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Visible Light-induced Oxidation of Ascorbic Acid and Formation of Hydrogen Peroxide

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Photosensitized oxidation of ascorbic acid and the formation of hydrogen peroxide using tris(2,2′-bipyridine)-ruthenium(II), $Ru(bpy)_3^{2+}$, proceed simultaneously in oxygen containing an aqueous solution of ascorbic acid with the illumination of visible light. The mechanism of the reaction has been suggested from the rate dependence on the solute concentrations and from quenching experiments. The charge separation could be achieved as the result of scavenging $Ru(bpy)_3^{3+}$, which is formed by the reaction of the lowest excited state species of $Ru(bpy)_3^{2+}$ with O_2.

The luminescence quenching of $Ru(bpy)_3^{2+}$ by various substances is a subject of much current interest.[1–12] The lowest excited state of $Ru(bpy)_3^{2+}$, $^*Ru(bpy)_3^{2+}$, is able to react with an electron-transfer reagent.[13,14] The oxidative and reductive quenchings of $Ru(bpy)_3^{2+}$ give $Ru(bpy)_3^{3+}$ as a strong oxidant and $Ru(bpy)_3^{+}$ as a strong reductant, respectively. In most photosystems the utilization of the redox properties of photo-generated $Ru(bpy)_3^{3+}$ or $Ru(bpy)_3^{+}$ is prevented because of fast back-electron-transfer reactions.[12]

The ability of $^*Ru(bpy)_3^{2+}$ to act as an electron donor or acceptor has been utilized in several prototype models of solar energy conversion.[15–18] Hydrogen evolution by water splitting with the irradiation of visible light has been extensively studied.[19,20] However, relatively little attention has been paid to the productions of superoxide ion,[21,22] and hydrogen peroxide[22] in the reaction of $^*Ru(bpy)_3^{2+}$ with molecular oxygen. The reductions of O_2 to O_2^- and H_2O_2 are both up-hill reactions, *e. g.*, the standard free energy changes for the production of O_2^- and H_2O_2 from O_2 are 129 kJ mol^{-1} ($E_0'(O_2/O_2^-) = -0.32$ V)[23] and 274 kJ mol^{-1} , ($E_0(O_2/H_2O_2) = -0.68$ V),[23] respectively. The excited state of $Ru(bpy)_3^{2+}$ is rapidly quenched by O_2 to produce O_2^-: the quenching rate constants obtained were 3.3×10^9 $M^{-1}\,s^{-1}$ [24] and 3.7×10^9 $M^{-1}\,s^{-1}$ [25] (1 M=1 mol dm^{-3}) in neutral aqueous solution and 3.0×10^9 $M^{-1}\,s^{-1}$ in 0.5 M HCl.[22] Fast back-reaction of the $Ru(bpy)_3^{3+}$ with O_2^-, however, occurs and the production of hydrogen peroxide could not be observed in the $Ru(bpy)_3^{2+}/O_2$ system.

We found that hydrogen peroxide was formed in the solution containing oxygen, using ascorbate ion as a scavenger of $Ru(bpy)_3^{3+}$. So we have investigated the mechanism of visible-light induced formation of hydrogen peroxide in the $Ru(bpy)_3^{2+}$/ascorbic acid/O_2 system.

Experimental

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was prepared according to the literature method[26] and recrystallized twice from water. Ascorbic acid from Kanto Kagaku was used without further purification.

The ionic strength of the irradiated samples were maintained at 0.2 by sodium chloride. The hydrogen ion concentration was adjusted by acetate buffers. An oxygen- or air-saturated aqueous solution containing $Ru(bpy)_3^{2+}$ and ascorbic acid in a cylindrical glass cell (40-mm diameter and 15-mm thickness) with a glass cap was liluminated by a 150 W tungsten lamp with a UV cut-off filter (Kenko, Skylight L-40, UV) at 25±0.2 °C.

The irradiation sample (2 ml) was poured into a column (10-mm diameter and 30-mm length) of cation-exchange resins (Dowex 50 W, X-8, 100—200 mesh, the hydrogen form), followed by washing with water. The concentrations of hydrogen peroxide[27] and dehydroascorbic acid[28] in the eluant were determined by a colorimetric method. The absorption spectra were observed with a Hitachi Model 320 spectrophotometer.

