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An Interpretation of the Photochemical Behavior of a Dye - Reducing Agent - Oxygen System on the Basis of a Switch-over of the Primary Processes

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An example is presented in which the complicated photochemical behavior of a system involving dye, a reducing agent, and oxygen is interpreted on the basis of the rate constants of the elementary reactions, which predict the change in mechanism from a D-D (or D-O) to a D-R mechanism. The dye chosen is eosine, and the reducing agent is EDTA. Investigations have been made of the quantity of oxygen consumed by the aerated aqueous dye solution, of the rate of oxidative photobleaching, and of the photochemical yield of hydrogen peroxide; the influence of the EDTA concentration on these quantities has been studied in particular. This influence was especially remarkable on the third phenomenon; the yield of hydrogen peroxide shows a sharp maximum at a certain EDTA concentration, $\sim 1\times 10^{-2}$ M for 1.0×10^{-3} M and 1.0×10^{-4} M of dye, and $\sim 6\times 10^{-2}$ M for 1.0×10^{-5} M of dye. To give a quantitative account of the above phenomena, the rate constants for the following elementary reactions have been determined tentatively by the flash technique:

$$\mathrm{D^T + O_2} \begin{array}{l} \nearrow \\ \searrow \end{array} \left.\begin{array}{l} \mathrm{D^+\cdots O_2^-} \\ \mathrm{D + O_2} \end{array}\right\} \quad 2.5\text{—}3.1\times 10^{8}\,\mathrm{M^{-1}\,sec^{-1}}$$

$$\mathrm{D^+\cdots O_2^-} \quad \rightarrow \qquad \sim 1\times 10^{3}\,\mathrm{sec^{-1}}$$

$$\mathrm{D^+\cdots D^-} \quad \rightarrow \qquad \sim 1\times 10^{3}\,\mathrm{sec^{-1}}$$

Although further evidence for the existence of $\mathrm{D^+\cdots O_2^-}$ and $\mathrm{D^+\cdots D^-}$ would be desirable, the above data as well as those already reported by Lindqvist and by our group, are well correlated with the present results.

In a series of papers we have established that a switch-over of the primary process occurs in the photochemical reaction of dyes when the concentration of dye is increased relative to that of a reducing or oxidizing agent.[1] Thus, at low concentrations of dye the reaction starts with interaction between the triplet-state dye, D^T, and a reagent (the D–R or D–O mechanism, depending on whether the reagent is a reductant or an oxidant respectively), whereas in the opposite case the reaction is initiated by the interaction of the ground-state dye with D^T (the D–D mechanism). Hence, in some cases different reaction products will result depending on the mechanism. We have found that, in the oxidative photobleaching of eosine by oxygen in the aqueous solution, the D–D mechanism produces hydrogen peroxide, perhaps via $D_T+D \rightarrow D^- + D^+$, $D^- + O_2 \rightarrow D + O_2^-$, whereas the D–O mechanism does not. Further, the above switch-over of the mechanism has been well correlated with the rate constants of the elementary reactions obtained from the flash-photolysis experiment.[2]

This paper is an extension of our previous papers. Its main purpose is to show how we can interpret the seemingly very anomalous behavior in a rather complicated system by taking into account a switch-over of the primary process and in terms of the rate constants of the elementary reactions. Besides, some suggestive proposals concerning transient intermediates will be presented. The system chosen is an aerated solution of eosine containing various amounts of ethylenediamine tetraacetic acid disodium salt (EDTA); studies will be made of the effect of the EDTA concentration on the rate of oxygen consumption, on the yield of hydrogen peroxide, and on the rate of the oxidative bleaching of dye. As to the production of hydrogen peroxide, the effect of dye concentration will also be investigated.

Some supplementary data obtained by the flash-photolysis experiment will also be presented in order to make the interpretation more substantial.

Experimental

Materials. Eosine (Merck's G. R. sample) was recrystallized twice from an ethanol solution. The maximum molar absorbance, ε_{max}, at 516 mμ for an aqueous solution is 9.6×10^4. The ethylenediamine tetraacetic acid disodium salt (EDTA) was from Dotite-2Na of Tokyo Kasei (G. R. sample).

