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Mechanistic Interpretations of the Dye-sensitized Formation of Hydrogen Peroxide in an Aqueous Solution

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Kinetic studies of the photosensitized formation of hydrogen peroxide and hyperoxide ions in a mixed aqueous solution of eosine, oxygen, and EDTA have been attempted on the basis of a switch-over of the primary processes, *i.e.*, the so-called DD, DR, and DO mechanisms. The rate constants for reactions of $E^{+}\cdots E^{-}$ and $E^{+}\cdots O_2^{-}$ intermediates with oxygen and EDTA were obtained. The yield of hydrogen peroxide *via* the DO-initiated mechanism was enhanced as much as one order of magnitude ($\approx$0.012) by the addition of 0.15 mol dm^{-3} of sodium borate or sodium carbonate. The maximum yield, 0.08, of hydrogen peroxide was obtained in an aerated aqueous solution of 1.0×10^{-4} mol dm^{-3} of eosine, 5.0×10^{-2} mol dm^{-3} of EDTA, and 8.8×10^{-2} mol dm^{-3} of sodium borate.

The investigation of the mechanism of a photosensitized oxidation is important from the point of view of photodynamic action, and several reaction mechanisms have been proposed to account for these reactions, as have been reviewed by Grossweiner,1) Foote,2,3) Spikes,4) and one of the present authors.5) As for the dye-sensitized photooxidation, the relationship between a structure and its susceptibility to photooxidation has recently been investigated by the kinetic treatment of the eosine-sensitized photooxidation of phenylalanine and tyrosine derivatives.6)

A reaction mechanism involving the triplet state of an organic dye should be altered with the concentrations of the dye, the reductant, and the oxidant. We have previously established that a switch-over of the primary processes can occur in the photochemical reactions of dyes, *i.e.*, the so-called DD, DR, and DO mechanisms.5,7) The classification of the primary processes for such photoredox reactions is of significance in the interpretation of the mechanism for the dye-sensitized reactions.

On the other hand, if the hyperoxide ion, O_2^{-}, can be efficiently produced in the course of a photosensitized oxidation in an aerated solution, it will be synthetically useful for the purpose of the specific oxidation of an organic compound by O_2^{-}.

This paper is an extension of our previous papers.8,9) Its main purpose is to show we can interpret kinetic behavior in a rather complicated system by taking a switch-over of the primary processes into account. Besides, some suggestions concerning the reaction of the transient intermediates on DD and DO mechanisms will be presented.

Experimental

Materials. Eosine (Merck) (E) was recrystallized twice from ethanol. Disodium dihydrogen ethylenediaminetetraacetate (Dotite-2Na of Wako Junyaku) (EDTA) and Tetranitro Blue Tetrazolium (Sigma Chemical Co.) (TNBT) were used without further purification.

Apparatus and Procedure. To determine the yield of H_2O_2, an irradiation apparatus was set up: ten cylindrical reaction cells (1.5 cm in radius) with an optically flat bottom were placed on a filter plate in a thermostat. The filter, made of a plastic plate, cut off any absorbance below 480 nm and was turned round at 1 rpm above the light source of a daylight fluorescent circleline (10 cm in radius) outside the thermostat set up with the transparent plastic box. The depth of the sample solutions being about 2 cm in the reaction cells, the absorption of light is practically complete in the region of the visible absorption. The quantity of light absorbed by the solutions was 1.3×10^{-9} mol cm^{-3} s^{-1}, which was estimated from the values of the photobleaching rate of eosine in a plain aqueous solution and the quantum yield. The details of the method have been described in previous papers.8,9) For the H_2O_2-accumulation experiment, air or oxygen gas was bubbled through the solution. The determination of the concentration of H_2O_2 was performed by the spectroscopic method with titanium complexing after the separation of a precipitate of eosine by the addition of sulfuric acid. The concentration of O_2^{-} was determined by the measurement of the absorbance of the formazan at the wavelength of 560 nm using $\varepsilon_{560}=5.0\times10^{4}$ mol^{-1} cm^{2}, when a sample containing a small amount of TNBT was irradiated.

