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Determination of S*–T Transition Probabilities of Some Xanthene and Thiazine Dyes on the Basis of T-Energy Transfer. II. Results in the Aqueous Solution

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Intersystem crossing probability φ_{ST}^{A} for fluorescein, eosin, erythrosin, methylene blue and thionine in the aqueous solution of pH 7.2 (only for fluorescein 0.05N NaOH solution) has been determined by comparing the quantum yield of the nonsensitized (Φ) and the sensitized photoreduction (Φ^S) on the basis of the relations

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

where β^A is the fraction of triplet dye molecules that undergo reduction, φ_{ST}^{A} and φ_{ST}^{D} are respectively for acceptor (dye) and donor (sensitizer), and γ is the energy transfer efficiency. This was assumed as unity. ATU and EDTA were used as a reducing agent. 1,5-Naphthalenedisulfonic acid and 1-anthracenesulfonic acid were used as sensitizers. The above relations and assumption have been found to hold satisfactorily. The φ_{ST}^{D} values for two sensitizers were determined using erythrosin as a reference substances for which φ_{ST}^{A} was assumed to be unity. φ_{ST}^{D} obtained was 0.88 for 1,5-naphthalenedisulfonic acid, and 0.82 for 1-anthracenesulfonic acid. φ_{ST}^{A} values for dyes obtained were: fluorescein (0.021) eosin (0.64) erythrosin (1.0) methylene blue (0.52) thionine (0.55). Using these φ_{ST}^{A} values, the rate constants for the following elementary reactions have been evaluated (A, dye: RH_2, reducing agent): $A^T + RH_2 \rightarrow$reaction, $A^T + RH_2 \rightarrow$deactivation, $A^T + A \rightarrow$reaction or deactivation.

In a previous paper[1] the application of the T-energy transfer was successfully applied to the determination of the S*-T transition probabilities of some xanthene and thiazine dyes in ethanol solutions. The method consists of comparison of the quantum yield for the direct photoreduction of dyes (Φ), with that of the sensitized reduction in otherwise similar conditions (Φ^S), using suitable aromatic hydrocarbons as sensitizers (donors). In an ideal case, Φ and Φ^S are written as

$$\Phi = -\mathrm{d}[A]/\mathrm{d}t/I_{ab} = \varphi_{ST}^{A}\beta^{A} \tag{1}$$

$$\Phi^{S} = -\mathrm{d}[A]/\mathrm{d}t/I_{ab} = \varphi_{ST}^{D}\gamma\beta^{A}, \tag{2}$$

where φ_{ST}^{A} and φ_{ST}^{D} are respectively the transition probabilities of S*–T transition for acceptor (dye) and donor, and β^A the fraction of the triplet dye which undergoes the reaction. γ is the efficiency of T-energy transfer between donor and acceptor and is regarded to be unity when the T-energy level of donor is much higher than that of acceptor. By combining (1) and (2) one can easily evaluate φ_{ST}^{A}, since the value of φ_{ST}^{D} is known for many aromatic hydrocarbons.

The purpose of the present paper is to extend the above method to the aqueous solutions. Hitherto there have been reported very few φ_{ST} values for dyes or for the substances dissolved in water. As far as we know, the only reliable data ever published for dyes are Bowers and Porter's.[2] However, their method which relies upon flash technique, appears to require some skill and caution in experiments.

Our method is very simple in principle and requires no particular technique but at present there is no report concerning the suitable sensitizers with the known φ_{ST}^{D} values. Once a set of such sensitizers are found, the method will have a wider scope of application.

As sensitizers, we have employed 1-anthracenesulfonic acid and 1,5-naphthalenedisulfonic acid. To determine the φ_{ST}^{D} value of the latter, erythrosin has been chosen as a reference substance, because its φ_{ST} value in the aqueous solution is, according to Bowers and Porter,[2] 1.0 and the same value has also been found by our experiment in ethanol.[1] In practice, the φ_{ST} value of 1,5-naphthalenedisulfonic acid has been determined by comparing Φ^S and Φ for the photoreduction of erythrosin using allylthiourea (ATU) or EDTA as a reducing agent. Then with the use of this φ_{ST}^{D} value, the φ_{ST}^{A} values

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[1] M. Nemoto, H. Kokubun and M. Koizumi, This Bulletin, **42**, 1223 (1969).