Apparatus and Procedure. The oxygen consumption was measured by a Warburg apparatus. The details of the method have been described in a previous paper.[1] A sample (20 m*l*) was irradiated with three 30W-daylight fluorescent lamps 60 cm long at 30.0±0.01°C. A filter made of a 30×100 cm^2 plastic plate cut off any absorbance below 480 mμ. To determine the yield of hydrogen peroxide, another apparatus was set up; eight reaction cells were placed on a filter plate which was turned round at 1 rpm above a daylight fluorescent circline, 10 cm in radius, used as a light source. Its intensity was about three times as strong as that of the Warburg apparatus.

Results

Concentration Effect of EDTA on the Rate of Oxygen Consumption. With the concentration of eosine fixed at 1.0×10^{-3} M, the effect of the EDTA concentration on the rate of oxygen consumption was investigated over the wide range from 4.0×10^{-6} M to 1.0×10^{-1} M. Figure 1 shows some typical runs for the time dependence of the oxygen consumption in air-saturated solutions ($[O_2] \simeq 2.3 \times 10^{-4}$ M*1) of eosine containing various amounts of EDTA. These runs are linear below 6.0×10^{-2} M of EDTA, just as for the solution containing no EDTA,[1] but at 8.0×10^{-2} M and 1.0×10^{-1} M of EDTA the rate gradually decreases as the reaction proceeds. The rate evaluated from the slope at the time origin increases with the EDTA concentration up to 8.0×10^{-2} M, but it is appreciably smaller at 1.0×10^{-1} M of EDTA.

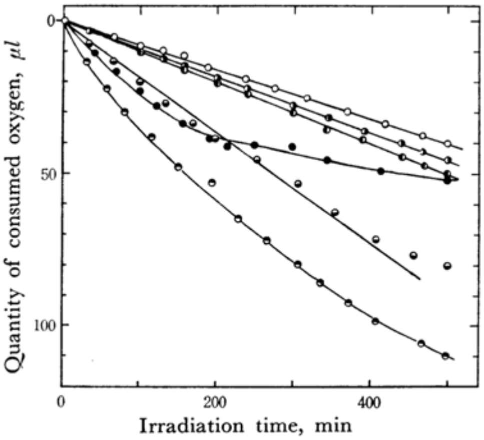

Fig. 1. Oxygen consumption rates in the air saturated solutions of eosine containing various amounts of EDTA.
[EDTA]= 0 M (-○-) 6.0×10^{-2}M (-◒-)
1.0×10^{-3}M (-◑-) 8.0×10^{-2}M (-◓-)
1.0×10^{-2}M (-◐-) 1.0×10^{-1}M (-●-)

In Fig. 2, the oxygen consumption rate (in the case of a nonlinear run, as evaluated from the tangent at the initial state) and the ratio of the yield of hydrogen peroxide against the amount of oxygen consumed*2 ($\Delta[O_2]/\Delta[H_2O_2]$, both quantities being measured after 530 minutes irradiation) are plotted against the concentration of

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[1] Y. Usui, K. Itoh and M. Koizumi, This Bulletin, **38**, 1017 (1965); T. Ohno, Y. Usui and M. Koizumi, *ibid.*, **38**, 1023 (1965); N. Kosui, K. Uchida and M. Koizumi, *ibid.*, **38**, 1959 (1965).

[2] T. Ohno, S. Katô and M. Koizumi, *ibid.*, **39**, 232 (1966).

*1 By a polarographic method, the concentration of oxygen in the 0.1 M EDTA aqueous solution was analyzed and was found to be 2.3×10^{-4} M.

*2 Measured in the solutions submitted to the Warburg experiments.