Results and Discussion

A considerable amount of H_2O_2 is really formed for eosine-sensitized photoredox reactions in aerated aqueous solutions containing EDTA. We have already studied the switch-over of the primary processes by means of oxygen-consumption experiments; *i.e.*, as is shown in Fig. 1, the processes of a, b, and c on triplet eosine, which correspond to the DD, DO, and DR mechanisms respectively, are known where the values of $k_{\mathrm{D}}^{\mathrm{s}}$ (4.0×10^{8} mol dm^{-3} s^{-1}), $k_{\mathrm{O}}^{\mathrm{s}}$ (1.1×10^{9} mol dm^{-3} s^{-1}), and $k_{\mathrm{E}}^{\mathrm{s}}$ (5.0×10^{5} mol dm^{-3} s^{-1}) are obtained respectively.7,8) The consecutive processes can be assumed to be competitive reactions of EDTA and oxygen with the intermediate irrespective of the mechanisms of DD, DO, and DR.

Effect of EDTA and Oxygen Concentrations upon the Yield of H_2O_2 Formation via *the DD-initiated Mechanism* ($\Phi_{\mathrm{h}}^{\mathrm{DD}}$). With the concentration of eosine fixed at 2.0×10^{-3} mol dm^{-3}, the effect of the EDTA concentration on the quantum yield of H_2O_2 formation was investigated over the wide range from 0 to 0.10 mol dm^{-3}. Figure 2 shows that $\Phi_{\mathrm{h}}^{\mathrm{DD}}$ tends to the constant value of the maximum yield ($\approx1.7\times10^{-2}$). See the scheme for DD mechanism shown in Fig. 1 in an air-saturated solution, assuming the relation of $k_{\mathrm{D}}^{\mathrm{s}}[\mathrm{E}]\gg k_{\mathrm{d}}$, $k_{\mathrm{D}}^{\mathrm{s}}[O_2]$, and $k_{\mathrm{E}}^{\mathrm{s}}[\mathrm{EDTA}]$:

$$\Phi_{\mathrm{h}}^{\mathrm{DD}}=\frac{\phi_{\mathrm{st}}k_{\mathrm{D}}^{\mathrm{r}}}{2k_{\mathrm{D}}^{\mathrm{s}}}\,\frac{k_{\mathrm{O}}^{\prime\mathrm{r}}[O_2]+\gamma(O_2)k_{\mathrm{E}}^{\prime\mathrm{r}}[\mathrm{EDTA}]}{k_{\mathrm{d}}^{\prime}+k_{\mathrm{O}}^{\prime\mathrm{s}}[O_2]+k_{\mathrm{E}}^{\prime\mathrm{s}}[\mathrm{EDTA}]}. \tag{1}$$

Denoting $\Phi_{\mathrm{h}}^{\mathrm{DD}}$ at [EDTA]=0 as Φ_{0}^{DD}, we can obtain

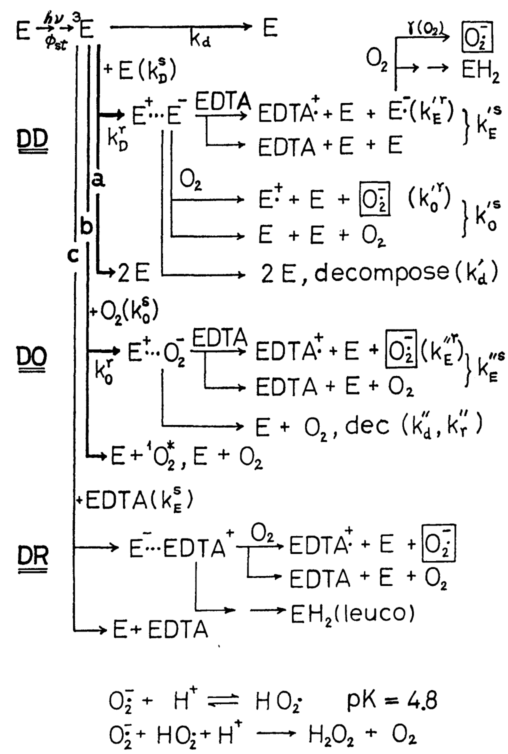

Fig. 1. The reaction scheme for eosine (E) photosensitized formation of hydrogen peroxide.