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

Table 1. Quantum yield of photoreduction

Reducing agent, EDTA

EDTA	Fluorescein	Eosin	Erythrosin	Methylene blue	Thionine
2.0×10^{-2}M	—	—	4.52×10^{-2}	8.4×10^{-2}	3.7×10^{-1}
1.5×10^{-2}	—	—	4.26×10^{-2}	6.6×10^{-2}	3.5×10^{-1}
1.0×10^{-2}	1.1×10^{-3}	5.25×10^{-2}	3.76×10^{-3}	4.6×10^{-2}	2.95×10^{-1}
5.0×10^{-3}	0.64×10^{-3}	2.42×10^{-2}	1.9×10^{-2}	2.6×10^{-2}	1.9×10^{-1}
2.5×10^{-3}	0.30×10^{-3}	—	1.05×10^{-2}	—	—
1.0×10^{-3}	—	0.53×10^{-2}	—	0.54×10^{-2}	0.6×10^{-1}

Reducing agent, ATU

ATU	Fluorescein	Eosin	Erythrosin	Methylene blue	Thionine
2.0×10^{-2}M	—	—	2.1×10^{-2}	2.9×10^{-3}	1.14×10^{-2}
1.5×10^{-2}	—	—	1.7×10^{-2}	2.1×10^{-3}	1.1×10^{-2}
1.0×10^{-2}	4.7×10^{-4}	1.4×10^{-2}	1.4×10^{-2}	1.4×10^{-3}	0.93×10^{-2}
5.0×10^{-3}	2.9×10^{-4}	0.89×10^{-2}	1.02×10^{-2}	—	—
3.0×10^{-3}	1.8×10^{-4}	—	—	—	—
2.5×10^{-3}	—	0.45×10^{-2}	0.56×10^{-2}	—	—

of other dyes have been determined. Erythrosin can not be used as a reference substance for 1-anthracenesulfonic acid, because its T-state has almost the same energy as that of the dye. Hence its φ_{ST} value has been determined in reference to methylene blue. The results have been found to be quite consistent and satisfactory.

Experimental

Materials. All the dyes and ATU are the same as in the previous paper.[1] EDTA (Dotile 2NA) of G. R. grade was used without further purification. 1-Anthracenesulfonic acid sodium salt of G. R. grade of Wakojunyaku was passed through a column of activated alumina. 1,5-Naphthalenedisulfonic acid sodium salt of G. R. grade of Wakojunyaku was subjected to recrystallization from 3N HCl solution twice.

Apparatus and Procedures. The apparatus and the method of measurement are the same as in the previous paper.[1] The measurement was usually made at pH 7.2 by employing a phosphate buffer except fluorescein for which 0.05N NaOH solution was used. The concentrations of substances are as follows unless otherwise described: xanthene dyes, 1.0×10^{-5}M; thiazine dyes, 1.5×10^{-5}M; 1,5-naphthalenedisulfonic acid, 2.25×10^{-4}M; 1-anthracenesulfonic acid, 1.0×10^{-4}M; EDTA, 2.0×10^{-2}—1.0×10^{-3}M; ATU, 2.0×10^{-2}—2.5×10^{-3}M. Temperature was 30±0.5°C. The fluorescence measurement was made by a Hitachi MPF-2A spectrofluorimeter whose spectral response was calibrated using standard substances.[3]

Results

Quantum Yields for the Direct Photoreduction of Dyes. Quantum yields for the photoreduction of fluorescein, eosin, erythrosin, methylene blue and thionine by EDTA and ATU in several concentrations are summarized in Table 1. The data for fluorescein,[4] eosin,[5] erythrosin[6] and methylene