The quenching experiments were carried out by using a Shimadzu Model RF-500 spectrofluorometer at 25±0.1 °C. For the luminescence experiments, the excitation was carried out at 455 nm. If necessary, dissolved oxygen in the samples was removed by flushing nitrogen gas, which was passed through an alkanine pyrogallol solution. The concentration of the dissolved oxygen in the solutions was adjusted by saturations of air and pure oxygen under atmospheric pressure at 25±0.2 °C.

Results

In the air- and oxygen-saturated solutions containing $Ru(bpy)_3^{2+}$ and ascorbic acid (AH_2) at pH 3.1—5.5, the formation reaction of hydrogen peroxide and the oxidation reaction of ascorbic acid proceeded simultaneously with the illumination of visible light, while the absorption spectrum of the solution in the visible

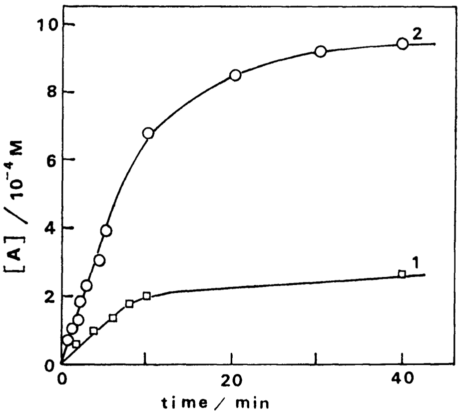

Fig. 1. Plots of [A] *vs.* time in $Ru(bpy)_3^{2+}/AH_2$ solutions at pH 4.6 and 25 °C.
$[Ru(bpy)_3^{2+}] = 1.0 \times 10^{-4}$ M, $[AH_2]_T = 1.0 \times 10^{-3}$ M, 1: air-saturated solution, 2: O_2-saturated solution.

region was unchanged during 1 h illumination. These results show that the $Ru(bpy)_3^{2+}$ photosensitized production of hydrogen peroxide occurs in the $Ru(bpy)_3^{2+}/AH_2/O_2$ system.

The plots of the concentration of dehydroascorbic acid (A) against the illumination time in oxygen-saturated and air-saturated solutions are shown in Fig. 1. The oxidation rates of ascorbic acid to dehydroascorbic acid, d[A]/d*t*, were determined from the slopes of [A] *vs.* time plots. The saturation of [A] *vs.* time curves is seen in Fig. 1 as the result of consumption of the dissolved oxygen in the solutions.

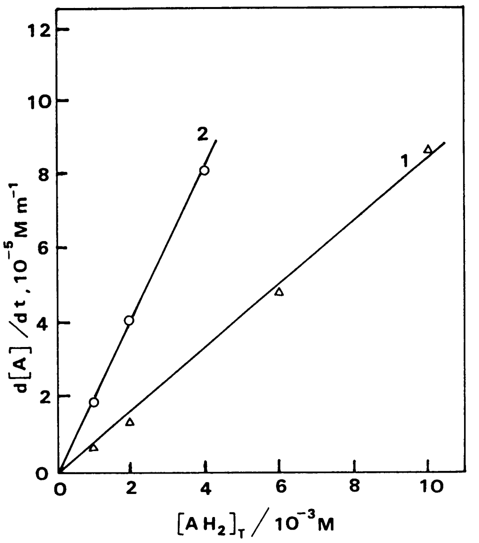

Fig. 2. Dependence of rate on ascorbic acid concentration in air-saturated (1) and O_2-saturated (2) solutions at pH 4.6 and 25 °C.
$[Ru(bpy)_3^{2+}]=1.0\times10^{-4}$ M.

The dependence of the rate on the total concentration of ascorbic acid, $[AH_2]_T$, is shown in Fig. 2. The oxidation rate of ascorbic acid was found to be proportional to the ascorbic acid concentration in the lower concentration region of the acid at a given pH.