Eq. 2:

$$\frac{1}{\Phi_h^{DD}-\Phi_0^{DD}}=\frac{1}{\Phi_0^{DD}(\beta-\alpha)}\left(\alpha+\frac{1}{[EDTA]}\right) \tag{2}$$

where $\alpha=k_E^{\prime s}/(k_d^\prime+k_0^{\prime s}[O_2])$ and $\beta=k_E^{\prime r}\,\gamma(O_2)/k_0^{\prime r}[O_2]$. A linear relationship of $1/(\Phi_h^{DD}-\Phi_0^{DD})$ against 1/[EDTA] was obtained, as is shown in Fig. 2. This suggests that EDTA reacts with the intermediate, $E^+\cdots E^-$, competitively. From the values of Φ_0^{DD} (4.5×10^{-3}) and the slope and intercept of the line, the α and β values can be estimated. Using the value of $\phi_{st}k_D^r/k_D^s$ (0.112),[10,11) the values of $k_0^{\prime r}/k_E^{\prime s}$ and $\gamma(O_2)k_E^{\prime r}/k_E^{\prime s}$ are estimated to be 0.665 and 0.22 respectively.

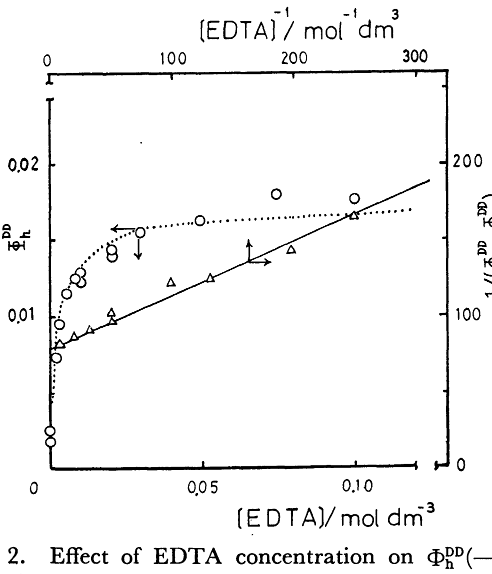

Fig. 2. Effect of EDTA concentration on Φ_h^{DD}(—○—) and the double reciprocal plots (—△—). [E]: 2×10^{-3} mol dm^{-3}, $[O_2]$: 2.4×10^{-4} mol dm^{-3}, pH=4.9.

At a lower concentration of EDTA $(1.0\times10^{-4}$ mol $dm^{-3})$ the effect of the oxygen concentration on Φ_h^{DD} was investigated under the condition of a DD-initiated mechanism. The results can be analysed by means of Eqs. 3 and 3′, which are approximate to Eq. 1 as $k_0^{\prime r}[O_2]\gg k_E^{\prime r}[EDTA]\gamma(O_2)$ and $(k_d^\prime+k_0^{\prime s}[O_2])\gg k_E^{\prime s}[EDTA]$. Equation 3 should hold without EDTA:

$$\Phi_h^{DD}\simeq\frac{\phi_{st}k_D^r}{2k_D^s}\,\frac{k_0^{\prime r}[O_2]}{k_d^\prime+k_0^{\prime s}[O_2]} \tag{3}$$

$$1/\Phi_h^{DD}=(2k_D^s/\phi_{st}k_D^r k_0^{\prime r})(k_0^{\prime s}+k_d^\prime/[O_2]) \tag{3'}$$

Judging from the data shown in Fig. 3, oxygen also reacts with the intermediate, $E^+\cdots E^-$, competitively. The slope and intercept of the linear line in Fig. 3 give the numerical values of $k_0^{\prime s}/k_d=2\times10^4$ mol dm^{-3} and $k_0^{\prime r}/k_0^{\prime s}=0.10$. Therefore, the maximum yield of Φ_h^{DD} *via* the reaction of oxygen with $E^+\cdots E^-$ should be equal to 5.5×10^{-3}, which is about one-third to that (0.017) *via* the reaction of EDTA with $E^+\cdots E^-$. Estimating the k_d value to be $1.8\times10^3\ s^{-1}$ from the data previously reported,[12,13) the rate constant for the reaction of