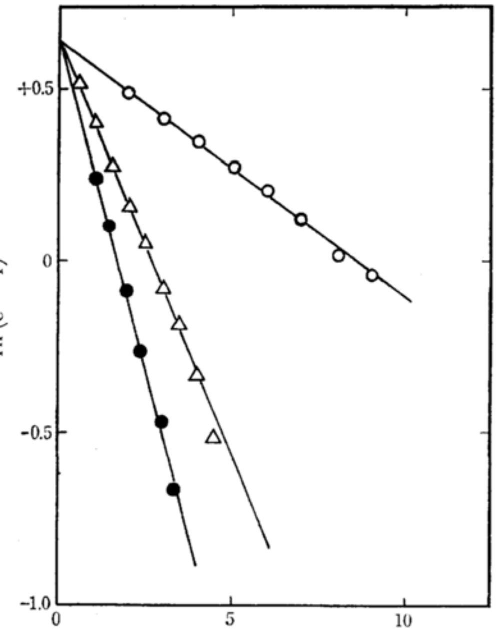

Fig. 1. Plots of ln (e^E-1) *vs.* t for thionine.
[thionine]$=1.5\times10^{-5}$ M
concentration of EDTA
○, 1.0×10^{-3}M △, 5.0×10^{-3}M
●, 1.0×10^{-2}M

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[3] E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger and W. Voss, *Z. Anal. Chem.*, **170**, 1 (1959).

[4] Y. Momose, K. Uchida and M. Koizumi, This Bulletin, **38**, 1601 (1965).

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

[6] A. H. Adelman and G. Oster, *J. Am. Chem. Soc.*, **78**, 3977 (1956).

Table 2. Some reference data for the donors

	Solvent	Absorption cm^{-1}	Phosphorescence cm^{-1}	Decay d) const. of T sec^{-1}	Quantum yield of fluorescence
Anthracene	EtOH	26700	14700 a)	7.0×10^2	0.3 e)
1-Anthracenesulfonic acid	H_2O (pH 7.2)	25900	—	1.0×10^3	0.18
Naphthalene	EtOH	31400	21250 b)	$\gtrsim10^4$	0.19 f)
1,5-Naphthalenedisulfonic acid	H_2O (pH 7.2)	29400	20800 c)	1.0×10^3	0.12

a) D. P. Craig and I. G. Ross, *J. Chem. Soc.*, **1954**, 1589.
b) in EPA at 77°K
c) in ethanol-water mixture
d) from the decay of T–T absorption at room temp.
e) T. Medinger and F. W. Wilkinson, *Trans. Faraday Soc.*, **61**, 620 (1965).
f) C. A. Parker *et al.*, *Proc. Chem. Soc.*, **1962**, 142.

blue7) agree with the published ones within experimental error. There is no value in literature to compare with for thionine. Figure 1 gives the $\ln(e^E-1)$ *vs.* t plot (E, optical density), the linearity of which supports the occurrence of D-R mechanism.

Examination on the Applicability of the Method. For the present method to be applicable, there should be no interaction between donor and other components including transient intermediates, except for the energy transfer between donor and acceptor. Thus in the first place, reducing agents must in no sense react with donors. Secondly, donors must react neither with the triplet state of dye nor with any other transient intermediates such as semiquinones of dyes. In addition, high efficiency of the energy transfer is very much desired. In these respects, nothing is known on the system consisting of the present donors and dyes.

Table 2 gives some reference data on the present donors as compared with the mother hydrocarbons.

The fluorescence quantum yields of the two sulfonic acids have been determined by comparing the fluorescence intensities of the aqueous solutions of these two substances with those of the ethanol solutions of naphthalene and anthracene.