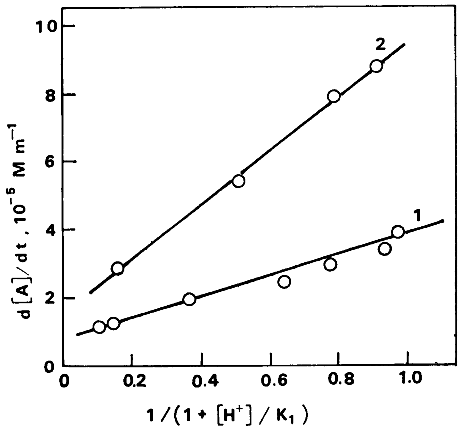

Fig. 3. Plots of d[A]/dt *vs.* $1/(1+[H^+]/K_1)$ in air-saturated (1) and O_2-saturated (2) solutions at 25 °C. $[Ru(bpy)_3^{2+}]=1.0\times10^{-4}$ M, $[AH_2]_T=1.0\times10^{-3}$ M.

In Fig. 3 the rates are plotted as a function of $1/(1+K_1/[H^+])$ where K_1 is the dissociation constant of Reaction 1: the value of $1/(1+K_1/[H^+])$ is proportional to the concentration of ascorbate monoanion, $[AH^-]$. Under the conditions employed, Reaction 2 can be neglected. The acid dissociation constants of

$$AH_2 \overset{K_1}{\rightleftharpoons} AH^- + H^+ \quad (1)$$

$$AH^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \quad (2)$$

Reactions 1 and 2 are reported to be $K_1=9.16\times10^{-5}$ M and $K_2=4.57\times10^{-12}$ M at 25 °C, respectively.[29)]

The rate is also dependent on the concentration of the dissolved oxygen: the ratios of the rates in the oxygen-saturated and air-saturated solutions range from 2.4 to 2.6 (Fig. 3).

The values of product distribution, $[H_2O_2]/[A]$, in the illuminated solutions under various conditions are shown in Table 1. This table shows that the observed $[H_2O_2]/[A]$ ratio are around 0.6.

TABLE 1. PRODUCT DISTRIBUTIONS IN THE IRRADIATED SOLUTIONS[a)]

pH	$[H_2O_2]/10^{-4}$ M	$[A]/10^{-4}$ M	$[H_2O_2]/[A]$	Sat. gas
3.5[b)]	1.86	2.68	0.69	Air
3.6[c)]	1.14	1.79	0.64	Air
4.5[c)]	1.66	2.61	0.64	Air
5.4[c)]	1.32	2.13	0.62	Air
3.3[c)]	4.18	8.34	0.50	Oxygen
4.1[e)]	4.20	7.99	0.53	Oxygen
4.6[c)]	5.68	9.85	0.58	Oxygen
5.0[c)]	4.88	8.23	0.59	Oxygen

a) 1.0×10^{-3} M AH_2, 1.0×10^{-4} M $Ru(bpy)_3^{2+}$, $\mu=0.2$, 25 °C. b) Illumination time 25 min. c) Illumination time 10 min. d) Illumination time 60 min. e) Illumination time 30 min.

By the determination of the concentration of ascorbic acid or hydrogen peroxide in the solutions at pH 5.5 and 25 °C, it was observed that a) the oxidation reaction of ascorbic acid by dissolved oxygen in the O_2-saturated solution can be neglected compared with the photosensitized oxidation of ascorbic acid and b) no appreciable

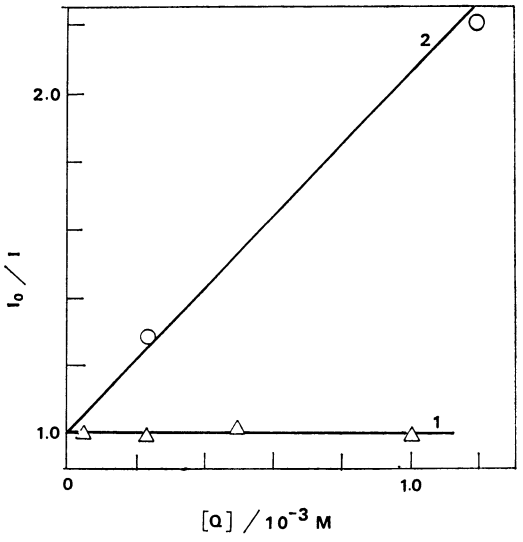

Fig. 4. Stern-Volmer plots at pH 4.6 and 25 °C.
1: Q; ascorbic acid, 2: Q; oxygen.

decomposition of hydrogen peroxide occurred during 30 min illumination of an oxygen-saturated solution containing 2.0×10^{-4} M $Ru(bpy)_3^{2+}$ and 1.0×10^{-3} M H_2O_2.

