Kinetics and Mechanisms of the Photo-Induced Oxidation of Ascorbic Acid by Molecular Oxygen Catalyzed by Ruthenium(II) Complexes Containing 2,2′-Bipyridine and 2,2′-Bipyrazine

Keiichi TSUKAHARA,* Yuuko WADA, and Masaru KIMURA*
Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630
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Hydrogen peroxide was efficiently produced by the irradiation of visible light on aqueous acid solutions containing ascorbic acid, molecular oxygen, and ruthenium(II) complexes: $[Ru(bpy)_x(bpz)_{3-x}]^{2+}$ (x=0—3, bpy=2,2′-bipyridine, and bpz=2,2′-bipyrazine). The formation of hydrogen peroxide and the decay of ascorbic acid were followed by polarography during continuous irradiation by visible light of the solution. The rate constants of the quenching reaction of the excited triplet state of the ruthenium(II) complexes by ascorbate and molecular oxygen obtained from the initial rate method were in good agreement with those obtained from luminescence quenching experiments. The initiation reaction in the photo-induced reaction mechanism changes from the oxidative quenching of $*[Ru(bpy)_3]^{2+}$ by molecular oxygen to the reductive quenching of $*[Ru(bpy)_2(bpz)]^{2+}$, $*[Ru(bpy)(bpz)_2]^{2+}$, or $*[Ru(bpz)_3]^{2+}$ by ascorbate. Such a change in the mechanism arises from a difference in the redox potentials, $E^0(Ru^{3+}/*Ru^{2+})$ and $E^0(*Ru^{2+}/Ru^{+})$, for each ruthenium(II) species containing bpy and bpz. The detailed mechanisms are discussed.

Photo-induced electron-transfer reactions involving ruthenium(II) polypyridine complexes have received considerable attention for both fundamental reasons and their practical application to solar energy conversion.[1,2] Tris(2,2′-bipyridine)ruthenium(II) ion ($[Ru(bpy)_3]^{2+}$) has been one of the most studied photosensitizers. Visible-light irradiation of aqueous solutions of $[Ru(bpy)_3]^{2+}$, triethanolamine, and methylviologen (1,1′-dimethyl-4,4′-bipyridinium cation, MV^{2+}) yielded the methylviologen radical cation (MV^{+}) with a quantum yield of 0.19;[3] the production of MV^{+} led to hydrogen evolution from water by the use of PtO_2 or colloidal Pt.[4,5] A tris(2,2′-bipyrazine)ruthenium(II) ion ($[Ru(bpz)_3]^{2+}$) is a superior photosensitizer over the $[Ru(bpy)_3]^{2+}$ ion for the production of MV^{+}, with a quantum yield of 0.77.[3] The reaction mechanisms are quite different. The photo-excited state of the $[Ru(bpy)_3]^{2+}$ ion, i.e., $*[Ru(bpy)_3]^{2+}$, is oxidatively quenched by a quencher (Q), such as MV^{2+} (Reaction 1):

$$*[Ru(bpy)_3]^{2+} + Q \longrightarrow [Ru(bpy)_3]^{3+} + Q^{-}. \quad (1)$$

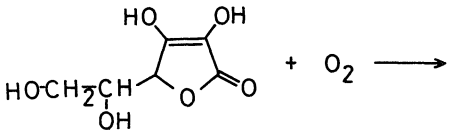
On the other hand, the $*[Ru(bpz)_3]^{2+}$ ion is reductively quenched by a quencher, such as triethanolamine (Reaction 2):

$$*[Ru(bpz)_3]^{2+} + Q \longrightarrow [Ru(bpz)_3]^{+} + Q^{+}. \quad (2)$$

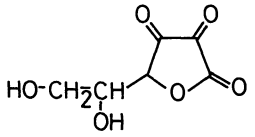
The difference in mechanisms is considered to arise from a positive shift of about 0.5 V in the redox potential of the ruthenium(II) complexes for the latter, compared with the former.[3]

We previously studied such visible-light induced redox and substitution reactions of inorganic compounds using $[Ru(bpy)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ ions.[6] Rillema et al.[7] have prepared the mixed-ligand ruthenium(II) complexes containing bpy and bpz, $[Ru(bpy)_2(bpz)]^{2+}$ and $[Ru(bpy)(bpz)_2]^{2+}$. Although the redox and excited-state properties of these complexes have been also investigated,[7-9] the redox quenching reaction has not been examined. It would be interesting to know the changing point from oxidative to reductive quenching mechanisms of the ruthenium(II) complexes by replacing 2,2′-bipyridine with 2,2′-bipyrazine. We therefore investigated the kinetics of the photo-induced oxidation of ascorbic acid by molecular oxygen catalyzed by the ruthenium(II) complexes, $[Ru(bpy)_x(bpz)_{3-x}]^{2+}$ (x=0—3), in an aqueous acid solution.

Although autoxidation of ascorbic acid to dehydroascorbic acid in an aqueous acid solution (Reaction 3)



ascorbic acid



(3)

dehydroascorbic acid

is very slow, in the presence of these ruthenium(II) complexes, irradiation with visible light induced the oxidation of ascorbic acid and the formation of hydrogen peroxide. Such a photo-induced oxidation of ascorbic acid by the $[Ru(bpy)_3]^{2+}$ ion has already been studied by Kurimura et al.,[10] in which an oxidative quenching mechanism of $*[Ru(bpy)_3]^{2+}$ by

molecular oxygen has been proposed. In the present work we have also found that the formation of hydrogen peroxide by use of the $[Ru(bpz)_3]^{2+}$ ion as a photocatalyst is most efficient among the four ruthenium(II) complexes.