The conditions mentioned above have been examined for all the systems. Firstly, it was ascertained that the triplet decays of the donors are not affected by $\sim1.0\times10^{-2}$M of ATU or EDTA of the same concentration. However, it was found by flash experiment that the decays of the triplet state for some dyes are affected by the existence of donor to some extent. In line with this finding, the quantum yield for the direct photoreduction of erythrosin, methylene blue and thionine was found to decrease with the addition of a larger quantity of donor. Figure 2 gives the result for erythrosin. The type of this deactivation seemed to be a mere deactivation, because no decrease in donor concentration was observed after reaction. It was ascertained, however, that in the system of 1,5-naphthalenedisulfonic acid and erythrosin, for example, the concentration of donors two or three times larger than that of the standard concentration, does

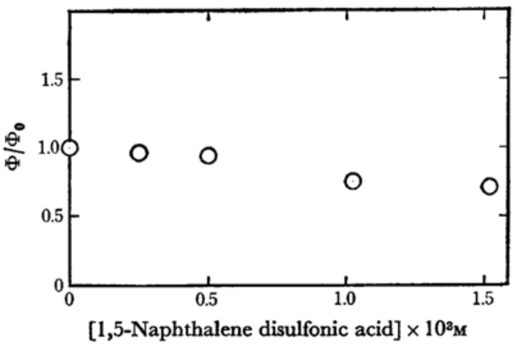

Fig. 2. Effect of the sensitizer's concentration on quantum yield of direct photoreduction.
[erythrosin]$=1.0\times10^{-5}$M
[EDTA]$=1.0\times10^{-2}$M

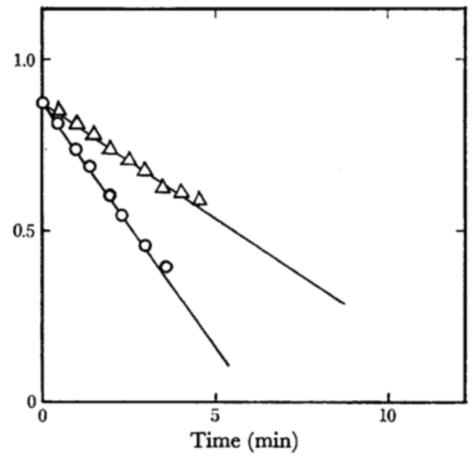

Fig. 3. An example of the plots of E *vs.* t for the sensitized reaction.
[eosin]$=11.0\times10^{-5}$M
[1,5-naphthalenedisulfonic acid]$=2.25\times10^{-4}$M
concentration of EDTA : △, 5.0×10^{-3}M
○, 1.0×10^{-2}M

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7) N. Kosui, K. Uchida and M. Koizumi, This Bulletin, **38**, 1958 (1965).

not affect the Φ^S value, if the concentration of reductant is larger than 1.0×10^{-2}M.

Lastly, mention should be made on the behavior of energy transfer. Figure 3 gives the plots of optical density against time for eosin as an example, under different conditions.

The linearity of the plot for [dye] $>1.0\times10^{-5}$M ensures that I_{ab}, φ^D_{ST} γ and β^A remain constant during the run. In view of the triplet lifetime given in Table 2, the constancy of γ is expected to be secured, if the energy transfer occurs as a diffusion controlled process. Figure 4 gives the decay of the donor triplet in the absence and in the presence of erythrosin; from these data the rate constant for deactivation by erythrosin is estimated to be of the order of 10^9M^{-1} sec^{-1}. Although the exact value of the energy transfer efficiency is yet unknown, the assumption will be made in the following that γ is unity in view of a large difference in triplet energy level between donor and dye.

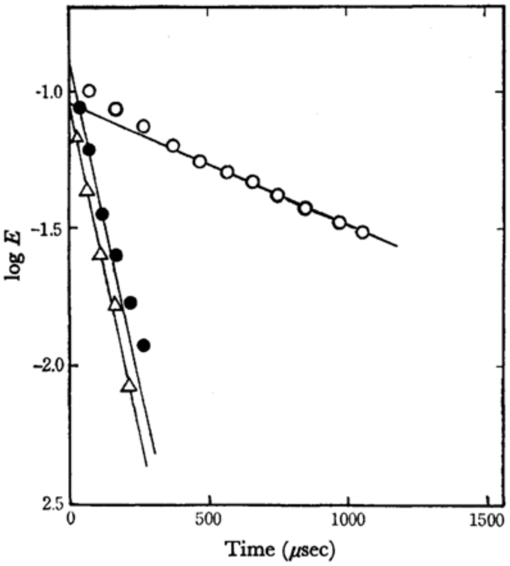


Fig. 4. Effect of the addition of the acceptor on the donor's triplet decay.
[1,5-naphthalenesulfonic acid]$=2.25\times10^{-4}$M
●, [erythrosin]$=1.0\times10^{-5}$M at 440 nm
△, at 580 nm
○, [erythrosin]=0 at 440 nm