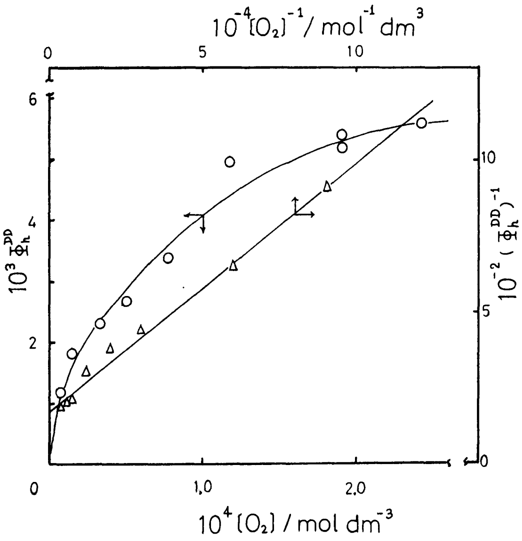

Fig. 3. Effect of oxygen concentration on Φ_h^{DD} (—○—) and the double reciprocal plots (—△—). [E]: 2×10^{-3} mol dm^{-3}, [EDTA]: 1×10^{-4} mol dm^{-3}, pH=4.9.

TABLE 1. RATE CONSTANTS OF ELEMENTARY PROCESSES FOR THE DD INTERMEDIATE

Reaction	Rate constant / $mol^{-1}\ dm^3\ s^{-1}$
$E^+\cdots E^-+EDTA\longrightarrow$ $E+EDTA^++E^-\ (k_E^{\prime r})$ $E^-+O_2\longrightarrow E+O_2^-(\gamma(O_2))$	$\gamma(O_2)k_E^{\prime r}=$ 8.4×10^5
$E^+\cdots E^-+EDTA\longrightarrow$ $\left.\begin{matrix}2E+EDTA\\E+EDTA^++E^-\end{matrix}\right\}(k_E^{\prime s})$	2.8×10^6
$E^+\cdots E^-+O_2\longrightarrow E^++E+O_2^-\ (k_0^{\prime r})$	3.7×10^6
$E^+\cdots E^-+O_2\longrightarrow\left.\begin{matrix}2E+O_2\\E^++E+O_2^-\end{matrix}\right\}(k_0^{\prime s})$	3.7×10^7

EDTA or oxygen with $E^+ \cdots E^-$ listed in Table 1 are obtained.

By substituting the experimental values into Eq. 1, one can obtain the following equation:

$$\Phi_h^{DD} = (2.1 \times 10^5[O_2] + 4.7 \times 10^4[\mathrm{EDTA}])/$$
$$(1.8 \times 10^3 + 3.7 \times 10^7[O_2] + 2\ 8 \times 10^6[\mathrm{EDTA}])$$

The calculated values of Φ_h^{DD} are shown with a dotted curve in Fig. 2. By comparing the $k_O'^s$ value with that of $k_E'^s$, it can be seen that oxygen can competitively attack $E^+ \cdots E^-$ faster than EDTA by one order of magnitude, resulting in the production of O_2^-, as is shown in Fig. 1.

Effect of EDTA Concentration upon the Yield of H_2O_2 *Formation* via *DO-initiated Mechanism* (Φ_h^{DO}). When the DO-initiated mechanism is operative, Eq. 4 can be derived from the scheme in Fig. 1:

$$\Phi_h^{DO} = \phi_{st} \frac{k_O^r}{k_O^s} \frac{k_E''^r[\mathrm{EDTA}]}{k_d'' + k_r'' + k_E''^s[\mathrm{EDTA}]} \quad (4)$$