Experimental

Materials. Tris(2,2′-bipyrazine)ruthenium(II) chloride 3.5 hydrate ($[Ru(bpz)_3]Cl_2 \cdot 3.5H_2O$),[11] 2,2′-bipyrazinebis(2,2′-bipyridine)ruthenium(II) hexafluorophosphate ($[Ru(bpy)_2(bpz)](PF_6)_2$),[7] and bis(2,2′-bipyrazine)(2,2′-bipyridine)ruthenium(II) hexafluorophosphate ($[Ru(bpy)(bpz)_2](PF_6)_2$)[7] were prepared and purified as in previously reported methods. Tris(2,2′-bipyridine)ruthenium(II) chloride hexahydrate ($[Ru(bpy)_3]Cl_2 \cdot 6H_2O$) obtained from Aldrich Chemical Company, Inc. was used without further purification. L-Ascorbic acid and sodium L-ascorbate were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. All other chemicals used were of guaranteed grade. All of the solutions used for measurements were prepared from redistilled water. A solution of ascorbic acid and sodium ascorbate was freshly prepared just before measurements.

Procedure. Kinetic measurements during irradiation with visible light were employed by using the same method as reported previously.[6a] A sample solution was continuously irradiated with visible light from two 100 W tungsten lamps at 30 °C under various pH conditions (an acetate buffer); ionic strengths (adjusted with sodium perchlorate); and concentrations of Ru(II), ascorbic acid, and oxygen. Oxygen or air was continuously bubbled through the solution. Aliquot samples were withdrawn at appropriate times after reaction initiation; a Dowex 50W-X8 cation-exchange resin (200—400 mesh, H^+ form) was added in order to remove the ruthenium(II) complexes. After filtration and washing the resins with water, the concentrations of hydrogen peroxide formed and of ascorbic acid remaining in the solutions were measured using a Yanagimoto PA-102 polarograph at 25 °C and pH 4.6 (a 0.1 mol dm^{-3} acetate buffer containing a 0.01% gelatin) under nitrogen gas. The potentials were set at −1.25 V and 0.15 V vs. SCE (a saturated calomel electrode) for hydrogen peroxide and ascorbic acid, respectively. The concentrations of ruthenium(II) ions were determined spectrophotometrically by the use of Shimadzu UV-200S and UV-240 spectrophotometers. The light intensity absorbed in the solution was determined by the use of potassium tris(oxalato)ferrate(III) trihydrate as an actinometer.[12] The iron(II) content was determined spectrophotometrically in the form of a tris(1,10-phenanthroline)iron(II) ion at 510 nm with a molar absorption coefficient of 1.11×10^4 dm^3 mol^{-1} cm^{-1}.

The luminescence quenching experiments of the ruthenium(II) complexes with ascorbic acid and molecular oxygen were carried out at 30 °C, pH 4.6 (a 0.1 mol dm^{-3} acetate buffer), and an ionic strength (I) of 0.10 mol dm^{-3} ($NaClO_4$) under argon gas by the use of a Hitachi 850 spectrofluorometer. The exciting wavelengths were 450 nm ($[Ru(bpz)_3]^{2+}$), 469 nm ($[Ru(bpy)(bpz)_2]^{2+}$), 406 nm ($[Ru(bpy)_2(bpz)]^{2+}$), and 452 nm ($[Ru(bpy)_3]^{2+}$), respectively. The emission intensities were monitored at wavelengths of 604 nm ($[Ru(bpz)_3]^{2+}$), 646 nm ($[Ru(bpy)(bpz)_2]^{2+}$), 707 nm ($[Ru(bpy)_2(bpz)]^{2+}$), and 608 nm ($[Ru(bpy)_3]^{2+}$), respectively.

The pH of the solutions was measured on a Hitachi-Horiba F-7LC pH meter. The internal solution of the reference electrode was a 3.33 mol dm^{-3} NaCl solution saturated with AgCl.

Results and Discussion

Although the oxidation of ascorbic acid by molecular oxygen at pH 3.9—5.6 was very slow in the absence of the ruthenium(II) complexes, or in the presence of the complexes in the dark, it was accelerated by irradiation with visible light of the solution in the presence of the ruthenium(II) complexes (Fig. 1). The absorption spectra of the ruthenium(II) complexes did not change during the reactions, indicating that the ruthenium(II) complexes act as homogeneous catalysts.

Both plots of the concentrations of ascorbic acid remained, and those of hydrogen peroxide formed against time were linear during the initial part of the reaction (up to 1 h). The initial reaction rate was, therefore, obtained from the initial slope of this line. The ratio of the concentrations of ascorbic acid reacted

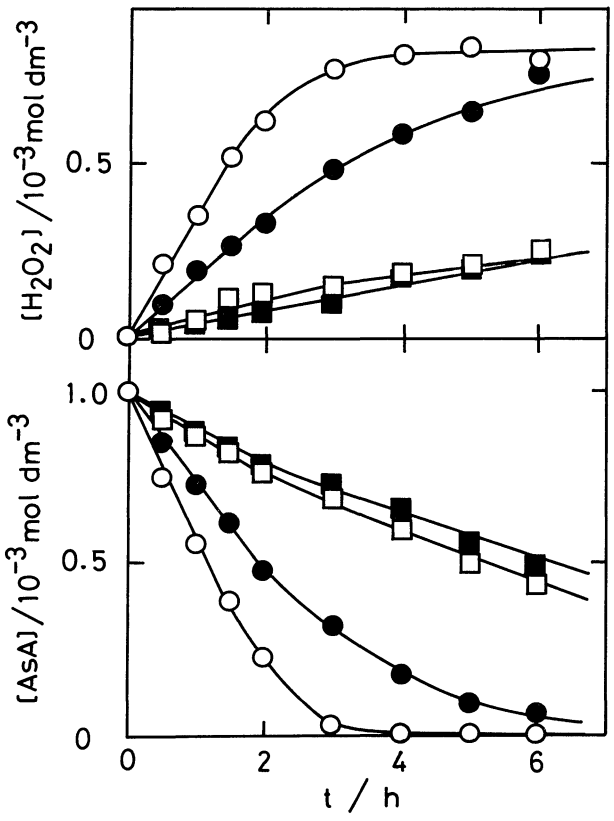


Fig. 1. The formation of hydrogen peroxide and the decay of ascorbic acid during the photo-induced oxidation of ascorbic acid by molecular oxygen in the presence of the ruthenium(II) complex at 30 °C, pH 4.60, and I=0.10 mol dm^{-3}. $[Ru(II)]=5.00 \times 10^{-5}$ mol dm^{-3}, $[AsA]_i=1.00 \times 10^{-3}$ mol dm^{-3}, and $[O_2]=2.28 \times 10^{-4}$ mol dm^{-3}. ○: $[Ru(bpz)_3]^{2+}$, ●: $[Ru(bpy)(bpz)_2]^{2+}$, □: $[Ru(bpy)_2(bpz)]^{2+}$, and ■: $[Ru(bpy)_3]^{2+}$.

