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The Occurrence of a D-D Mechanism in the Ethanol Solution of Eosine

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The occurrence of a D-D mechanism in which the photochemical reaction is initiated by the interaction of the triplet dye and the ground-state dye molecules, has been established for the ethanol solution of eosine. Chief evidence for it has been afforded by: 1) the predominance of the second-order reaction at high dye concentrations, 2) the dependence of the quantum yield of the photoreduction upon the dye concentration, and 3) the effect of the dye concentration on the photochemical oxygen absorption and on the oxydative photobleaching of dye. Assuming no simple deactivation between the triplet dye and allylthiourea, the quantum yield for the formation of the triplet dye has been evaluated as 0.056. Then the rate constants for the following elementary reactions, $D^T+D-\left|\begin{matrix}\rightarrow\text{intermediate}\\ \rightarrow\text{deactivation}\end{matrix}\right\}$ and $D^T+\text{ATU}\rightarrow$ intermediate, are, respectively, $1\times10^8\ \text{M}^{-1}\text{sec}^{-1}$ and $1—2\times10^5\ \text{M}^{-1}\text{sec}^{-1}$. It seems that the reaction between oxygen and the triplet dye is chiefly an eventual deactivation of the latter, with no appreciable decomposition of the dye or of ethanol.

In a series of papers1) our group has thoroughly established that the photoreduction of eosine in an aqueous solution by allylthiourea can, under suitable conditions, start from the attack of the ground-state dye molecule upon the excited one. Such a mechanism, which we have designated as a D-D mechanism, also takes place in some thiazine dyes.2) It is the purpose of the present paper to ascertain whether a similar mechanism occurs in the case of the ethanol solution of eosine and, further, to compare the kinetics in ethanol with that in water.

As early as 1956 Imamura and Koizumi6) found that the solution of eosine in ethanol undergoes photoreduction with a quantum yield of about 5×10^{-4}. However, since then no attention has been paid to the possibility of the occurrence of the D-D mechanism in ethanol. Flash photolysis studies of the ethanol solution of eosine have also been made by our group,4) and some findings have been reported by Kira and Kato5) which suggest the transient formation of a certain molecular complex composed of a half-reduced and a half-oxidized dye molecule.[*1] It seemed of great interest, therefore, to extend the two types of experiments which had already been made on the aqueous solution to the ethanol solution; one type is a study of the effect of the dye concentration on the quantum yield of photoreduction and on the type of the decay kinetics, and the other is a study of the similar effect on the rate of the photochemical consumption of oxygen. Allylthiourea (ATU) was used as a reducing agent for the purpose of increasing the quantum yield, thus making the quantitative studies more feasible.

Photoreduction of Eosine by ATU in Ethanol

The materials and procedures are quite similar to those used in the studies of the aqueous solution1b) except for the use of various cells to shorten the optical path to 0.1 mm. The reaction was followed by the fall of the maximum peak of eosine at 528 mμ. The concentrations of AUT and of the dye were changed from 2×10^{-2} to 5×10^{-4} M and from 5×10^{-6} to 8×10^{-5} M respectively.

Decay Curves. So long as the dye concentration is $10^{-6}—10^{-5}$ M, the $\ln(e^{\tilde{\alpha}cd}-1)$ *vs. t* plot, where $\tilde{\alpha}$, c and d are, respectively, the molar absorbance, the dye concentration, and the optical path, is linear, irrespective of the ATU concentration. This implies that the rate is proportional to the absorption of light. At lower concentrations

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1) a) Y. Usui, K. Itoh and M. Koizumi, This Bulletin, **38**, 1015 (1965). b) T. Ohno, Y. Usui and M. Koizumi, *ibid.*, **38**, 1022 (1965). c) T. Ohno, S. Kato and M. Koizumi, *ibid.*, **39**, 232 (1966).

2) S. Kato, M. Morita and M. Koizumi, *ibid.*, **37**, 117 (1964); N. Kosui, K. Uchida and M. Koizumi, *ibid.*, **38**, 1958 (1965).