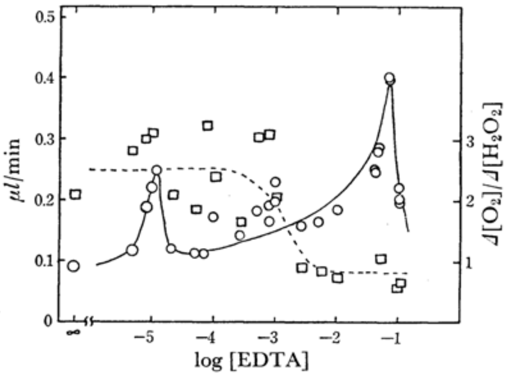

Fig. 2. Dependence of the rate of oxygen consumption (-○-) and $\Delta[O_2]/\Delta[H_2O_2]$ (-□-) on the EDTA concentration.

EDTA. Although the data are not very accurate, there is clearly a general tendency for the former quantity to increase gradually with the addition of EDTA; the increase is particularly remarkable above ~10^{-2} M of EDTA, but it suddenly falls at ~10^{-1} M of EDTA after passing through a maximum near 8×10^{-2} M of EDTA. As for $\Delta[O_2]/\Delta[H_2O_2]$, there seems to be a sudden drop near ~10^{-3} M of EDTA. In $\Delta[O_2]/\Delta[D]$, however, there is no such tendency to be seen from 4.0×10^{-6} M to 1.0×10^{-2} M; the average value in this range is 2.0 ± 0.7.

The Influence of the Addition of EDTA on the Yield of Hydrogen Peroxide. This was studied in more detail using a specially-designed apparatus and at three dye concentrations, 1.0×10^{-3} M, 1.0×10^{-4} M, and 1.0×10^{-5} M. The solutions in the cells were deep enough to assure a practically complete absorption of light in all cases. The number of photons absorbed at the initial stage was *ca.* $4.8\times10^{14}\ l^{-1}\ \text{sec}^{-1}$.

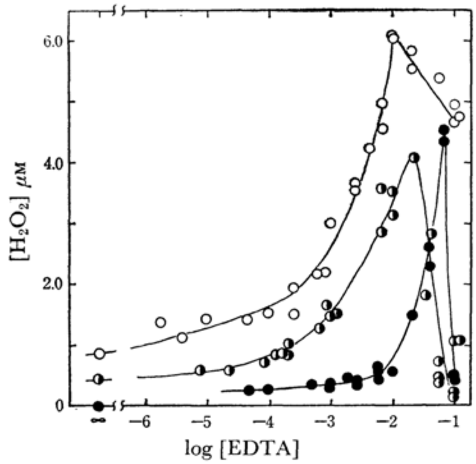

Fig. 3. Plots of the yield of hydrogen peroxide after 300 min-irradiation against the EDTA concentration.

-○- [Eosine]$=1.0\times10^{-3}$M
-◐- [Eosine]$=1.0\times10^{-4}$M
-●- [Eosine]$=1.0\times10^{-5}$M

Figure 3 shows the plots of the yields of hydrogen peroxide after 300 minutes irradiation against the EDTA concentrations, using for the latter a logarithmic scale to cover its wide range. This figure shows a tendency in all the cases for the yield of hydrogen peroxide to increase with the quantity of EDTA and a tendency for it to pass through a maximum and then to decline rather suddenly. Although the general behavior is similar, the features of the curve for 1.0×10^{-5} M of dye are apparently different from those of that for 1.0×10^{-4} M and 1.0×10^{-3} M of dye in regards to the concentration of EDTA at which the maximum point is reached and also that at which a notable increase becomes apparent. The main features can be summarized as follows:

1) In the cases of 1.0×10^{-4} M and 1.0×10^{-3} M of dye, the elevation becomes appreciable near ~10^{-4} M of EDTA, whereas at 1.0×10^{-5} M of dye it is observable only above ~10^{-2} M.

2) For 1.0×10^{-5} M of dye, the addition of less than 10^{-2} M of EDTA causes a certain small amount of hydrogen peroxide to be produced, while no production of it occurs in the absence of EDTA as Imamura³⁾ has already established and as is confirmed in the present investigation. Even for 1.0×10^{-3} M of dye, there seems to be a similar effect below ~10^{-4} M of EDTA, although this effect is not so apparent as in the case of 1.0×10^{-5} M of dye.