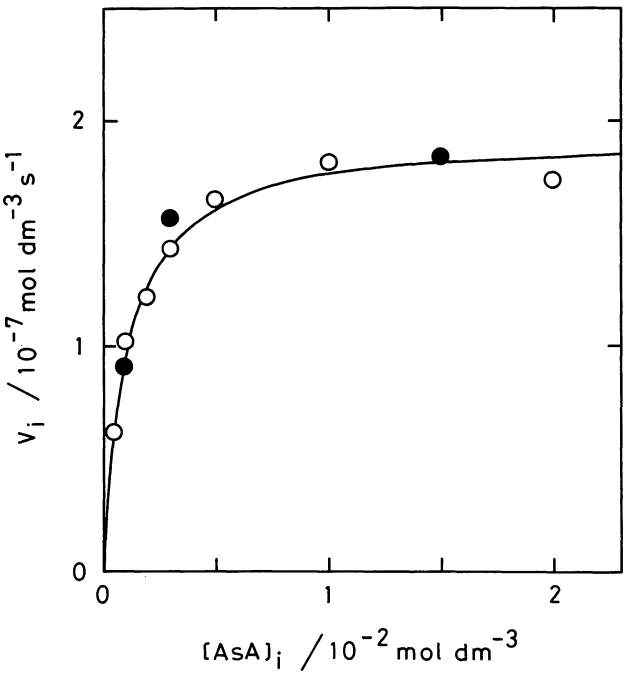


Fig. 2. Plots of V_i vs. [AsA]$_i$ for the photo-induced oxidation of ascorbic acid by molecular oxygen in the presence of $[Ru(bpz)_3]^{2+}$ ions. The initial rate V_i is the mean value for the formation of hydrogen peroxide and the decay of ascorbic acid. ○: $[O_2]=2.28\times10^{-4}$ mol dm^{-3} and ●: $[O_2]=1.16\times10^{-3}$ mol dm^{-3}. Other conditions are the same as in Fig. 1.

to those of hydrogen peroxide formed was near unity at low concentrations of ascorbic acid, but increased to about 2.5 at high concentrations. This indicates that the reaction of ascorbic acid with hydrogen peroxide occurs slowly. We found that the initial rate of the reaction between ascorbic acid and hydrogen peroxide with 1.00×10^{-3} mol dm^{-3} in each was $(9.0\pm1.0)\times10^{-9}$ mol dm^{-3} s^{-1} at pH 4.6, 30 °C, and I=0.10 mol dm^{-3} in an air-saturated solution. The autoxidation of ascorbic acid in the dark was accelerated by decreasing the ionic strength. Moreover, the reaction between ascorbic acid and hydrogen peroxide was accelerated by increasing the ionic strength. Therefore, most of the experiments in the present study were carried out at I=0.10 mol dm^{-3}, adjusted with $NaClO_4$.

Dependence of Concentrations of Ascorbic Acid. The reaction rate increased with increasing concentrations of ascorbic acid, and reached a constant value at higher concentrations of ascorbic acid. One of the examples is shown in Fig. 2 for the $[Ru(bpz)_3]^{2+}$ system. Numerical rate data are given in Table 1 for the ruthenium(II) complexes.

Effect of Oxygen. In the absence of oxygen the reaction did not occur for all of the ruthenium(II) systems. In the $[Ru(bpz)_3]^{2+}$ and $[Ru(bpy)(bpz)_2]^{2+}$ systems the reaction rate in the air-saturated solution was close to that in the oxygen-saturated solution. On the other hand, the rate of reaction in the oxygen-saturated solution was greater than that in the air-saturated solution for the other ruthenium(II) systems, $[Ru(bpy)_2(bpz)]^{2+}$ and $[Ru(bpy)_3]^{2+}$.

Table 1. Initial Rate of Reaction for the Formation of Hydrogen Peroxide and the Decay of Ascorbate in the Photo-Induced Oxidation of Ascorbic Acid by Molecular Oxygen Catalyzed by Ruthenium(II) Complexes[a]

[AsA]$_i$	$V_i(H_2O_2)$		V_i(AsA)	
10^{-3} mol dm^{-3}	10^{-7} mol dm^{-3} s^{-1}		10^{-7} mol dm^{-3} s^{-1}	
	Air satd[b]	O_2 satd[c]	Air satd[b]	O_2 satd[c]
	$[Ru(bpz)_3]^{2+}$			
0.50	0.57		0.66	
1.00	0.89	0.81	1.14	1.00
2.00	1.04		1.40	
3.00	1.16	1.33	1.69	1.80
5.00	1.27		2.03	
5.00	1.70[d]		2.50[d]	
5.00	0.61[e]		1.10[e]	
10.0	1.35		2.28	
10.0	2.00[d]		3.10[d]	
10.0	0.72[e]		2.00[e]	
15.0		1.30		2.37
20.0	1.28		2.20	
	$[Ru(bpy)(bpz)_2]^{2+}$			
1.00	0.44	0.69	0.70	0.82
2.00	0.91		1.30	
5.00	1.37		1.94	
10.0	1.38		2.77	
20.0	1.78	2.90	4.80	5.25
	$[Ru(bpy)_2(bpz)]^{2+}$			
1.00	0.21	0.23	0.26	0.30
2.00	0.29		0.41	
5.00	0.51		1.07	
10.0	0.85		1.73	
20.0	1.45	1.97	2.81	3.70
	$[Ru(bpy)_3]^{2+}$			
1.00	0.13	0.20	0.25	0.30
2.50	0.20	0.40	0.40	0.65
5.00	0.26	0.53	0.56	0.93
10.0	0.32	0.60	0.72	1.23
20.0	0.36	0.70	0.95	1.50