Determination of φ^D_{ST} of the Two Donors. Firstly, φ^D_{ST} of 1,5-naphthalenedisulfonic acid has been determined by comparing the Φ^S values of the photoreduction of erythrosin sensitized by this donor, with those of the direct photoreduction of erythrosin listed in Table 1.

Table 3 gives the values of Φ^S of erythrosin and those of φ_{ST} of 1,5-naphthalenedisulfonic acid obtained on the assumption that φ_{ST} of erythrosin is unity.

TABLE 3. φ_{ST} OF 1,5-NAPHTHALENE-DISULFONIC ACID AND Φ^S

Reductant	[Reductant]	Φ^S	φ_{ST}
EDTA	2.0×10^{-2}M	4.0×10^{-2}	0.89
	1.5×10^{-2}	3.8×10^{-2}	0.89
	1.0×10^{-2}	3.5×10^{-2}	0.93
	5.0×10^{-3}	1.55×10^{-2}	0.82
ATU	2.0×10^{-2}	1.9×10^{-2}	0.83
	1.5×10^{-2}	1.4×10^{-2}	0.90
	1.0×10^{-2}	1.25×10^{-2}	0.92
		Average	0.88 ± 0.05

Next, φ_{ST} of methylene blue was determined using 1,5-naphthalenedisulfonic acid as a donor. Then from the combination of methylene blue and 1-anthracene sulfonic acid, φ_{ST} of the latter was obtained by use of φ_{ST} of methylene blue, 0.52 ± 0.01. The result was that φ_{ST} of 1-anthracene-

TABLE 4. QUANTUM YIELD OF SENSITIZED PHOTOREDUCTION OF XANTHENE DYES
donor; 1,5-naphthalenedisulfonic acid

Reductant	[EDTA]	Fluorescein	Eosin	Erythrosin
EDTA	2.0×10^{-2}M	—	—	4.0×10^{-2}
	1.5×10^{-2}	—	—	3.8×10^{-2}
	1.0×10^{-2}	4.04×10^{-2}	7.6×10^{-2}	3.5×10^{-2}
	5.0×10^{-3}	2.25×10^{-2}	3.4×10^{-2}	1.6×10^{-2}
	2.5×10^{-3}	1.3×10^{-2}	—	—
	1.0×10^{-3}	—	0.66×10^{-2}	—
	[ATU]			
ATU	2.0×10^{-2}	—	—	1.95×10^{-2}
	1.5×10^{-2}	—	—	1.43×10^{-2}
	1.0×10^{-2}	2.3×10^{-2}	2.1×10^{-2}	1.25×10^{-2}
	5.0×10^{-3}	1.17×10^{-2}	1.28×10^{-2}	—
	3.0×10^{-3}	0.75×10^{-2}	—	—
	2.5×10^{-3}	—	0.66×10^{-2}	—

Table 5. Quantum yield of sensitized photoreduction of thiazine dyes

Donor / Reductant	[Reductant]	I Methylene blue	I Thionine	II Methylene blue
EDTA	2.0×10^{-2}M	1.4×10^{-1}	5.7×10^{-1}	1.24×10^{-1}
	1.5×10^{-2}	1.14×10^{-1}	5.4×10^{-1}	1.1×10^{-1}
	1.0×10^{-2}	0.79×10^{-1}	5.0×10^{-1}	0.88×10^{-1}
ATU	2.0×10^{-2}	4.87×10^{-3}	1.79×10^{-2}	4.46×10^{-3}
	1.5×10^{-2}	3.45×10^{-3}	1.70×10^{-2}	3.38×10^{-3}
	1.0×10^{-2}	2.36×10^{-3}	1.49×10^{-2}	2.12×10^{-3}

I, 1,5-naphthalenedisulfonic acid
II, 1-anthracensulfonic acid

sulfonic acid is 0.82±0.02 (As to the experimental data, see below).