3) The position of the maximum point is ~1×10^{-2} M of EDTA for 1.0×10^{-3} M and 1.0×10^{-4} M of dye, whereas for 1.0×10^{-5} M of dye it is ~6×10^{-2} M. It must be added, however, that a sharp decrease for 1.0×10^{-4} M and 1.0×10^{-5} M of dye after the line passes through a maximum may be partially due to the fact that in these cases the solution has been bleached to a great extent during illumination.

Concentration Effect of EDTA on the Dye Bleaching. This was studied only at one dye concentration, 1.0×10^{-5} M. In the absence of EDTA, the oxidative bleaching occurs *via* the D–O mechanism, as has already been fully confirmed by Imamura.³⁾ The reaction proceeds at a rate simply proportional to the absorption of light. Figure 4 shows the plot of $\ln(e^{\alpha cd}-1)$ against the time for solutions containing various quantities of EDTA.

It may be seen that as long as the concentration of EDTA is less than ~2×10^{-2} M, the rate is not essentially affected. Above 2×10^{-2} M, however, the initial rate gradually increases with the amount of EDTA, as is shown in the figure. A remarkable fact is that at these high concentrations of

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3) M. Imamura and M. Koizumi, This Bulletin, **28**, 117 (1957).

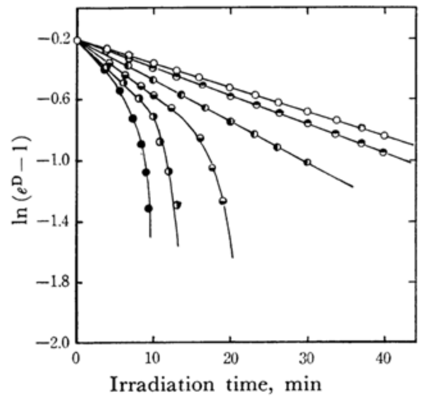

Fig. 4. Photobleaching of eosine at various concentrations of EDTA (Eosine 10 μM).

[EDTA]
-○- 1×10^{-3}M (Same in 6.0×10^{-3}—1.0×10^{-2}M)
-◓- 2×10^{-2}M
-◐- 4×10^{-2}M
-◒- 6×10^{-2}M
-◑- 8×10^{-2}M
-●- 1×10^{-1}M

EDTA the slopes of the curves in Fig. 4 begin to increase after a certain time, becoming quite large in a short time. This phenomenon is considered to be due to the reduction of dye by EDTA; this becomes a dominant reaction as the oxygen in solution is consumed.*3 This view has been confirmed in the following way. According to our previous results,4) leuco eosine is photooxidized to the colored form with a suitable sensitizer, for instance, acridine. Hence, 10^{-4} M of acridine was added to a bleached solution containing 1.0×10^{-1} M of EDTA, and then the solution was irradiated with a 365 mμ light from a mercury lamp (in the presence of oxygen). The spectra before and after the irradiation are shown in Fig. 5. It is apparent that the absorption of eosine at 525 mμ is remarkably recovered by this irradiation; *i. e.*, the photosensitized oxidation of the photoproduct (leuco eosine) has occurred by acridine addition. The decline of acridine absorption is perhaps due to the reduction by EDTA. A similar experiment showed that, in the case of 4×10^{-2} M of EDTA, the recovery of dye does not occur at all. Thus the photoreduction of eosine by EDTA can occur even in an aerated solution when the concentration of EDTA is large enough.

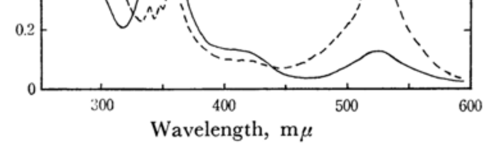

Fig. 5. Spectra showing the recovery of eosine by acridine sensitized photoxidation.
—— the bleached sample+acridine 10^{-4}M
---- after 20 min-irradiation by Hg 3650Å

Supplementary Experiments and Discussion

In order to interpret the results obtained above, it is necessary to refer to the rate constants of the elementary reactions. Most of them have already been reported by Lindqvist *et al.*5) and by our group2), but it is desirable to obtain some additional information; for this purpose, some supplementary flash experiments have been made.

