k_5+k_6 obtained by using the k_4 values in Table 2 were 10^9—$10^{10}\text{M}^{-1}\,\text{sec}^{-1}$. This assures that the energy transfer occurs as diffusion controlled.

As seen in Table 5, the φ_{ST}^{A} values obtained in the present research are much larger than the tentative values already published,[2–4] and of course, the ones of Oster. They are compared with the values of Porter and Bowers[6] (in the aqueous solution of pH 9), for fluorescein (0.05), eosine (0.71), erythrosine (1.07) and Schenck's values for fluorescein (0.03), eosine (0.3) and erythrosine[10] (0.6) (in methanol at 20°C). Somewhat smaller values of Schenck may be due to the method being similar as the Oster's one. Thus it can now be concluded that the values evaluated by Oster's method are in general smaller than the real ones due to the participation of the deactivation reaction between D^T and ATU.

The φ_{ST}^{A} values of xanthene dyes increase in the order, fluorescein$<$eosine$<$erythrosine. This is interpreted in terms of the internal heavy atom effect.

The magnitude of the mere deactivation of triplet dye by the attack of ATU which largely influences the quantum yield can simply be evaluated as follows. Thus the values of $\beta_{\max}^{A}$, as obtained from the intercepts of the $1/\Phi^S$ (or $1/\Phi$) *vs.* $1/[RH_2]$ plots, using the φ_{ST}^{D} (or φ_{ST}^{A}) values and assuming $\gamma=1$, give $(k_9+k_{10})/k_9$. Table 7 lists the values of k_9/k_{10}, *i. e.*, the ratio of the mere deactivation and the genuine reaction between triplet dye and ATU. It is seen that for each dye, the values are about the same for different sensitizers and also for the direct reaction. This verifies again the assumption, $\gamma=1$.

Table 7 shows that the mere deactivation of triplet dye by ATU increases in the order, fluorescein $<$eosine$<$erythrosine. Thus it has been established unequivocally that the magnitude of the photoreduction quantum yield largely depends on such a deactivation process and that the internal conversion does not matter as once Oster proposed.[1] All the values of $\Phi_F+\Phi_T$ for fluorescein (0.9_3), eosine (0.9_5) and erythrosine ($\sim 1._0$) are close to unity.

Finally, correction will be made on the previously reported rate constants of some elementary reactions involved in the photoreduction of eosine in ethanol,[*2] using the present value of φ_{ST} (0.40).[*2]

TABLE 8. RATE CONSTANTS OF SOME ELEMENTARY REACTIONS INVOLVED IN THE PHOTOREDUCTION OF EOSINE IN ETHANOL

From the reactions in pure ethanol	
$k_7'/k_7=3.8\times10^{-3}$ (3×10^{-2})	
	$k_7(\approx k_7'')=2.3\times10^{3}\,\text{sec}^{-1}$
	$k_7'=\sim10\,\text{sec}^{-1}$ $(70\,\text{sec}^{-1})$
$k_8'/k_8=\sim2\times10^{-3}$ $(\sim4\times10^{-3})$	
	$k_8=\sim2\times10^{8}\text{M}^{-1}\,\text{sec}^{-1}$
	$k_8'=\sim9\times10^{4}\text{M}^{-1}\,\text{sec}^{-1}$
From the reactions with ATU in ethanol	
$k_8'/k_8=1$—3×10^{-3}	$k_8=1.3$—$3.7\times10^{8}\text{M}^{-1}\,\text{sec}^{-1}$
	$k_8'=1$—$5.5\times10^{5}\text{M}^{-1}\,\text{sec}^{-1}$
$k_9'/k_9=0.7$—5×10^{-1}	$k_9=1.1$—$4\times10^{5}\text{M}^{-1}\,\text{sec}^{-1}$
	$k_9'=2.6$—$5.5\times10^{4}\text{M}^{-1}\,\text{sec}^{-1}$

′: genuine reaction

no superscript: sum of the genuine and deactivation reaction.

The values in parentheses are the previous ones.

These values are very approximate.

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

[*2] It is to be noted that some of the previous notations are changed to fit the present system.