The sums of Φ_F and φ_{ST} for 1,5-naphthalenedisulfonic acid and 1-anthracenesulfonic acid are respectively $0.88+0.12=1.0$ and $0.82+0.18=1.0$. Thus the internal conversion is negligible in these two donors.

Quantum Yields of the Sensitized Photoreduction Φ^S and the φ_{ST} Values of Dyes. Tables 4 and 5 give respectively the quantum yields of the sensitized photoreduction of xanthene and thiazine dyes. The experimental condition was always so selected that the reaction took place in an ideal way. The 1-anthracenesulfonic acid-thionine system was omitted, since the concentration of thionine in the aerated solution gradually decreased even in dark.

In Table 6 are summarized the φ_{ST} values of fluorescein, eosin, methylene blue and thionine obtained by applying Eqs. (1) and (2) to a set of two corresponding experimental data given in Tables 1, 4 and 5. The φ_{ST} values of methylene blue listed in the column of 1-anthracenesulfonic acid are the ones recalculated by putting φ_{ST} for 1-anthracenesulfonic acid as 0.82. Table 6 clearly shows that the φ_{ST} value of each dye is essentially the same independent of reducing agent and donor.

Discussion

Table 7 gives the comparison of the φ_{ST} values of the present work (pH 7.2) with the published data.

The values for xanthene dyes in the aqueous solution are somewhat larger than those in ethanol. The values for thiazine dyes on the other hand are about the same in both solvents. The present value for eosin is very close to Bowers and Porter's in spite of the entirely different method. Gollnick and Schenck's values are somewhat smaller than the present ones (except fluorescein). Their values were based on the assumption that the reaction $A^T+{}^3O_2\rightarrow A+{}^1O_2$ occurs in the presence of ample oxygen, with efficiency 1. It is unlikely that this assumption is correct.

According to our previous investigations, the

Table 6. φ_{ST} Values of dyes

Donor / Reductant	[Reductant]	I Fluorescein	I Eosin	I Methylene blue	I Thionine	II Methylene blue
EDTA	2.0×10^{-2}M	—	—	0.52	0.55	0.55
	1.5×10^{-2}	—	—	0.51	0.57	0.50
	1.0×10^{-2}	0.022	0.64	0.51	0.52	—
	5.0×10^{-3}	0.025	0.63	—	—	—
	2.5×10^{-3}	0.021	—	—	—	—
	1.0×10^{-3}	—	0.70	—	—	—
	Average	0.022±0.003	0.66±0.03	0.51±0.01	0.54±0.03	0.52±0.03
ATU	2.0×10^{-2}	—	—	0.52	0.56	0.53
	1.5×10^{-2}	—	—	0.51	0.57	0.51
	1.0×10^{-2}	0.018	0.60	0.53	0.55	0.55
	5.0×10^{-3}	0.021	0.61	—	—	—
	3.0×10^{-3}	0.022	—	—	—	—
	2.5×10^{-3}	—	0.61	—	—	—
	Average	0.020±0.002	0.61±0.01	0.53±0.01	0.56±0.02	0.53±0.02