Rate Constant of the D^T+O_2 Reaction. By a flash apparatus (1μF, 10.5 kV) the decay of the triplet state was measured at 610 mμ and at different oxygen concentrations. The first-order rate formula holds quite well in all cases, and the rate constant increases with the oxygen concentration. The rate formula can be written as follows2);

$$-\frac{d[D^T]}{dt}=\{k_{sp}+k_D[D]_O+k_{O_2}[O_2]\}[D^T]$$

where k_{sp} is a unimolecular rate constant and $[D]_O$ is the concentration of dye. Figure 6 shows the relation between the first-order decay constant and the concentration of oxygen.

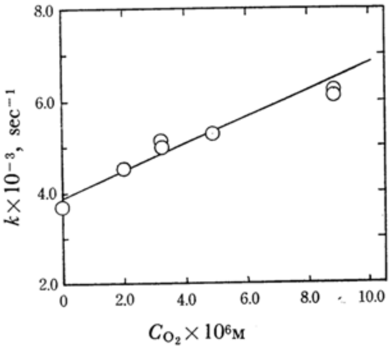

Fig. 6. Decay constants of triplet state for various oxygen concentrations.

From the plot, one obtains the second-order rate

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*3 The experiment was done under static conditions so that the rate of the dissolution of the gaseous oxygen could be neglected.

4) K. Uchida, S. Katô and M. Koizumi, This Bulletin, **35**, 16 (1962).

5) V. Kasche and L. Lindqvist, *Photochem. Photobiol.*, **4** (5), 923 (1965).

constant, k_{O_2}, for $D^T + O_2 \rightarrow$: 2.5—3.1×10⁸ M^{-1} sec^{-1}.

Decay Constant of $D^+\cdots O_2^-$. Figure 7 shows the transient absorption spectra for the aerated solution of dye (1.0×10^{-5} M) containing 1.0×10^{-3} M of EDTA.

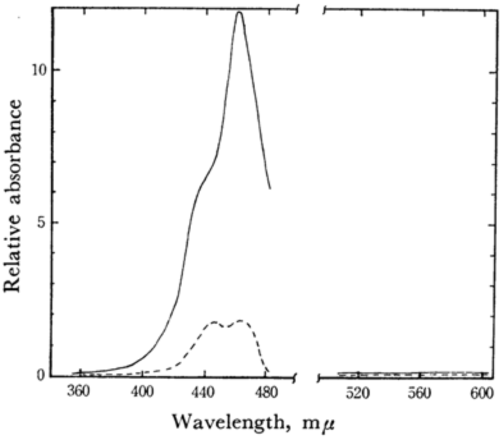

Fig. 7. Absorption spectra of transient species in the presence of 1.0×10^{-3}M EDTA at 65 μsec (——) and at 1420 μsec (----) after flashing. (Eosine 10μM)

It is apparent that: (1) a peak at ∼463 mμ due to the half-oxidized dye, Ox, exists with quite a high intensity 63 μ sec after flashing, but (2) after 1420 μ sec it is scarecely observed. Similar results were obtained for the solutions containing 0—4×10^{-2} M of EDTA. The first finding is very important because it strongly supports the view that the main reaction in this case is an electron transfer between D^T and oxygen. Further, the second finding favors the view that some kind of a transient complex is formed between D^+ and O_2^-, because if the two species were to exist separately, they would recombine bimolecularly and the rate for this could not be so large.[*4] It is plausible to attribute this transient spectrum to $D^+\cdots O_2^-$. The first-order decay constants, measured at 463 mμ in various oxygen concentrations were almost constant, being all in the range of $0.9—1.2\times10^3$ sec^{-1}. A few examples of the decay curves are shown in Fig. 8.

An Attempt to Establish the Existence of $D^+\cdots D^-$. Hitherto the existence of $D^+\cdots D^-$ has not been established. In a previous paper[1)] dealing with steady-light experiments, its existence was assumed rather conventionally and it was suggested that its lifetime might be $\sim10^{-4}$sec. On the other hand, the flash experiments showed that the transients decay (partly) according to the second order; this favors the view that D^+ and D^- exist as separate species. There remained a great deal of uncertainty about the behavior of D^+ and D^-.