A linear relationship of $1/\Phi_h^{DO}$ against 1/[EDTA] was obtained by taking account of the EDTA concentration effect. The result indicates that the DO-initiated mechanism shown in Fig. 1 is operative and that the reaction of EDTA with the intermediate, $E^+ \cdots O_2^-$, to produce the O_2^- ion may occur in competition with the deactivation and decomposition. Inserting the ϕ_{st} value (0.64) into the intercept of the line in Fig. 4, we obtain $k_O^r k_E''^r / k_O^s k_E''^s \simeq 6.2 \times 10^{-3}$, which leads to the inequality of $k_O^r/k_O^s \leqq 0.11$ and $0.056 \leqq k_E''^r/k_E''^s \leqq 1$, since the probability of singlet oxygen formation by the reaction of triplet eosine with oxygen equals 0.89.[14] The value of $(k_d'' + k_r'')/k_E''^s$ is also obtained as 2.4 $(\pm 0.3) \times 10^{-3}$ mol dm^{-3} from the intercept and slope in Fig. 4. Using the numerical value of 7.0×10^5 for $k_E''^s$, we obtain 1.7×10^3 s^{-1} for $(k_d'' + k_r'')$, which coinsides with the value of 1.2×10^3 s^{-1} for the decay constant of $E^+ \cdots O_2^-$ previously reported in the experiment by means of flash photolysis.[7,9]

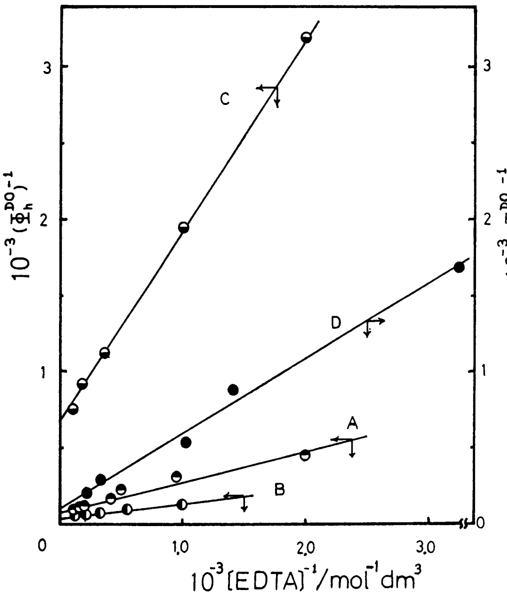

Fig. 4. Plots of $1/\Phi_h^{DO}$ (or $1/\Phi_s^{DO}$) against 1/[EDTA] for the EDTA concentration effect on Φ_h^{DO} (or Φ_s^{DO}) in 2×10^{-2} mol dm^{-3} borate buffer solution (A), 1.5×10^{-1} mol dm^{-3} borate buffer solution (B), 1×10^{-2} mol dm^{-3} acetate buffer solution (C), and 1×10^{-2} mol dm^{-3} phosphate buffer solution (D). [E]: 2×10^{-5} mol dm^{-3} and [O_2]: 2.4×10^{-4} mol dm^{-3}.

In the course of H_2O_2 production, singlet oxygen is formed simultaneously by the energy transfer between triplet eosine and oxygen. Since the yield of H_2O_2 was scarcely affected by the addition of the singlet oxygen quencher (NaN_3, 7.0×10^{-3} mol dm^{-3}), it can be said that singlet oxygen is not directly concerned in the mechanism of H_2O_2 production.

H_2O_2 Formation via *the DR-initiated Mechanism.* With the concentrations of eosine, oxygen, and EDTA fixed under condition when the DR mechanism is operative, the yields of H_2O_2 formation (Φ_h^{DR}) and of eosine reduction were measured. The value of Φ_h^{DR} is equal to 0.057 in the concentrations of 0.2 mol dm^{-3} of EDTA, 5.0×10^{-5} mol dm^{-3} of oxygen, and 5.0×10^{-5} mol dm^{-3} of eosine. However, the photoreduction of eosine takes place at the same time, and H_2O_2 decomposes rather rapidly after it is produced. When the deaerated solution containing 5.0×10^{-5} mol dm^{-3} of eosine, 5.0×10^{-4} mol dm^{-3} of H_2O_2, and 0.2 mol dm^{-3} of EDTA was irradiated, H_2O_2 was decomposed in the initial stage of the photoreduction of the dye. Although further investigations will be needed in order to treat Φ_h^{DR} kinetically, it may be supposed that the eosine semiquinone produced *via* the DR-initiated mechanism reacts with H_2O_2, leading to its decomposition.