3) M. Imamura and M. Koizumi, *ibid.*, **29**, 899 (1956).

4) S. Kato and M. Koizumi, *Nature*, **184**, 1620 (1959); S. Kato, T. Watanabe, S. Nagaki and M. Koizumi, This Bulletin, **33**, 262 (1960).

5) A. Kira and S. Kato, *Sci. Rep. Tohoku Univ. Ser.* 1, **48**, 142 (1965).

[*1] The peak at 410 mμ in the transient spectra was assigned to the semiquinone of eosine. The peak at 450 mμ was suggested to be due to a semioxidized form. These two peaks decay according to the first order, with a common rate constant of $6\times10^2\ \text{sec}^{-1}$.

of ATU, *e. g.*, at 5×10^{-4} M, the linearity is not so good and the 1/[D] *vs. t* plot becomes more satisfactory. This suggests the preponderance of the second-order reaction. This behavior, which is quite similar to that in the aqueous solution, supports the view that a switch-over from the D-R to the D-D mechanism is occurring with the increase in the dye concentration.

The Effect of the ATU Concentration on the Quantum Yield of Photoreduction. Figure 1 gives the effect of the ATU concentration on the quantum yield of photoreduction, Φ.

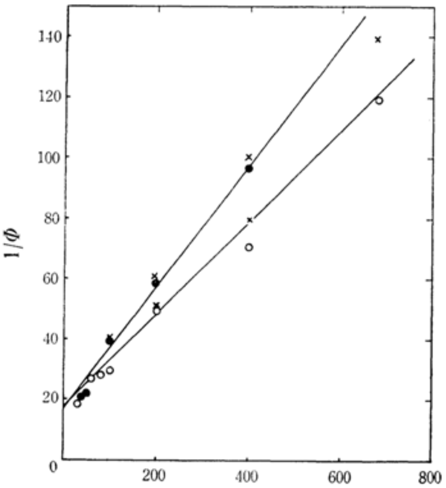

Fig. 1. Effect of ATU concentration on the quantum yield of photoreduction.
● [D]; 8×10^{-6} M, ○ [D]; 5×10^{-6} M
× Corrected value (see discussion in the text)

The dependence of Φ on [ATU] is reproduced by the following relation:

$$\frac{1}{\Phi}=\alpha+\frac{\beta}{[\mathrm{ATU}]} \qquad (1)$$

where α and β are, respectively, the intercepts and the slopes of the curves in Fig. 2. The values of α and β are listed in Table 1.

TABLE 1. VALUES OF α AND β

[D], M	α	β
5×10^{-6}	17.2	0.21_2
8×10^{-6}	17.5	0.16_3

The Effect of the Dye Concentrationon Φ. Figure 2 gives the dependence of Φ on the dye concentration. The linear plots in Fig. 2 are expressed by the following relation:

$$\frac{1}{\Phi}=\alpha'+\beta'[\mathrm{D}] \qquad (2)$$

where α' and β' depend upon the ATU concentration; β' in particular is inversely proportional to the ATU concentration, as may be seen in Table 2. Figure 3 shows that the deviation from the linear

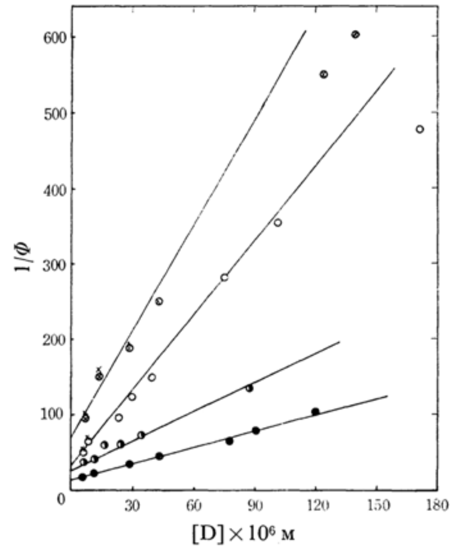

Fig. 2. Effect of dye concentration on the quantum yield of photoreduction for the ATU containing solution.
● [A]; 2×10^{-2} M ◑ [A]; 1×10^{-2} M
○ [A]; 5×10^{-3} M ⊗ [A]; 2.5×10^{-3} M
× Corrected value