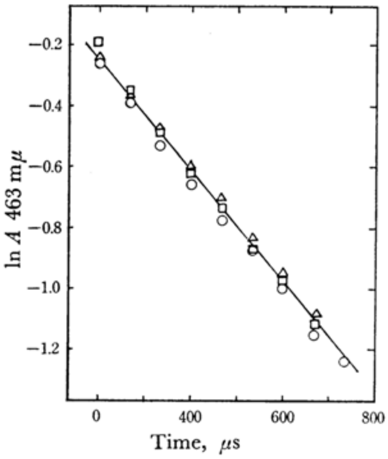

Fig. 8. Decay of $D^+\cdots O_2^-$ at various concentration of oxygen.
-□- 4.8×10^{-6}M -○- 8.8×10^{-6}M
-△- 2.3×10^{-4}M

In view of this, further flash studies were made in order to confirm the existence of $D^+\cdots D^-$. After several attempts had been in vain, a reinvestigation of the decay of the transients gave some support for its existence although not conclusive. Thus the early portions of the decay curves for the transient absorption spectra at 408 and 450 mμ in 10^{-5} M deaerated solutions of eosine were found to be reproduced by the first-order rate formula; furthermore, they were all found to have a rate constant of about ≈10^3 sec^{-1}.[*5] This does not contradict the previous result, since the former result was concerned chiefly with the decay in a later stage, ∼1 msec after the flashing.

It is likely that some transients exist in the bound state, $D^+\cdots D^-$, and others in the free state. If most of the former revert to the original dye with the rate constant of $\sim10^3$ sec^{-1}, the succeeding decay will follow the second-order formula, since the free species mainly recombine bimolecularly with a rather small rate constant of 8×10^7 M^{-1} sec^{-1}, resulting in a fractional rate[*6] of less than 8×10^2 sec^{-1} under usual conditions.

Below it will be assumed that some of the redox intermediates exist as a bound species with the decay constant of $\sim10^3$ sec^{-1}, while the remainder exist as free species.

[*4] *Cf.* Ref. 2. No effect of the EDTA addition upon H_2O_2 production, rules out the posibility of the reaction $D^+ + EDTA \rightarrow$. The small shift in the peak as compared with that reported in Ref. 2 may be due to the complexing of D^+ with O_2^-.

[*5] Since the triplet dye seems to have a small absorbance[5)] in the above spectral region, there remains some doubt for considering this rate constant as the one for the decay of $D^+\cdots D^-$.

[*6] The fractional rate of the $D^T + D \xrightarrow{k} 2D$ reaction, for instance, is defined as $[-d[D^T]/dt]/[D] = k[D^T]$.

TABLE 1. RATE CONSTANTS OF ELEMENTARY REACTIONS

(i)	process	k_i	Ref.
(1)	$D^T+D \rightarrow Rd+Ox\ (D^+\cdots D^-)$	0.7×10^8 M^{-1} sec^{-1}	5)
(2)	$D^T+D \rightarrow D+D$	3×10^8 M^{-1} sec^{-1}	5)
(3)	$D^T+O_2 \rightarrow D^+\cdots O_2^-\ (k_{O_2}\sim10^8)$	2.5—$3.1\times\underline{10^8}$ M^{-1} sec^{-1}	
(4)	$D^T+O_2 \rightarrow D+O_2$		
(5)	$D^T+EDTA \rightarrow D^-+EDTA^+$	5×10^5 M^{-1} sec^{-1}	2)
(6)	$Rd+Ox \rightarrow$	8.8×10^8 M^{-1} sec^{-1}	2)
(7)	Ox decay of the first order	9×10^2 sec^{-1}	2)
(8)	$Ox+EDTA \rightarrow$	8×10^5 M^{-1} sec^{-1}	2)
(9)	$D^+\cdots O_2^- \rightarrow$	$(\sim1\times10^3$ sec$^{-1})$	
(10)	$D^+\cdots D^- \rightarrow$	$\sim10^3$ sec^{-1}	
(11)	Rd''*	1 sec^{-1}	2)

* Rd'' is a certain molecular complex of Rd^+ with D^-

All the rate constants for the elementary reactions necessary for the present purpose are listed in Table 1. We feel that the process (10) should be substantiated more conclusively.