The luminescence quenching studies were carried out in $Ru(bpy)_3^{2+}/O_2$ and deaerated $Ru(bpy)_3^{2+}/$ascorbic acid solutions at pH 4.6. The Stern-Volmer plots for these systems are shown in Fig. 4. From the results shown in this figure, we conclude that the predominant species that reacts with $^*Ru(bpy)_3^{2+}$ is the dissolved oxygen. The Stern-Volmer constant estimated from slope 2 in Fig. 4 was 1900 M^{-1} and the quenching rate constant, k_q, for $^*Ru(bpy)_3^{2+}$ by O_2 was 3.2×10^9 $M^{-1}\,s^{-1}$ at 25 °C, since the excited state life time of $^*Ru(bpy)_3^{2+}$ is known to be 6.0×10^{-7} s.[30)]

Discussion

The rate profiles shown in Figs. 1 to 3 indicate that the rates depend on the concentrations of ascorbic acid and O_2 and that the reactive species of the acid is the ascorbate anion, AH^-. The results of the quenching experiments (Fig. 4) show that the reaction of $^*Ru(bpy)_3^{2+}$ with AH^- can be ignored compared with that of $^*Ru(bpy)_3^{2+}$ with O_2 under the conditions employed.

The proposed reaction mechanism responsible for the experimental results is given by Reactions 3 to 13.

$$Ru(bpy)_3^{2+} \xrightarrow{h\nu} {}^*Ru(bpy)_3^{2+} \quad (3)$$

The $^*Ru(bpy)_3^{2+}$ reacts with O_2 to give a superoxide

$$^*Ru(bpy)_3^{2+} + O_2 \longrightarrow Ru(bpy)_3^{3+} + O_2^- \quad (4)$$

ion. At low pH the superoxide ion becomes an HO_2

$$O_2^- + H^+ \rightleftharpoons HO_2 \qquad pK\,4.8^{31)} \quad (5)$$

radical. The scavanging reaction of $Ru(bpy)_3^{3+}$ by ascorbate anion competes for the back-electron-transfer reaction.

$$Ru(bpy)_3^{3+} + AH^- \rightleftharpoons Ru(bpy)_3^{2+} + AH\cdot \quad (6)$$

$$Ru(bpy)_3^{3+} + O_2^-(\text{or } HO_2) \longrightarrow Ru(bpy)_3^{2+} + O_2(\text{or } O_2 + H^+), \quad (7)$$

where AH· is the ascorbic acid radical. The superoxide

$$AH^- + O_2^- + 2H^+ + \longrightarrow AH\cdot + H_2O_2 \quad (8)$$

$$AH_2 + HO_2 \rightleftharpoons AH\cdot + H_2O_2 \quad (9)$$

ion and HO_2 radical oxidize the ascorbic acid.[29)] When the concentration of ascorbic acid is low, the disproportionation reactions of O_2^- and HO_2 occur.[32,33)] The

$$O_2^- + O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2 \quad (10)$$

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (11)$$

ascorbic acid radicals are, presumably, decomposed by Reactions 12 and 13.[29)] The rate constant of Reaction 13

$$AH\cdot + O_2 \longrightarrow A + HO_2 \quad (12)$$

$$AH\cdot + AH\cdot \longrightarrow A + AH_2 \quad (13)$$

was estimated to be 8×10^7 $M^{-1}\,s^{-1}$ in the pH range 2.5—4.0.[34)]

The rate constants for the forward reaction, k_{14} (Eq. 14), and backward reaction, k_{15} (Eq. 15), were determined by means of flash photolysis by Creutz and Sutin[35)] to be $k_{14}=2\times10^7$ $M^{-1}\,s^{-1}$ and $k_{15}=1\times10^9$ $M^{-1}\,s^{-1}$ at 25 °C.

$$^*Ru(bpy)_3^{2+} + AH^- \xrightarrow{k_{14}} Ru(bpy)_3^{3+} + AH\cdot \quad (14)$$

$$Ru(bpy)_3^{2+}\ AH\cdot \xrightarrow{k_{15}} Ru(bpy)_3^{3+} + AH^- \quad (15)$$