a) At 30 °C, pH 4.60, I=0.10 mol dm^{-3} ($NaClO_4$), and [Ru(II)]=5.00×10^{-5} mol dm^{-3}. b) In air-saturated solutions which contain 2.28×10^{-4} mol dm^{-3} O_2. c) In O_2-saturated solutions which contain 1.16×10^{-3} mol dm^{-3} O_2. d) At I=0.050 mol dm^{-3}. e) At I=0.50 mol dm^{-3}.

Dependence of Concentrations of Ruthenium(II). The effect of the concentrations of the $[Ru(bpz)_3]^{2+}$ ions on the reaction rate is shown in Fig. 3, indicating that it gradually increases with increasing concentrations of $[Ru(bpz)_3]^{2+}$ ions, reaching a constant at more than 5.00×10^{-5} mol dm^{-3} of ascorbic acid. This behavior can be accounted for by a Lambert–Beer's law (Eq. 4):

$$I_a = I_0(1 - \exp(-\gamma[[Ru(bpz)_3]^{2+}]), \quad (4)$$

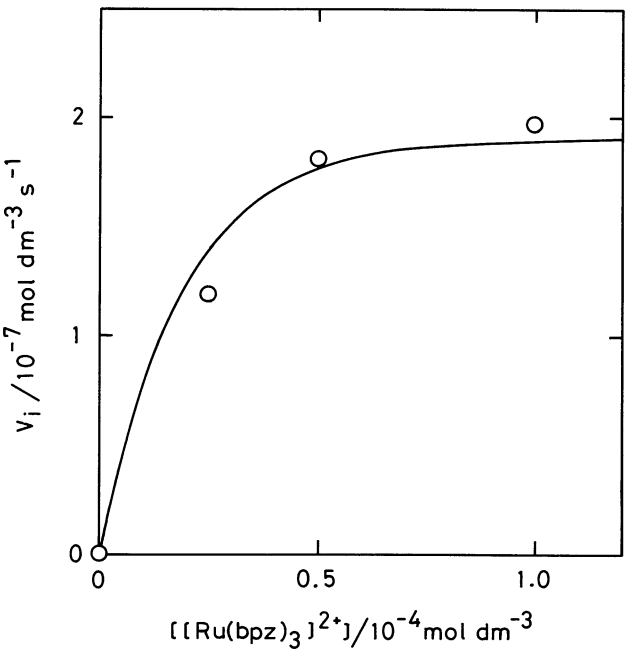


Fig. 3. Plots of V_i vs. [[Ru(bpz)$_3$]$^{2+}$] for the photo-induced oxidation of ascorbic acid by molecular oxygen at [AsA]$_i$=1.00×10^{-2} mol dm^{-3}. Other conditions are the same as in Fig. 1. The solid curve is calculated according to Eq. 4 with γ=5.3×10^4 dm^3 mol^{-1} and I_0=1.85×10^{-7}mol dm^{-3} s^{-1}.

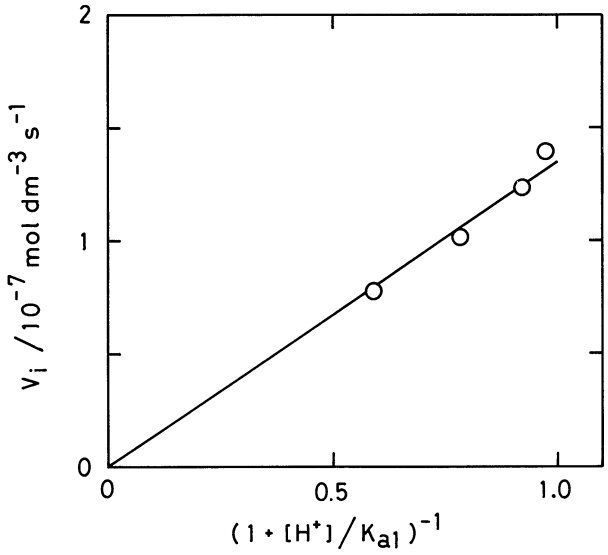


Fig. 4. Plots of V_i vs. $(1+[H^+]/K_{a1})^{-1}$ for the photo-induced oxidation of ascorbic acid by molecular oxygen in the presence of [Ru(bpz)$_3$]$^{2+}$ ions at [AsA]$_i$=1.00×10^{-3} mol dm^{-3}. Other conditions are the same as in Fig. 1.

where I_a and I_0 are the light intensities absorbed and irradiated, respectively, and γ is a constant including a molar absorption coefficient of the [Ru(bpz)$_3$]$^{2+}$ ion and the optical path length of the reacting solution. Saturation of the initial reaction rate corresponds to that of the light intensity absorbed in the [Ru(bpz)$_3$]$^{2+}$ solution. The solid line in Fig. 3 is a calculated one according to Eq. 4 with γ=5.3×10^4 dm^3 mol^{-1} and I_0=1.85×10^{-7} mol dm^{-3} s^{-1}. The light intensity absorbed in a reacting solution containing 5.0×10^{-5} mol dm^{-3} of the [Ru(bpz)$_3$]$^{2+}$ ion was determined to be (1.76±0.09)×10^{-7} mol dm^{-3} s^{-1} by using a tris(oxalato)-ferrate(III) actinometer. This value is very close to the mean value of the initial rates of reaction obtained from the decay of ascorbic acid and the formation of hydrogen peroxide at high concentrations of ascorbic acid ((1.8±0.4)×10^{-7} mol dm^{-3} s^{-1}).