One datum, that underlined, is purely hypothetical. Although a chief reason for adoption $k_3\simeq10^8$ M^{-1} sec^{-1} for $D^T+O_2\rightarrow D^+\cdots O_2^-$ is that it can give a consistent interpretation of the present results, it is not altogether unreasonable for the following reason. As has already been reported, the quantum yield for oxidative bleaching of dye in an aerated solution as well as the one for oxygen consumption is several times larger in a D–D mechanism (when the dye concentration is $>10^{-4}$M) than in a D–O mechanism (when the dye concentration is $<10^{-5}$ M). Provided $D^+\cdots D^-$ and $D^+\cdots O_2^-$ once produced mostly lead to the oxidative bleaching, then the rate constant for process (1) in Table 1 should be several times larger than that for process (3), resulting in k_3 being $\sim10^7$. However, some of the two transient species revert to the original species,[*7] and the k_3 value could be larger than $\sim10^7$M^{-1}sec^{-1}.

I. The Rate of Oxygen Consumption. In this experiment the concentrations of dye and oxygen are, respectively, 1.0×10^{-3} M and 2.3×10^{-4} M. From the rate constants of processes (1) and (3) in Table 1, one can say that a D–D mechanism instead of a D–O mechanism predominates when [EDTA] is not exceedingly high, whereas at high enough concentrations of EDTA a switch-over to a D–R mechanism will occur.

The sudden decrease in the rate constant at $\sim10^{-1}$ M of EDTA (R) in Figs. 1 and 2 is attributed to this switch-over of the mechanism on the basis of the following comparison. The rate constants for reaction (1) $D^T+D\rightarrow D^+\cdots D^-$ and reaction (5) $D^T+R\rightarrow D^-\cdots R^+$ are, respectively, 0.7×10^8 and 5×10^5 M^{-1} sec^{-1}. Hence, the fractional rate for (1) and (5) at $[D]=1.0\times10^{-3}$ M and [EDTA] $\sim10^{-1}$ M are, respectively, $0.7\times10^8\times10^{-3}=7\times10^4$ sec^{-1} and $5\times10^5\times10^{-1}=5\times10^4$. *i. e.*, at $\gtrsim10^{-1}$ M of EDTA, a D–R mechanism predominates and the rate of oxygen consumption by this mechanism becomes smaller.

The gradual increase in the rate from around 10^{-3} M of EDTA in Fig. 2 can be attributed to the attack of EDTA on $D^+\cdots D^-$ in such a way that $R+D^+\cdots D^-\rightarrow R^++D+D^-$ occurs and oxygen is consumed by the reaction with D^-. Since the lifetime of $D^+\cdots D^-$ is $\sim10^{-3}$ sec, such an attack may become effective when the fractional rate of reaction (8) becomes approximately equal to 10^3 sec^{-1} (thus, $10^{-3}\times8\times10^5=8\times10^2$ sec^{-1}).

As to the ratio of the oxygen consumption to the yield of hydrogen peroxide, the following interpretation may be given. In the region of low EDTA concentrations ($\lesseqgtr10^{-3}$ M), the reaction proceeds as follows; $D^+\cdots D^-+O_2\rightarrow D^++O_2^-+D$, $D^++O_2\rightarrow$ dye destruction. This leads to the above ratio, ~2. When $[EDTA]>10^{-3}$ M, $D^+\cdots D^-+R\rightarrow D+R^++D^-$; then $D^-+O_2\rightarrow D+O_2^-$ occurs, leading to the ~1 ratio.

The gradual decrease in the oxygen consumption rate at 1.0×10^{-1} M and 8.0×10^{-2} M of EDTA (Fig. 1) may be attributed to the increase in the contribution of the D–R mechanism as the dye is bleached.