TABLE 2. VALUES OF α' AND β'

[ATU], M	α'	β'	$\beta'\times$[ATU]
2×10^{-2}	20	7×10^5	1.2×10^4
1×10^{-2}	34	10.6×15^5	1.0×10^4
5×10^{-3}	38	29.5×10^5	1.5×10^4
2.5×10^{-3}	90	35×10^5	0.8×10^4
			Av. $1.1\times10^4\pm0.1$

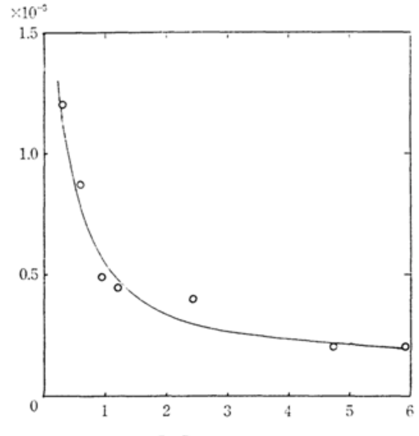

Fig. 3. Effect of dye concentration on the quantum yield of photoreduction for the plain ethanol solution.

plot becomes apparent with the increase in the dye concentration when the ATU concentration is small. This is similar to the case with the aqueous solution and may be attributed to the participation of the D-D mechanism under such conditions. The value of α' and β' are given in Table 2.

In connection with the above results, the effect of the dye concentration on the quantum yield of the photoreduction of eosine in a plain ethanol solution was also investigated. The results are given in Fig. 3.

Although the data are still preliminary, there is a clear tendency for Φ to decrease monotonicly, with an increase in the dye concentration, but to approach a constant limiting value. This result also supports the view that the interaction between the ground-state dye and the triplet dye is, for the most part, a simple deactivation, but the reaction through the D-D mechanism also occurs.

Absorption of Oxygen by the Irradiated Solution of Eosine in Ethanol and the Oxidative Photobleaching of the Dye

A Warburg apparatus was used in order to measure the quantity of oxygen absorbed by the aerated solution of eosine in ethanol when irradiated. The procedures are similar to those reported in a previous paper.[1a)] The dye concentration was varied from 10^{-5} to 10^{-3} M.

The Effect of the Dye Concentration on the Rate of Oxygen Consumption. The rate of oxygen absorption was determined from the slope of the plot of the quantity of absorbed oxygen against the time, which was linear, as in the aqueous solution. The results are shown in Fig. 4 as a function of the dye concentration. For comparison, the curve for the aqueous solution is also given.[1a)] As may be seen from the figure, the features of the two curves are quite similar. Thus the rate is practically constant beyond a certain dye concentration (somewhat larger than the concentration of the dissolved oxygen), whereas when the dye concentration becomes smaller, the rate decreases remarkably. As in the previous paper, this is to be interpreted by a switch-over from the D-O to the D-D mechanism. It may be worthwhile to note that the quantum yield of oxygen consumption by the D-D mechanism in ethanol is about one-half that in the aqueous solution. Another difference as compared with the aqueous solution is that the quantum yield of oxygen consumption by the D-O mechanism, Φ_{O_2} (D-O), is exceedingly small, perhaps less than 10^{-4}.