pH Dependence. The effect of pH on the reaction rate for the [Ru(bpz)$_3$]$^{2+}$ system was studied at 30 °C, pH 3.9—5.6 (a 0.10 mol dm^{-3} acetate buffer), and I=0.10 mol dm^{-3} (NaClO$_4$) in an air-saturated solution. The reaction rate increased with increasing pH at the initial concentration of ascorbic acid, [AsA]$_i$= 1.00×10^{-3} mol dm^{-3}. The acid-dissociation constant of the *[Ru(bpz)$_2$(Hbpz)]$^{3+}$ ion is 10^{-2} mol dm^{-3},[3b] indicating that the predominant species is the *[Ru(bpz)$_3$]$^{2+}$ ion at pH 3.9—5.6. The pH dependence can be explained by considering the following acid-base equilibrium of ascorbic acid (H$_2$A):

$$H_2A \rightleftharpoons HA^- + H^+ \quad [K_{a1} = 9.16 \times 10^{-5} \text{ mol dm}^{-3}].^{13)} \quad (5)$$

The molar fraction of the HA$^-$ ion is represented by

$$[HA^-]/([H_2A] + [HA^-]) = (1 + [H^+]/K_{a1})^{-1}. \quad (6)$$

Plots of the initial reaction rate vs. $(1+[H^+]/K_{a1})^{-1}$ was linear with a zero intercept (Fig. 4), indicating that the reacting species is the HA$^-$ ion. At a 1.00×10^{-2} mol dm^{-3} ascorbic acid the reaction rate was independent of pH, consistent with the results that the initial reaction rate is independent of the concentrations of ascorbic acid at more than 1.00×10^{-2} mol dm^{-3}.

The effect of the ionic strength on the initial reaction rate for the [Ru(bpz)$_3$]$^{2+}$ system, in which the reaction rate decreases with an increase in the ionic strength, also supports the idea that the reactive species are oppositely charged (Table 1).

Quenching of Excited State of Ruthenium(II) Complexes by Ascorbic Acid and Molecular Oxygen. The metal-to-ligand excited triplet state of [Ru(bpy)$_3$]$^{2+}$ and [Ru(bpz)$_3$]$^{2+}$ ions is quenched by ascorbic acid and molecular oxygen through an oxidation-reduction mechanism.[3,14-16] We also measured the luminescence quenching by ascorbic acid and molecular oxygen of *[Ru(bpy)$_2$(bpz)]$^{2+}$ and *[Ru(bpy)(bpz)$_2$]$^{2+}$ ions along with *[Ru(bpy)$_3$]$^{2+}$ and *[Ru(bpz)$_3$]$^{2+}$ ions under our experimental conditions.

Stern–Volmer plots for quenching by ascorbic acid are shown in Fig. 5. The rate constants of the quenching by ascorbic acid and molecular oxygen (k_{q1} and k_{q2}, respectively) were obtained by the use of the lifetime for the excited triplet state of ruthenium(II) complexes (Table 2). The lifetime of the *$[Ru(bpy)(bpz)_2]^{2+}$ ion in an aqueous solution is unknown and was therefore estimated from the value in propylene carbonate, compared with data for the *$[Ru(bpy)_2(bpz)]^{2+}$ ion in aqueous and propylene carbonate solutions.[7,9] The lifetime of the *$[Ru(bpy)_2(bpz)]^{2+}$ ion at pH 4.6 (a 0.1 mol dm^{-3} acetate buffer) was estimated from the ratio of the luminescence intensity at pH 4.6 to that in H_2O. The lifetime of the *$[Ru(bpy)_2(bpz)]^{2+}$ ion in H_2O has been reported to be 88 ns.[9]

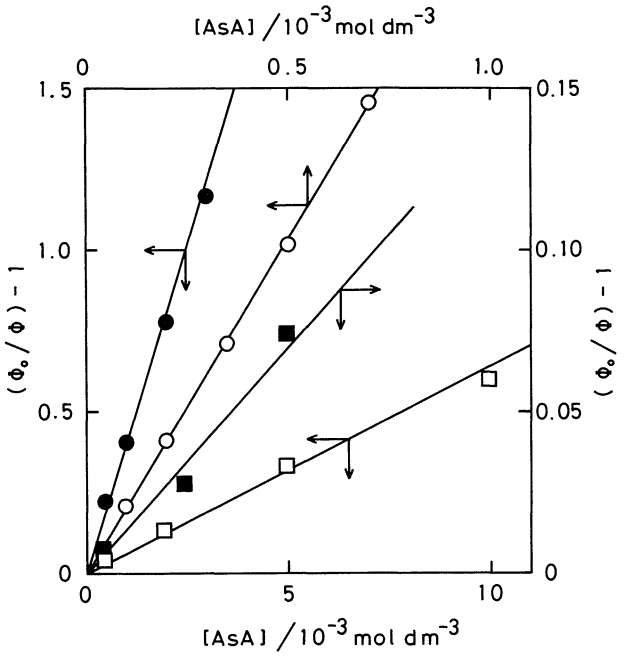


Fig. 5. Stern–Volmer plots for the luminescence quenching of the excited-triplet states of the ruthenium(II) complexes by ascorbic acid at 30 °C, pH 4.60, and I=0.10 mol dm^{-3} under an argon atmosphere. ○: $[Ru(bpz)_3]^{2+}$, ●: $[Ru(bpy)(bpz)_2]^{2+}$, □: $[Ru(bpy)_2(bpz)]^{2+}$, and ■: $[Ru(bpy)_3]^{2+}$.