Influence of Inorganic Salts on Φ_h^{DO} via *the DO-initiated Mechanism.* It was observed that the formation of H_2O_2 *via* the DO-initiated mechanism was enhanced by the addition of some inorganic salts. This effect is confirmed in the case of the DO-initiated mechanism, but not in the DD mechanism. As is shown in Table 2, the increment in the Φ_h^{DO} value was as high as one order of magnitude with 0.15 mol dm^{-3} of sodium borate or 0.16 mol dm^{-3} of sodium carbonate.

Using Eq. 4 we can analyse the effect of EDTA concentration on Φ_h^{DO} similarly and see that the DO-initiated mechanism in Fig. 1 is still operative. From the results of the kinetic analysis shown in Fig. 4, A and B, it can be seen that the value of $\phi_{st} k_O^r k_E''^r / k_O^s k_E''^s$ in

TABLE 2. INORGANIC SALT EFFECT ON Φ_h^{DO}

Added compound $\left(\frac{\text{concentration}}{\text{mol dm}^{-3}}\right)$	pH	Φ_h^{DO}
None	9.5	1.1×10^{-3}
$Na_2B_4O_7$ (0.15)	9.2	12×10^{-3}
Na_2CO_3 (0.16)	10.3	10×10^{-3}
Na_2SiO_3 (0.10)	11.4	5.0×10^{-3}
$Na_2P_2O_7$ (0.10)	9.9	4.5×10^{-3}
$(NH_4)_2SO_4$ (0.10)	8.5	3.4×10^{-3}
Na_2SO_4 (0.10)	8.6	2.7×10^{-3}
NaCl (0.10)	9.2	2.2×10^{-3}
CH_3COONa (0.10)	9.6	2.2×10^{-3}
Na_2HPO_4 (0.10)	7.6	2.0×10^{-3}

[E]$=5.0 \times 10^{-5}$ mol dm^{-3}, [EDTA]$=3.0 \times 10^{-3}$ mol dm^{-3}, [O_2]$=2.4 \times 10^{-4}$ mol dm^{-3}.

the presence of sodium borate is greater than that without the salt. For the solution to which sodium borate has been added, the yields of the triplet eosine and the semioxidized radical were checked by a flash photolysis experiment. Since no influence of the salt on these yields was observed, it may be supposed that the values of ϕ_{st} and k_0^r/k_0^s with sodium borate are equal to those without the salt. By comparing the two values of $\phi_{st}k_0^r k_E''^r/k_0^s k_E''^s$, we learn that the values of $k_E''^r/k_E''^s$ with sodium borate are seven times (at 10 °C) and twenty-five times (at 25 °C) greater than those without sodium borate. The results are shown in Table 3. The effect of the addition of sodium borate may be attributed to the enhancement of the reaction probability between $E^+\cdots O_2^-$ and EDTA.