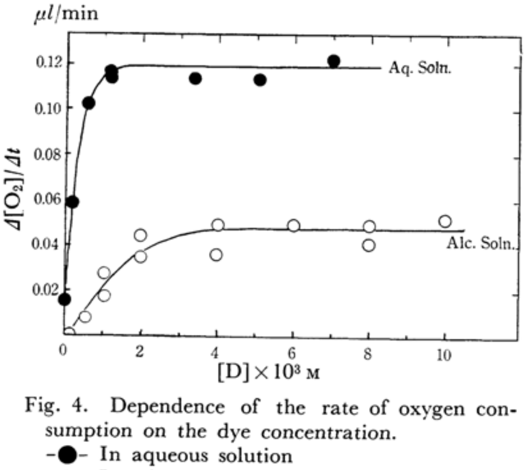

Fig. 4. Dependence of the rate of oxygen consumption on the dye concentration.
-●- In aqueous solution
-○- In ethanol solution

In connection with the above experiment, the oxidative photobleaching of eosine in the aerated ethanol solution was investigated, varying the dye concentration from 10^{-5} to 10^{-6} M.*2 The $\ln(e^{\tilde{\alpha}cd}-1)$ *vs.* t plots for various dye concentrations are shown in Fig. 5. As may be seen from the figure, the oxidative photobleaching practically does not occur below 8×10^{-4} M of the dye. However, when the dye concentration exceeds 1×10^{-3} M, which is near the concentration of the dissolved oxygen, the rate becomes measurable.*3 The $\ln(e^{\tilde{\alpha}cd}-1)$ *vs.* t plots are not linear; the slope increases rather rapidly as the reaction proceeds. This feature is quite similar to that of the aqueous solution.

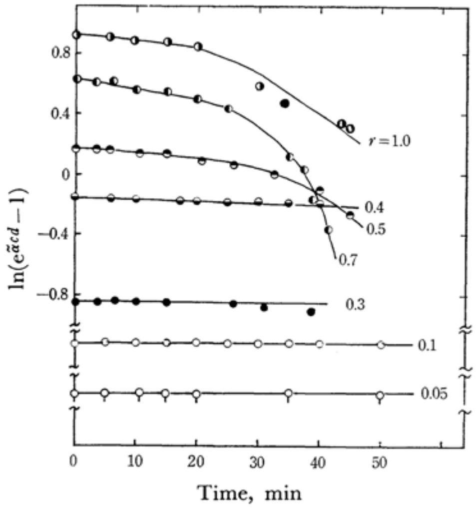

Fig. 5. Photobleaching of eosine at various concentration [D] in air-saturated ethanol solution. $r=[D]/[O_2]$

[D] (M)	[D] (M)
◑ 2.0×10^{-3}	● 6.0×10^{-4}
◐ 1.4×10^{-3}	○ 2.0×10^{-4}
◓ 1.0×10^{-3}	ϙ 1.0×10^{-5}
◒ 8.0×10^{-4}	

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*2 Three types of cell, the optical paths of which are 10, 1, and 0.1 mm, were used.

*3 In this case the final product is not a leuco dye; the dye structure is perhaps decomposed.

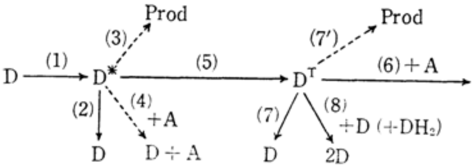
The above result can also be interpreted by a switch-over from the D-O to the D-D mechanism as the dye concentration exceeds that of the dissolved oxygen; in the former mechanism there is practically no net reaction, whereas in the latter mechanism an irreversible bleaching occurs in a complicated fashion.

Discussion

The general features of all the reactions resemble those of the corresponding reactions in the aqueous solution, especially with respect to the effect of the dye concentration not only on the decay kinetics and the quantum yield of the photoreduction, but also on the photochemical oxygen consumption and on the oxidative photobleaching. Hence, it may be said that the participation of the D-D mechanism at low ATU and at high dye concentrations as well as in the plain ethanol solution has been qualitatively substantiated. However, it is felt that the data are rather scanty and that, moreover, they are not accurate enough for the exact quantitative analysis. Below we will give the order of the magnitude evaluation of the rate constants for the elementary reactions on the basis of the D-R and D-D mechanisms.