Mechanism of Reaction. The obtained results are accounted for by the following reaction mechanism:

$$Ru(II) \xrightarrow{h\nu} *Ru(II) \qquad I_a\phi \quad (7)$$

$$*Ru(II) \longrightarrow Ru(II) \qquad k_0 \quad (8)$$

$$*Ru(II) + HA^- \longrightarrow Ru(I) + A^{\cdot-} + H^+ \qquad k'_{q1} \quad (9)$$

$$[HA\cdot \rightleftarrows H^+ + A^{\cdot-} \quad pK_a = -0.45]^{17)}$$

$$*Ru(II) + O_2 \longrightarrow Ru(III) + O_2^{\cdot-} \qquad k'_{q2} \quad (10)$$

$$[HO_2 \rightleftarrows H^+ + O_2^{\cdot-} \quad pK_a = 4.8]^{18)}$$

$$Ru(III) + HA^- \longrightarrow Ru(II) + A^{\cdot-} + H^+ \qquad k_1 \quad (11)$$

$$Ru(I) + O_2 \longrightarrow Ru(II) + O_2^{\cdot-} \qquad k_2 \quad (12)$$

$$2A^{\cdot-} \xrightarrow{H^+} A + HA^- \qquad k_3 \quad (13)$$

$$2O_2^{\cdot-} \text{ (and/or } HO_2) \longrightarrow H_2O_2 + O_2 \qquad k_4 \quad (14)$$

$$HA^- + O_2^{\cdot-} \text{ (and/or } HO_2) \longrightarrow A^{\cdot-} + H_2O_2 \qquad k_5 \quad (15)$$

The reaction between the ascorbate radical and molecular oxygen might be very slow, on the basis of their redox potentials ($E^0(A/A^{\cdot-})$=−0.14 V and $E^0(O_2/O_2^{\cdot-})$=−0.16 V).[19,20] When the decays of the ascorbate radical and the superoxide anion are very fast and the steady state assumption for *Ru(II), Ru(III), and Ru(I) is adopted, the following rate law can be derived:

$$-\frac{d[AsA]}{dt} = \frac{d[H_2O_2]}{dt} = \frac{(k'_{q1}[AsA] + k'_{q2}[O_2])I_a\phi}{k_0 + k'_{q1}[AsA] + k'_{q2}[O_2]}. \quad (16)$$

The rate constants of Reactions 11—15 have been reported: k_1=1.7×10^9 dm^3 mol^{-1} s^{-1} ($[Ru(bpy)_3]^{3+}$),[21] k_2=5.8×10^8 dm^3 mol^{-1} s^{-1} ($[Ru(bpz)_3]^+$),[22] k_3=1×10^8 dm^3 mol^{-1} s^{-1} (at pH 4.6),[23] k_4=9×10^7 dm^3 mol^{-1} s^{-1} (at pH 4.6),[24] and k_5=8×10^5 dm^3 mol^{-1} s^{-1} (at pH 4.6).[25] Then, Eq. 16 can be rewritten as

Table 2. Rate Constants of the Luminescence Quenching by Ascorbic Acid and Molecular Oxygen of the Excited-Triplet State of Ruthenium(II) Complexes at 30 °C, pH 4.60, and I=0.10 mol dm^{-3}

Complex	k_{q1}(AsA) dm^3 mol^{-1} s^{-1}	$k_{q2}(O_2)$ dm^3 mol^{-1} s^{-1}	$E^0(Ru^{*2+/+})$[a] V	$E^0(Ru^{3+/*2+})$[a] V
*$[Ru(bpz)_3]^{2+}$	(2.0±0.1)×10^9 3.0×10^9[b]	(3.8±0.1)×10^8 5.5×10^8[c]	1.64 (1.64)	0.14 (0.08)
*$[Ru(bpy)(bpz)_2]^{2+}$	(1.5±0.1)×10^9	(5.3±0.3)×10^8	(1.42)	(−0.03)
*$[Ru(bpy)_2(bpz)]^{2+}$	(2.3±0.1)×10^9	(2.3±0.1)×10^9	(1.28)	(−0.11)
*$[Ru(bpy)_3]^{2+}$	(2.2±0.6)×10^7 2×10^7[d]	(3.4±0.2)×10^9 3.3×10^9[e]	0.84 (0.78)	−0.84 (−0.87)

a) Ref. 2. The value in parentheses is in acetonitrile. b) At pH 5—10. Ref. 16. c) In H_2O. Ref. 16. d) In H_2O. Ref. 15. e) In H_2O. Ref. 14.

$$\frac{1}{V_i} = \frac{1}{I_a\phi} + \frac{k_0}{(k'_{q1}[AsA] + k'_{q2}[O_2])I_a\phi}, \quad (17)$$

where V_i denotes the initial rate of reaction. Since the condition $k'_{q1}[AsA] \gg k'_{q2}[O_2]$ holds for the $[Ru(bpz)_3]^{2+}$ and $[Ru(bpy)(bpz)_2]^{2+}$ systems (see Table 2), Eq. 17 can be simplified to

$$\frac{1}{V_i} = \frac{1}{I_a\phi} + \frac{k_0}{k'_{q1}I_a\phi} \cdot \frac{1}{[AsA]}. \quad (18)$$

Plots of V_i^{-1} vs. $[AsA]^{-1}$ were linear, as is shown in Fig. 6. The values of $I_a\phi$ and k'_{q1}/k_0 were, respectively, obtained from the intercept and slope of this line. The values of k'_{q1} are $(1.0\pm0.3)\times10^9$ dm^3 mol^{-1} s^{-1} and $(7.7\pm1.2)\times10^8$ dm^3 mol^{-1} s^{-1} for $[Ru(bpz)_3]^{2+}$ and $[Ru(bpy)(bpz)_2]^{2+}$, respectively. The value of $I_a\phi$ for the $[Ru(bpz)_3]^{2+}$ system ($(2.0\pm0.5)\times10^{-7}$ mol dm^{-3} s^{-1}) is in agreement with that obtained from an experiment using a tris(oxalato)ferrate(III) actinometer ($(1.76\pm0.09)\times10^{-7}$ mol dm^{-3} s^{-1}), suggesting that the quantum yield ϕ is ca. 1.