Temperature Effect on Φ_h^{DO}. Figure 5 shows the H_2O_2 formation curves of the DO-initiated mechanism at several temperatures. The initial yield of H_2O_2 generally increases with an increase in the temperature. The Arrhenius plots for the overall rate constant, k, in the H_2O_2 formation processes, *i.e.*, $\Delta[H_2O_2]/\Delta t = kt$, give similar activation energies both in the mixed solutions of 5.0×10^{-5} mol dm^{-3} eosine, 8.0×10^{-1} mol dm^{-3} sodium borate, and 6.0×10^{-3} mol dm^{-3} EDTA ($\approx$12 kcal deg, pH=9.4), and in 5.0×10^{-5} mol dm^{-3} eosine, 1.0×10^{-2} mol dm^{-3} acetate buffer, and 6.0×10^{-3} mol dm^{-3} EDTA ($\approx$17 kcal deg, pH=5.1). With an increase in the temperature, the reaction probability, $k_0^r k_E''^r/k_0^s k_E''^s$ for $E^+\cdots O_2^-$, increases as is listed in Table 3. However, at higher temperatures ($T \gtrsim 30$ °C), H_2O_2 formation curves give maximum values during irradiation and then fall, as is shown in Fig. 5. By a vacuum distillation of the irradiated solution containing the borate ion (pH=8.0), H_2O_2 was not distilled out completely; however, the residual H_2O_2 was quantitatively distilled as a result of the neutralization by the addition of hydrochloric acid. This suggests that a nonvolatile compound such as a peroxo salt of $[B_2(O_2)_2(OH)_4]^{2-}$ might be formed during the irradiation and partially dissociated.[15] It was confirmed that the peroxo compound is unstable in an aqueous solution and rapidly decomposes at temperatures higher than 20 °C. There is no maximum value in the formation curves without the borate ion even at 40 °C within the present observation time; rather, the curves rise straight. Therefore, the decomposition of H_2O_2 is negligible in this system. It may be suggested that O_2^- (or H_2O_2) makes the peroxo compound with borate ions and then decomposes at higher temperatures ($T \gtrsim 20$ °C).

Supplementally, we checked the pH dependency on Φ_h. The values of Φ_h^{DO} were not practically affected by the pH in the region of pH=5—10, but those of Φ_h^{DD} became relatively small at pH$\lesssim$7.

EDTA Concentration Effect on the Yield of O_2^- Ion Formation (Φ_s^{DO}). Using TNBT (16 μmol dm^{-3}) as the radical trap for O_2^-, the values of Φ_s^{DO} were determined by measuring the optical absorption of the formazan at the wavelength of 560 nm.[16] Since the relationship of the $\Phi_s^{DO}/2 = \Phi_h^{DO}$ is always obtained in the systems without sodium borate, it may be supposed that the disproportionation reaction between O_2^- ions occurs quantitatively in an alkaline solution. From the results of the EDTA-concentration effect on Φ_s^{DO}, a linear relationship of $1/\Phi_s^{DO}$ against 1/[EDTA] was obtained; the values of $k_0^r k_E''^r/k_0^s k_E''^s$ and $k_E''^r/(k_d''+k_r'')$ agree with those obtained from the same analytical treatment

TABLE 3. RATE CONSTANTS OF ELEMENTARY PROCESSES FOR THE DO INTERMEDIATE

Conditions (pH)	T/°C	$k_0^r k_E''^r/k_0^s k_E{}^s$	$k_E''^s/(k_r''+k_d'')$
A) 2×10^{-2} mol dm^{-3}			
Borate buffer (9.2)	10	4.4×10^{-2}	3.0×10^{-2}
B) 1.5×10^{-1} mol dm^{-3}			
Borate buffer (9.2)	25	1.56×10^{-1}	9.0×10^{-3}
C) 1.0×10^{-2} mol dm^{-3}			
Acetate buffer (4.9)	25	6.2×10^{-3}	4.1×10^{-2}
D) 1.0×10^{-2} mol dm^{-3}			
Phosphate buffer (8.9)	25	6.0×10^{-3}	4.2×10^{-2}

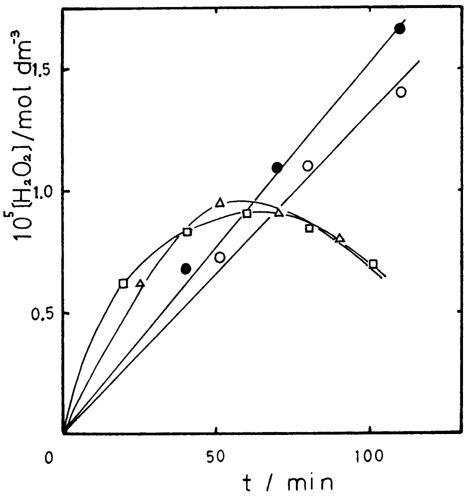

Fig. 5. H_2O_2 formation curves at several temperatures on DO started mechanism. [E]: 5×10^{-5} mol dm^{-3}, [EDTA]: 6×10^{-3} mol dm^{-3}, [O_2]: 2.4×10^{-4} mol dm^{-3}, and [$Na_2B_4O_7$]: 8×10^{-2} mol dm^{-3}. T=10 °C (—○—), 30 °C (—△—), 40 °C (—□— and —●— without $Na_2B_4O_7$).