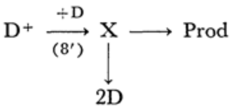
When the concentration of ATU is large enough, only the D-R mechanism occurs; the scheme for it may be written as follows[1b];

A.



where A and DH$_2$ are, respectively, ATU and the leuco dye. The processes denoted by dashed arrows are negligible for the case in question. When the concentration of ATU is rather small and the dye concentration is high, the D-D mechanism also participates; its essential processes succeeding the formation of D^T may be written as follows:

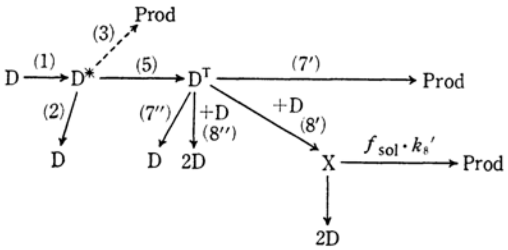
B.



where X represents a pair of half-reduced and half-oxidized dye molecules which exist as a molecular complex or as two separate species.

Before entering into an analysis of the data for the system containing ATU, it seems proper to consider here the results in a plain ethanol solution. It is evident that the reaction scheme presented by Imamura and Koizumi[3] should now be extended and should be written as follows:

C.*4



The quantum yield for the D-R or, more properly, the D-S mechanism (to distinguish the solvent from ATU) and the D-D mechanism in this case may then be given by the following relations:

$$\Phi_{D-S}=\frac{k_5}{k_2+k_5}\cdot\frac{k_7'}{k_7+k_8[D]} \tag{3}$$

$$\Phi_{D-D}=\frac{k_5}{k_2+k_5}\cdot\frac{f_{sol}\cdot k_8'[D]}{k_7+k_8[D]} \tag{4}$$

where $k_5/(k_2+k_5)=\varphi_{S-T}$ is a quantum yield for the production of the triplet dye and where f_{sol} is the fraction of X which ultimately goes to the product.

From the value of Φ for low dye concentrations, the value of $\varphi_{S-T}k_7'/k_7$ may be approximated about $\sim 1.5\times 10^{-3}$ and the value of k_8/k_7, roughly estimated as $\sim 1.0\times 10^6$ M. Using the value of $k_7=2.3\times 10^3$ sec^{-1} reported by Kira[5] and tentatively assuming $\varphi_{S-T}=0.05$ (see below), the approximate values of k_8, k_7'' and k_7' may be evaluated as $\sim 2\times 10^9$ M^{-1} sec^{-1}, $\sim 2.2\times 10^3$ sec^{-1} and 70 sec^{-1} respectively. When the dye concentration is $\sim 5\times 10^{-5}$ M, the reaction seems to proceed mainly *via* the D-D mechanism and Φ_{D-D} may be $\sim 2\times 10^{-4}$. Hence, the value of $f_{sol}\cdot k_8'/k_8$ is $\sim 4\times 10^{-3}$. The values obtained here are, rather, the order-of-magnitude values.

Returning now to the reactions in the system containing ATU, the entire Φ is generally written as follows:

$$\Phi=\Phi_{D-R}+\Phi_{D-S}+\Phi_{D-D}$$

Hence, in order to know the value of Φ_{D-R}, a small correction should be made in the experimental value of Φ to take the contribution of Φ_{D-S} into account. However, this correction was found to be necessary only when the ATU and dye concentrations are both very small. The corrected values (corrected by taking into account the values of k_6 and k_8 given below) are shown by the symbol X in Figs. 1 and 2. The rate constants of the elementary reactions involved in the D-R mechanism can now be evaluated in the following way by using the corrected Φ_{D-R} values. On the basis of the above Scheme A, the application of the steady-state method leads to the following equation:

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*4 In this paper and, respectively, denotes a genuine reaction and a simple deactivation. Notations without them signify the sum of the above two reactions.