In continuous photolysis, half of the ascorbic acid is consumed and half of the hydrogen peroxide is produced against the photo-excited state of the ruthenium(II) complexes. The values of $2k'_{q1}$ and $2k'_{q2}$, therefore, correspond to those of k_{q1} and k_{q2} for luminescence quenching of the excited state of the ruthenium(II) complexes, respectively. The former values are in good agreement with the latter ones, indicating that the above-mentioned mechanism is reasonable.

From luminescence-quenching experiments for the $*[Ru(bpy)_2(bpz)]^{2+}$ ion, the value of k_{q1} is nearly equal to that of k_{q2}. Therefore, Eq. 16 for the $[Ru(bpy)_2(bpz)]^{2+}$ system is simplified to

$$\frac{1}{V_i} = \frac{1}{I_a\phi} + \frac{k_0}{k'_{q1}([AsA] + [O_2])I_a\phi}. \quad (19)$$

Plots of V_i^{-1} vs. $([AsA]+[O_2])^{-1}$ were linear and the values of $I_a\phi$ and k'_{q1}/k_0 were, respectively, obtained from the intercept and slope of this straight line (Fig. 7): $I_a\phi=(1.7\pm0.8)\times10^{-7}$ mol dm^{-3} s^{-1} and $k'_{q1}=k'_{q2}=(3.1\pm1.9)\times10^9$ dm^3 mol^{-1} s^{-1}.

In the $[Ru(bpy)_3]^{2+}$ system the condition $k'_{q2}[O_2] \gg k'_{q1}[AsA]$ holds (see Table 2). Therefore, the reaction rate should therefore be independent of the concentrations of ascorbic acid, when Reaction 11 is very fast:

$$V_i = \frac{k'_{q2}[O_2]I_a\phi}{k_0 + k'_{q2}[O_2]}. \quad (20)$$

The initial reaction rate was, however, dependent on the concentrations of ascorbic acid and reached a constant value at high concentrations of ascorbic acid. A linear dependence of the initial of reaction rate on the concentrations of ascorbic acid for this system has already been reported by Kurimura et al.[10] They have suggested that the reaction rate must reach a constant value at high concentrations of ascorbic acid, and pro-

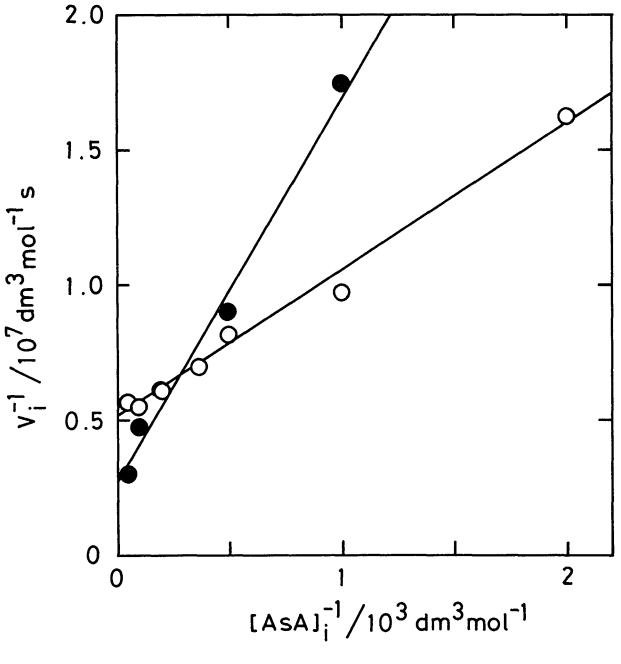


Fig. 6. Plots of V_i^{-1} vs. $[AsA]_i^{-1}$ for the photo-induced oxidation of ascorbic acid by molecular oxygen in the presence of the ruthenium(II) complexes. Experimental conditions are the same as in Fig. 1. ○: $[Ru(bpz)_3]^{2+}$ and ●: $[Ru(bpy)(bpz)_2]^{2+}$.

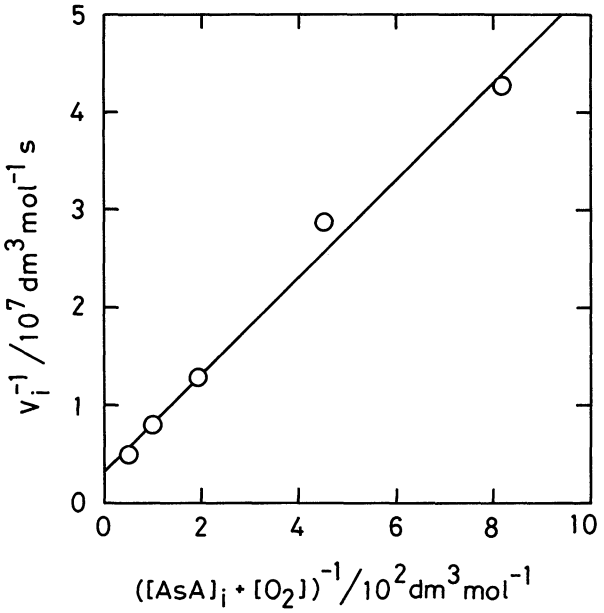


Fig. 7. Plots of V_i^{-1} vs. $([AsA]_i+[O_2])^{-1}$ for the photo-induced oxidation of ascorbic acid by molecular oxygen in the presence of $[Ru(bpy)_2(bpz)]^{2+}$ ions. Experimental conditions are the same as in Fig. 1.

posed a mechanism in which Reaction 11 competes with the back reaction for oxidative quenching by oxygen (Reaction 21):

$$[Ru(bpy)_3]^{3+} + O_2^{\cdot-} \longrightarrow [Ru(bpy)_3]^{2+} + O_2. \quad (21)$$

The rate constant of Reaction 21 has been reported to be 1.4×10^{10} dm^3 mol^{-1} s^{-1}.[26] The formation of hydrogen peroxide suggests that the reaction of superoxide ions with ascorbate and/or the disproportionation of superoxide ions must occur competitively in Reactions 11 and 21. At high concentrations of ascorbic acid, where the reaction rate is indenpendent of the concentrations of ascorbic acid, the initial rate can be simplified, as in Eq. 20. The value of k'_{q2}, obtained from air- and oxygen-saturated solutions, is $(3.0\pm 2.0)\times10^9$ dm^3 mol^{-1} s^{-1}, but has a large error due to the use of only two determinations.