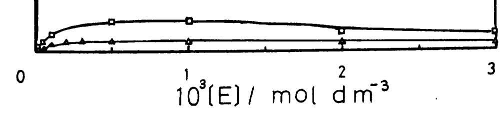

Fig. 6. Effect of eosine concentration on Φ_h in aerated aqueous solution. [EDTA]: 1×10^{-1} mol dm^{-3} (—○—), 3×10^{-3} mol dm^{-3} (—□—), and 0 mol dm^{-3} (—△—) without $Na_2B_4O_7$ (pH=4.9). [EDTA]: 5×10^{-2} mol dm^{-3} (—●—) with 8.8×10^{-2} mol dm^{-3} $Na_2B_4O_7$ (pH=7.8).

as that used for Φ_h^{DO} (*cf.* Fig. 4. and Table 3, D and C). These results support the idea that the H_2O_2 formation from the O_2^- ion is exclusively due to the disproportionation between O_2^- ions in this system and that the contribution of the reaction of TNBT with the triplet eosine to make the formazan is negligible at low concentrations of 16 μmol dm^{-3}.

However, as for the addition effect of the borate ion on Φ_s^{DO}, no significant increasing effect on Φ_s^{DO} was observed in the system with EDTA. Under the DO mechanism in the solution without EDTA, no free O_2^- is liberated from $E^+ \cdots O_2^-$; absolutely no H_2O_2 was detected.[17] In spite of such results, the formazan was still formed upon the irradiation of a sample without EDTA. It is considered that TNBT might react with $E^+ \cdots O_2^-$. Furthermore, the yield of the formazan was increased by the addition of the borate ion. In the case of EDTA addition, if the borate ion could stabilize the free O_2^- liberated by the following reaction:

$$\mathrm{EDTA} + E^+ \cdots O_2^- \longrightarrow \mathrm{EDTA} + E + O_2^-$$

the enhancement of Φ_s^{DO} by the borate ion would also be observed. Assuming that the borate ion stabilizes the O_2^- radical, which exists in an intermediate including EDTA in the above reaction, and that, in preference to the stabilization by the borate ion, TNBT reacts with O_2^- in the intermediate, no enhancement effect by the borate ion may appear. Further investigations of the reasons will be needed in the future.

Eosine Concentration Effect on Φ_h *and the Accumulation Experiment of* H_2O_2. In order to ascertain the conditions for the highest yield of H_2O_2 formation, Φ_h was measured at various concentrations of eosine and EDTA with or without the borate ion. As is shown in Fig. 6, the maximum yield of 0.04 (Φ_h^{max}) is obtained under the conditions of [E]: 1—2$\times 10^{-4}$ mol dm^{-3}, [O_2]: 2.4$\times 10^{-4}$ mol dm^{-3}, and [EDTA]: 0.1 mol dm^{-3} without the borate ion. Further, the value of Φ_h^{max} is close to 0.08—0.10 under the conditions of [E]: 1.0$\times 10^{-4}$ mol dm^{-3}, [O_2]: 2.4$\times 10^{-3}$ mol dm^{-3}, and [EDTA]: 0.05 mol dm^{-4} with 0.088 mol dm^{-3} of the borate ion, where the maximum concentration of H_2O_2 is ≈6$\times 10^{-3}$ mol dm^{-3}. Since is H_2O_2 decomposed by a catalytic reaction, the reversible fixation of gaseous oxygen was performed photochemically in the presence of EDTA, *i.e.*,

$$O_2 + 2\,\mathrm{EDTA} + 2H^+ \xrightarrow{h\nu/\mathrm{sensitizer}} H_2O_2 + 2\,\mathrm{EDTA}^+$$
$$\xrightarrow{\mathrm{catalysis}} (1/2)H_2O + (1/2)O_2.$$

This reaction leads to the consumption of EDTA.

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