TABLE 3. EVALUATED RATE CONSTANTS

	$k_8/\varphi_{S-T}k_6'$	$k_6/\varphi_{S-T}k_6'$	$k_7/\varphi_{S-T}k_6'$	$\varphi_{S-T}k_6'$ $\mathrm{sec^{-1}}$	k_6 $\mathrm{sec^{-1}}$	k_8 $\mathrm{M^{-1}sec^{-1}}$
from Eqs. (9) and (10) ([D] effect)	$\underline{1.14\times10^4}$	10—15	0.17—0.22	$1.1—1.4\times10^4$	$1.1—2.1\times10^5$	$1.3—1.6\times10^8$
from Eqs. (6) and (7) ([A] effect)	1.6×10^4	$\underline{17.2—17.5}$	0.1	2.3×10^4	$3.8—4.0\times10^5$	3.7×10^8

$$\Phi_{corr} = \Phi_{D-R} = \varphi_{S-T}\cdot\frac{k_6'[A]}{k_7 + k_6[A] + k_8[D]} \tag{5}$$

α and β in Eq. (1) are, respectively, given as follows:

$$\alpha = \frac{1}{\varphi_{S-T}}\cdot\frac{k_6}{k_6'} \tag{6}$$

$$\beta = \frac{1}{\varphi_{S-T}}\cdot\frac{k_7 + k_8[D]}{k_6'} \tag{7}$$

and

$$\frac{\beta}{\alpha} = \frac{k_7 + k_8[D]}{k_6} \tag{8}$$

Similarly, α' and β' in Eq. (2) are written as follows:

$$\alpha' = \frac{1}{\varphi_{S-T}}\cdot\frac{k_7 + k_6[A]}{k_6'[A]} \tag{9}$$

$$\beta' = \frac{1}{\varphi_{S-T}}\cdot\frac{k_8}{k_6'[A]} \tag{10}$$

As expected, the value of α (see Table 3) is approximately constant and the value of $k_6/\varphi_{S-T}k_6'$ is 17.2—17.5. The values of $k_7/\varphi_{S-T}k_6'$ and $k_8/\varphi_{S-T}k_6'$ can be evaluated from the dependence of β on [D] from (7). Alternatively, these three values can also be evaluated from the dependence of α' and β' on [A] (Table 4) using Eqs. (9) and (10). The values are given in Table 3.

The two series of values evaluated by different methods agree moderately well. The values of $k_8/\varphi_{S-T}k_6'$ and $k_7/\varphi_{S-T}k_6'$ from Eqs. (6) and (7) were evaluated from only two different concentrations of dye and are considered to be the least reliable. The values underlined are the most reliable. The values of $\varphi_{S-T}k_6'$ and k_6 and k_8 given in the table were evaluated by using the value of $k_7(=2.3\times10^3\ \mathrm{sec^{-1}})$. If one assumes $k_6=k_6'$, then φ_{S-T} is 0.056.

Next let us discuss the paticipation of the D-D mechanism. This can be deduced on the basis of deviations from the linear part (Fig. 2) of the $1/\Phi$ *vs.* [D] plots, deviations which are appreciable at high dye concentrations and at low ATU concentrations (2.5×10^{-3} and 5×10^{-3} M). In such cases no correction for Φ_{D-S} is necessary in a good approximation. Φ_{D-D} for the system containing ATU is given by the following relation:

$$\Phi_{D-D} = \varphi_{S-T}\left(\frac{k_8'[D]}{k_7 + k_6[A] + k_8[D]}\right)f \tag{11}$$

where f is factor similar to f_{sol} in Eq. (4). The order of magnitude of $k_8'\cdot f$ can now be evaluated by combining Eq. (5) and Eq. (11). Thus,

$$\frac{\Phi_{D-D}}{\Phi_{D-R}} = \frac{k_8'[D]}{k_6'[A]}f \tag{12}$$

The value of $k_8'\cdot f/k_6'$ evaluated at several points in the $1/\Phi$ *vs.* [D] plot in Fig. 2 is 4—10. If one assumes that $k_6\approx k_6'$, then $k_8'\cdot f$ is of the order of 10^6 and, hence, $k_8'\cdot f/k_8$ is of the order of $\sim$0.01 (see the values of k_6 and k_8 listed in Table 3) This agrees approximately with the $k_8'\cdot f_{sol}/k_8$ value for the plain ethanol solution; the attack of an ethanol molecule on the intermediate X seems to be as effective as that of an ATU molecule under the experimental conditions.