By assuming the competition between Reactions 4 and 14 the fraction of $^*Ru(bpy)_3^{2+}$ molecules scavenged by AH^-, f, is given by:

$$f = \frac{1}{1 + k_4[O_2]/k_{14}[AH^-]}. \quad (16)$$

Using $k_4=3.2\times10^9$ $M^{-1}\,s^{-1}$ and $k_{14}=2\times10^7$ $M^{-1}\,s^{-1}$,[34)] we can derive $f<0.03$ in the air-saturated solution and $f<0.006$ in the O_2-saturated solution under the conditions employed. The results seem to support the contention that the reaction of $^*Ru(bpy)_3^{2+}$ with AH^- could be essentially ignored.

The luminescence quenching efficiency of $^*Ru(bpy)_3^{2+}$ by O_2 and thus the rate would increase with an increase in the concentration of O_2. The ratio of the amounts of $^*Ru(bpy)_3^{2+}$ being oxidized to $Ru(bpy)_3^{3+}$ by Reaction 4 in the oxygen- and air-saturated solutions would correspond to $(I_0-I_{O_2})/(I_0-I_{air})$ where I_0, I_{O_2}, and I_{air} are the relative luminescence intensities in the deaerated, oxygen-saturated, and air-saturated $Ru(bpy)_3^{2+}$ solutions, respectively. The ratio was estimated to be about 2.8 from the results shown in Fig. 4. The ratio of the rates in O_2-saturated and air-saturated solutions, $(d[A]/dt)_{O_2}/(d[A]/dt)_{air}=2.6$, is essentially in agreement with the value of $(I_0-I_{O_2})/(I_0-I_{air})$.

Dependence of the rate on $[AH_2]_T$ (Fig. 3) would account for the competition between Reactions 6 and 7 for $Ru(bpy)_3^{3+}$. A linear dependence of the rate on $[AH_2]_T$ at lower $[AH_2]_T$ indicates that the rate of Reaction 7 increases almost linearly with $[AH^-]$. The relatively small increase in the rate in the higher concentration region of ascorbic acid is attributable to that $k_7[O_2^-]$ or $k'_7[HO_2]$, where k_7 and k'_7 are the rate constants of $Ru(bpy)_3^{3+}$ with O_2^- and $Ru(bpy)_3^{3+}$ with HO_2 respectively, is not so much different from $k_8[AH^-]$. When the concentration of the ascorbic acid becomes high enough for scavenging $Ru(bpy)_3^{3+}$, the rate would not depend on $[AH_2]_T$ any longer.

According to Reactions 3 to 13, the stoichiometric ratio of $[H_2O_2]/[A]$ should be about unity, whereas the observed product distributions (Table 1) show that the ratio was 0.5—0.7. This lower value of the observed ratio is probably attributable to the chain decomposition reaction of H_2O_2.[32)] Such cahin reactions would occur when the concentration of H_2O_2 becomes high enough for HO_2 to react with H_2O_2 instead of with ascorbic

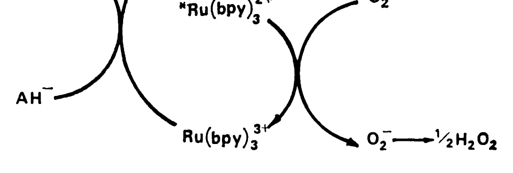

Fig. 5. Schematic representation of the photosensitized reaction.

acid (Eqs. 8 and 9) or with itself (Eqs. 10 and 11).

$$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH \quad (17)$$

$$H_2O_2 + OH \longrightarrow H_2O + HO_2 \quad (18)$$

Similar chain decomposition reactions would occur for O_2^- instead of HO_2. The reactions of OH radical with ascorbic acid and $Ru(bpy)_3^{2+}$ have to be considered.

The main features of the $Ru(bpy)_3^{2+}$ photosensitized reaction are illustrated schematically in Fig. 5. The ratio of the rate of the electron-transfer reaction (Eq. 4) to that of the back-electron-transfer reaction (Eq. 7) would determine the efficiency of the charge-separation of the reaction of $Ru(bpy)_3^{2+}$ with O_2 and thus that of the photosensitized reaction under study.

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