I, 1,5-naphthalenedisulfonic acid
II, 1-anthracensulfonic acid

TABLE 7. COMPARISON OF φ_{ST} VALUES

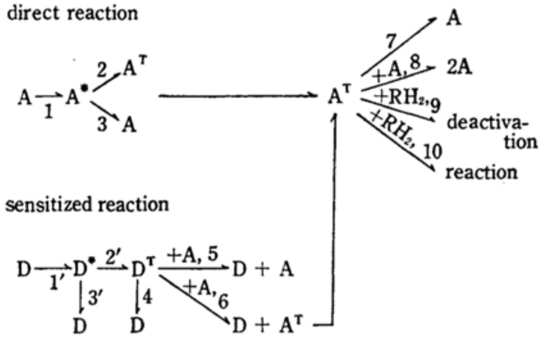
	Present work (pH 7.2)	Bowers and Porter[2] (pH 9.0)	in C_2H_5OH[1]	Gollinick and Schenck[8] in alcohols
Fluorescein	0.021 ± 0.02[a]	0.05	0.0045 ± 0.005[b]	0.03
Eosin	0.64 ± 0.02	0.71	0.42 ± 0.04	0.25~0.3
Erythrosin	(1.0)	1.07	1.05 ± 0.03	0.62~0.6
Methylene blue	0.52 ± 0.01		0.52 ± 0.03	
Thionine	0.55 ± 0.02		0.62 ± 0.4	

a) 0.05N NaOH
b) 30 vol.% aq. alkaline ethanolic solution

TABLE 8. COMPARISON OF THE $(k_9+k_{10})/(k_7+k_8[A])$ VALUES (R) AND β_{max}

Acceptor / Donor	Fluorescein		Eosin		Erythrosin		Methylene blue		Thionine	
	R	β_{max}	R	β_{max}	R	β_{max}	R	β_{max}	R	β_{max}
EDTA										
None	50	0.1	54	0.13	73	0.08	84	0.4	100	0.89
1,5-Naphthalenedisulfonic acid	30	0.11	47	0.19	86	0.08	115	0.3	160	0.91
1-Anthracenesulfonic acid	—	—	—	—	—	—	100	0.3	—	—
ATU										
None	60	0.09	55	0.067	60	0.035	100	0.032	50	0.04
1,5-Naphthalenedisulfonic acid	57	0.077	40	0.07	60	0.029	110	0.024	50	0.03
1-Anthracenesulfonic acid	—	—	—	—	—	—	100	0.024	—	—

scheme for the present reaction can be described as follows,



Then γ and β in Eqs. (1) and (2) are expressed as follows,

$$\gamma = \frac{k_6[A]}{k_4 + (k_5+k_6)[A]} \tag{3}$$

$$\beta_A = \frac{k_{10}[RH_2]}{k_7 + k_8[A] + k_9[RH_2] + k_{10}[RH_2]} \tag{4}$$

Insertion of (3) and (4) into Eqs. (1) and (2) allows us to expect that both the $1/\Phi$ *vs.* $1/[RH_2]$ plot and the $1/\Phi^S$ *vs.* $1/[RH_2]$ plot should give the same value for (intercept)/(slope), *i.e.* $(k_9+k_{10})/(k_7+k_8[A])$, if the donor does not interfere with the reaction scheme after the formation of A^T. Table 8 clearly shows that this really holds in all cases.

Furthermore the intercepts of the $1/\Phi$ *vs.* $1/[RH_2]$ plot and $1/\Phi^S$ *vs.* $1/[RH_2]$ plot give respectively $\varphi_{ST}^A\ \beta_{max}$ and $\varphi_{ST}^D\ \gamma\beta_{max}$, and if the relation $\gamma=1$ really holds, the same β_{max}, *i. e.* $k_{10}/(k_9+k_{10})$ should result irrespective of sensitized and nonsensitized reaction and also independent of the kind of sensitizer. In Table 8 are listed also the values of β_{max} evaluated from the intercepts by putting $\gamma=1$. It is evident that β_{max} for each dye-reductant system agree within experimental error. As in the ethanol solution mere deactivation is much larger for ATU than for EDTA. It is remarkable that mere deactivation scarcely occurs in the case of thionine-EDTA.

In the case of eosin and fluorescein, the (k_9+k_{10}) and k_7 values are known from the flash experiments and so the k_9, k_{10} and k_8 values are obtained. The results are given in Table 9.

Lastly, the tentative data reported in the previous papers will be corrected using the reliable φ_{ST} values obtained in the present paper. Since the equation

$$\frac{1}{\Phi} = \frac{1}{\varphi_{ST}^A}\left\{\frac{k_9+k_{10}}{k_9} + \frac{k_7}{k_{10}[RH_2]} + \frac{k_8[A]}{k_{10}[RH_2]}\right\}$$

holds, and $(k_9+k_{10})/k_9$ can be evaluated from the

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[8] K. Gollnick and G. O. Schenck, *Pure Appl. Chem.*, **9**, 507 (1964); K. Gollnick, *Advances in Photochem.*, Vol. 6, ed. by W. A. Noyes, Jr., G. S. Hammond and J. N. Pitts, John Wiley & Sons, New York (1968).