Lastly, let us discuss a switch over from the D-O to the D-D mechanism with reference to the oxygen-consumption experiment. As has been discussed in a previous paper,[1a)] when the concentration of oxygen is larger than that of the dye, the essential part of the scheme may be written as follows:

$$\left.\begin{array}{l} 9')\ \ D^T + O_2 \rightarrow X'\ (D\cdots O_2 \text{ or } D^+\cdots O_2^-)^{*5} \\ 9'')\ \ D^T + O_2 \rightarrow D + O_2 \end{array}\right\}\ k_9$$

However, in the opposite case, there are two possibilities to be considered, *i. e.*, the possibility of X' ($D^+\cdots D^-$) being attacked preferentially by ethanol or preferentially by oxygen. In the former case, ethanol will attack D^+, leaving D^-, which will yield the leuco dye in the absence of oxygen, but which in the presence of oxygen, will react with it. On the other hand, in the latter possibility oxygen will attack D^-, regenerating D, and the remaining D^+ will decompose. Hence, the quantum yield of the oxygen consumption in the former case may be expected to be smaller than that of the photoreduction *via* the D-D mechanism. This expectation is contrary to the result obtained above ($\Phi_{O_2}\cdot$(D-D)—5×10^{-3}, Φ(D-D) for reduction $\sim2—3\times10^{-4}$). Thus the most plausible scheme when the dye concentration is larger than that of the oxygen is:

[*5] Although the redox intermediate is denoted rather conventionally as $D\cdots O_2$ or $D^+\cdots O_2^-$, there is, of course, the possibility that the two components exist as separate species. However, there is some evidence for the formation of $D^+\cdots O_2^-$ (See Y. Usui and M. Koizumi, This Bulletin, **40**, 440 (1967); the discussion above is made on this assumption.

$$\left.\begin{array}{lll} 10') & D^{+}\cdots D^{-}+O_2 \rightarrow D^{+}+O_2{}^{-}+D & k_{10}' \\ 10'') & D^{+}\cdots D^{-}+O_2 \rightarrow 2D+O_2 & k_{10}'' \end{array}\right\} k_{10}$$

The quantum yield of oxygen consumption may now be simply given as follows: when $[D] \ll [O_2]$,

$$\Phi_{O2}(D\text{-}O) \approx \varphi_{S-T}\frac{k_9'}{k_9} \tag{13}$$

and when $[D] \gg [O_2]$

$$\Phi_{O_2}(D\text{-}D) \approx \varphi_{S-T}\cdot\frac{k_8'}{k_8}\cdot\frac{k_{10}'}{k_{10}} \tag{14}$$

From Eq. (14), in conjunction with the saturation value of Φ_{O_2} (5.5×10^{-3}) (Fig. 4) and the tentative value of φ_{S-T}, the value of $k_8'k_{10}'/k_8k_{10}$ may be evaluated as $\sim1\times10^{-1}$. Comparing this with the value of $f_{sol}k_8'/k_8$, it seems plausible that the D-D intermediate is attacked by oxygen about one order more efficiently than by ethanol in an air-saturated solution. From Eq. (13) combined with $\Phi_{O_2}(D\text{-}D) \ll 10^{-4}$, k_9'/k_9 is estimated to be less than -2×10^{-3}. Thus, in ethanol most of the attacks of oxygen molecules on D^T end in mere deactivation. This is consistent with the non-occurrence of the oxidative bleaching when $[D] \lesssim 8\times10^{-4}$ M.

The authors wish to express their thanks to Mr. I. Ono for his assistance in the measurements using the Warburg apparatus.