Difference in Mechanisms of Reaction for $[Ru(bpy)_x(bpz)_{3-x}]^{2+}$ Ions. Hydrogen peroxide was efficiently produced during the photo-induced oxidation of ascorbic acid by molecular oxygen catalyzed by $[Ru(bpy)_x(bpz)_{3-x}]^{2+}$ (x=0—3) ions. The $[Ru(bpz)_3]^{2+}$, $[Ru(bpy)_2(bpz)]^{2+}$, and $[Ru(bpy)(bpz)_2]^{2+}$ ions are superior to the $[Ru(bpy)_3]^{2+}$ ion for the formation of hydrogen peroxide. This can be explained by a difference in the quenching rate constants of the excited triplet state of these complexes by ascorbic acid and molecular oxygen. Under the present experimental conditions k'_{q1}[AsA] is larger than k'_{q2}[O_2] for the $[Ru(bpz)_3]^{2+}$, $[Ru(bpy)(bpz)_2]^{2+}$, and $[Ru(bpy)_2(bpz)]^{2+}$ ions, indicating that the reductive quenching process is predominant (Scheme 1). On the other hand, k'_{q2}[O_2] is larger than k'_{q1}[AsA] for the $[Ru(bpy)_3]^{2+}$ ion, in which the oxidative quenching process is predominant (Scheme 2). For the $[Ru(bpy)_2(bpz)]^{2+}$ ion the value of k_{q1} is the same as that of k_{q2}. Therefore, the change in the reaction mechanisms from the oxidative to reductive might occur in the $[Ru(bpy)_2(bpz)]^{2+}$ complex. The redox potentials of couples Ru^{3+}/Ru^{*2+} and Ru^{*2+}/Ru^{+} have been reported, as given in Table 2. The excited triplet state of the $[Ru(bpy)_2(bpz)]^{2+}$ ion is considered to be in the metal-to-ligand charge transfer (MLCT) state of $[Ru^{III}(bpy)_2(bpz^{\cdot-})]^{2+}$, where an electron is localized in the bpz ligand.[7,8] The value of E^0 ($Ru^{3+/*2+}$) for the $*[Ru(bpy)_3]^{2+}$ ion is much lower than that for the other ruthenium(II) complexes containing the bpz ligand, indicating that the $bpz^{\cdot-}$ ligand is more stable during electron transfer than is the $bpy^{\cdot-}$ ligand. Therefore, the electron of the $bpz^{\cdot-}$ ion in the MLCT state of the ruthenium(II) complexes might not be easily transferred, being compared with the $bpy^{\cdot-}$ ion in the $[Ru(bpy)_3]^{2+}$ system. The order of k_{q1} is almost parallel to that of the redox potential, $E^0(Ru^{*2+/+})$, and the order of k_{q2} is inversely dependent on $E^0(Ru^{3+/*2+})$. However, the quenching reaction between Ru(II) complexes, except for the $*[Ru(bpy)_3]^{2+}$ ion and ascorbate, is almost of a diffusion- controlled rate and, therefore, the difference in the rate is much smaller than that expected from the difference in the redox potentials. This trend is similar to the oxidative quenching reaction by molecular oxygen. For example, though the quenching rate constants (k_{q1} and k_{q2}) for the $[Ru(bpy)_2(bpz)]^{2+}$ system are the same, the values of the free energy change of the reaction are quite different: -0.60 eV (1 eV=9.65×10^4 J mol^{-1}) for reductive quenching by ascorbate ($E^0(HA^{\cdot}/HA^-)$= 0.68 V)[19] and 0.05 eV for oxidative quenching by O_2 ($E^0(O_2/O_2^{\cdot-})=-0.16$ V).[20]

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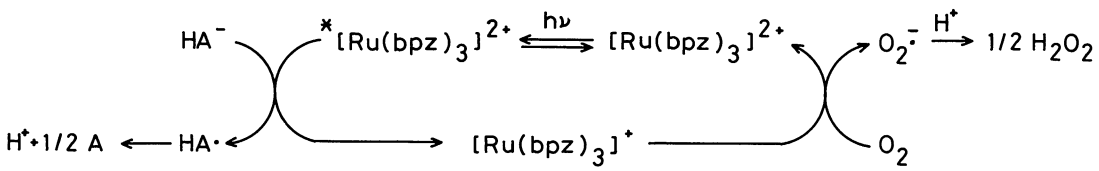
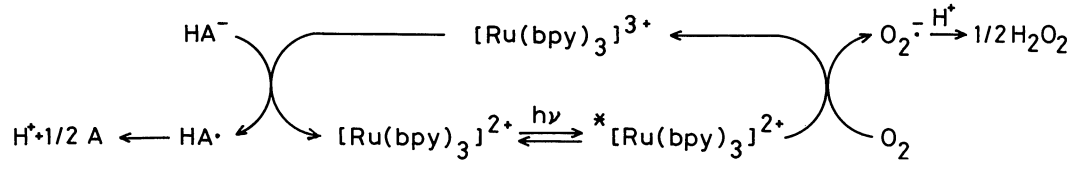


Scheme 1.



Scheme 2.

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