II. Yield of Hydrogen Peroxide. The sudden fall in the yield of hydrogen peroxide around 10^{-2} M of EDTA in the case of 1.0×10^{-3} M and 1.0×10^{-4} M concentrations of dye may be attributed to the replacement of a D–D mechanism with a D–R mechanism. This view is supported in a way similar to that in the case of the oxygen-consumption experiment. The fractional rates for reaction (1) in Table 1 and for reaction (5) are, respectively, $0.7\times10^8\times10^{-4}=7\times10^3$ sec^{-1} (for 1.0×10^{-4} M of dye) and $5\times10^5\times10^{-2}=5\times10^3$ sec^{-1} (for 10^{-2} M of EDTA). In the case of a 1.0×10^{-5} M concentration of dye, on the other hand, a D–O mechanism prevails at a low concentration of EDTA, and sudden fall of EDTA at $\sim10^{-1}$ M

[*7] It is more plausible to consider that most of $D^+\cdots O_2^-$ results to $D+O_2$.

is to be attributed to the change in the mechanism from D–O to D–R. The following data support this interpretation:

For reaction (3), $10^8\times 10^{-4}\times 2.3\approx 2.3\times 10^4$

For reaction (5), $5\times 10^5\times 10^{-1}\approx 5\times 10^4$

The gradual increase observed in the case of 1.0×10^{-3} M and 1.0×10^{-4} M concentrations of dye from above $\lesssim 10^{-3}$ M of EDTA may be attributed to $R+D^+\cdots D^-\rightarrow R^+ + D + D^-$, just as has been described in Sec. I. On the other hand, for a 1.0×10^{-5} M of concentration of dye where a D–O mechanism occurs, the $D^+\cdots O_2^-$ intermediate has a similar lifetime, 10^{-3} sec, and yet the increase becomes apparent only at a larger EDTA concentration. This might be due to the difference in efficiency with which R attacks the two species.

As to the production of hydrogen peroxide in the low concentration region of EDTA, it is probably due to the attack of EDTA on the free D^+, which otherwise would be expected to go back to the original dye by the $D^+ + O_2^- \rightarrow D + O_2$ reaction or to be decomposed by oxygen. Free D^+ and O_2^-, the concentrations of which are very small, have a rather long life; this may be the reason why this effect appears at a rather low concentration of EDTA. The effect is naturally constant over a wide range of EDTA concentrations. A similar interpretation seems to be applicable to the case of a 1×10^{-4} M concentration of dye, in which case, however, the free radical ions are D^+ and D^-.

III. The Rate of the Bleaching of Dye. The fact that the initial rate of bleaching begins to increase near $\sim 2\times 10^{-2}$ M of EDTA can be interpreted as being due to the participation of a D–R mechanism. The fractional rates for reactions (5) and (3) at $[\mathrm{EDTA}]=2\times 10^{-2}$ M and at $[O_2]\simeq 2.3\times 10^{-4}$ M are as follows;

For Reaction (5), $5\times 10^5\times 2\times 10^{-2}\simeq 10^4\ \mathrm{sec}^{-1}$

For Reaction (3), $\gtrsim 10^8\times 10^{-4}\times 2.3\approx 2.3 \times 10^4\ \mathrm{sec}^{-1}$

The increase in the bleaching rate as the reaction proceeds when the EDTA concentration is $>4.0\times 10^{-2}$ M, is due to a similar reason. It is worthwhile noting that the transient intermediate produced by the $D^T + R \rightarrow D^-\cdots R^+$ process, which perhaps corresponds to the Rd'' in a previous paper,2) is not entirely destroyed by oxygen, but yields leuco dye (at least partially), as has been established in the present paper.

To summarize, all the present results, apart from some minor points, can well be interpreted in terms of the rate constants obtained from the flash photolytic experiments, plus one additional rate constant assumed provisionally. Thus the assumed rate constant for $D^T + O_2 \rightarrow D^+\cdots O_2^-$, $\sim 10^8\ \mathrm{M}^{-1}\,\mathrm{sec}^{-1}$, has been supported to some extent. The existence of $D^+\cdots D^-$ with a lifetime of $\gtrsim 10^{-3}$ sec, is also consistent with the present results.

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