Table 9

	k_7 (sec^{-1})		k_8 (sec$^{-1}\cdot$M^{-1})	k_9+k_{10} (sec$^{-1}\cdot$M^{-1})	k_9 (sec$^{-1}\cdot$M^{-1})	k_{10} (sec$^{-1}\cdot$M^{-1})
Eosine	5.4×10^{2} a)	EDTA	7.3—10×10^{8}	5.0×10^{5} b)	4.2×10^{5}	8.3×10^{4}
		ATU	5.6—7.9×10^{8}	3.4×10^{5} b)	3.1×10^{5}	2.4×10^{4}
Fluorescein	5.10×10 c)	ATU	2.8—4.5×10^{8}	2.0×10^{5} c)	1.8×10^{5}	1.8×10^{4}

a) V. Kasche and L. Lindqvist, *Photochem. Photobiol.*, **4**, 923 (1965).
b) T. Ohno, S. Kato and M. Koizumi, This Bulletin, **39**, 232 (1966).
c) L. Lindqvist, *Arkiv för Kemi*, **16**, 79 (1960).

Table 10. Corrected values from the previous data

Reduction	[A]	$\dfrac{k_7+k_8[\mathrm{A}]}{k_{10}}$	$\dfrac{k_{10}}{k_9+k_{10}}$	k_{10} sec$^{-1}\cdot$M^{-1}	k_8 sec$^{-1}\cdot$M^{-1}
Eosin*					
ATU	1.16×10^{-5}M	5.75×10^{-1}	0.23	7.8×10^{4}	4.4×10^{9}
	8.0×10^{-6}	4.47×10^{-1}	0.08	2.7×10^{4}	1.2×10^{9}
	4.0×10^{-6}	1.41×10^{-1}	0.05	1.7×10^{4}	2.4×10^{8}
	2.4×10^{-6}	0.9×10^{-1}	0.05	1.7×10^{4}	1.0×10^{8}
EDTA	8.0×10^{-6}	9.1×10^{-2}	0.125	6.0×10^{4}	6.2×10^{8}
	5.5×10^{-6}	4.6×10^{-2}	0.125		2.1×10^{8}
Fluorescein4)					
ATU	0.09N NaOH	3.48×10^{-2}	0.23	4.52×10^{4}	1.5×10^{8}
	0.1N NaOH	2.6×10^{-2}	0.23		
EDTA	0.05N NaOH	1.79×10^{-2}	0.39		
	0.1N NaOH	2.04×10^{-2}	0.64		
Methylene blue7)					
EDTA	9.0×10^{-6}	8.3×10^{-3}	0.45	6.1×10^{6}	3.0×10^{9}
ATU	8.2×10^{-6}		0.024	1.3×10^{4}	2.7×10^{9}

* The values of intercept for the $1/\Phi$ *vs.* $1/[\mathrm{RH_2}]$ plot in the previous paper5) appears to depend on the dye concentration. But in view of the present result, this is most likely due to experimental error. Hence $\varphi_{\mathrm{ST}}=0.64$ was used in all the data.

intercept of the $1/\Phi$ *vs.* $1/[\mathrm{RH_2}]$ plot, k_8, k_9 and k_{10} can be evaluated from the experimental data for the dependence of Φ on $[\mathrm{RH_2}]$ and on [A], only if k_7 is known from the flash experiment. The knowledge of the (k_9+k_{10}) value from the flash experiment will make the evaluation of these constants more simple and more reliable. The corrected values from the previous data for fluorescein, eosin and methylene blue are given in Table 10.

It is seen that in general the previous k_{10} values are much too large while the k_8-value is correct in the order of magnitude. Moderate agreement is apparent between the data in Tables 9 and 10.

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