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Light-induced Electron-transfer Reactions.
Part 4. Kinetics of Formation of Hydrogen Peroxide and Acetone by Irradiation with Visible Light of Aqueous Solutions Containing Tris(2,2′-bipyridine)-ruthenium(II) Complex, 2-Propanol and Oxygen

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Abstract

Hydrogen peroxide and acetone are formed by the light-catalyzed reaction of tris(2,2′-bipyridine)-ruthenium(II) complex ($[Ru(bpy)_3]^{2+}$; bpy = 2,2′-bipyridine) in an aqueous diluted sulfuric acid solutions containing 2-propanol and oxygen. The overall reaction is $(CH_3)_2CHOH + O_2 \rightarrow H_2O_2 + (CH_3)_2CO$. The amounts of hydrogen peroxide and acetone formed increase with increasing concentrations of $[Ru(bpy)_3]^{2+}$, oxygen, 2-propanol, and hydrogen ion, and with increasing the amount of incident light intensity irradiated. No formation of hydrogen peroxide and acetone is found in the dark or in the absence of either $[Ru(bpy)_3]^{2+}$, 2-propanol, or oxygen. The formation of hydrogen peroxide and acetone is greatly retarded by the presence of copper(II) ion. A chain mechanism of reaction is presented to account for these results obtained.

Introduction

In a previous study we found that considerable amounts of hydrogen peroxide were formed by irradiation with visible light of aqueous acidic solutions containing tris(2,2′-bipyridine)ruthenium(II), oxalic acid, manganese(II), and oxygen [1]. In the present work it was found that acetone as well as hydrogen peroxide were formed by irradiation with visible light of the aqueous diluted sulfuric acid solutions containing the tris(2,2′-bipyridine)ruthenium(II) complex ion ($[Ru(bpy)_3]^{2+}$), 2-propanol, and oxygen. The overall reaction (or stoichiometric equation) is shown in eqn. (1).

$$(CH_3)_2CHOH + O_2 \longrightarrow H_2O_2 + (CH_3)_2CO \qquad (1)$$

The light-induced electron-transfer reactions with $[Ru(bpy)_3]^{2+}$ would be of interest in the context of a solar-energy conversion system including the complexed mechanisms of reaction.

Experimental

Chemicals

The $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ is the same as described in the previous paper [1]. 2-Propanol of reagent grade was distilled. Deinonized water was further distilled with and without addition of permanganate ion in a glass still. All other chemicals used were of guaranteed reagent grade of Wako Pure Chemical Co.

The concentration of oxygen dissolved in solutions was adjusted by the saturation of air, pure oxygen, or a mixture of air and oxygen with nitrogen gas and by bubbling them through the reaction solution.

Procedure

The procedures are essentially the same as in the previous work [1]. The concentration of hydrogen peroxide formed was measured by using polarography at −1.30 V *vs.* SCE (saturated calomel electrode) at 25 °C in acetate buffer of pH 4.8 (0.05 M each of acetic acid and sodium acetate, where M = mol dm^{-3} throughout this paper) and 0.01% gelatine. The concentration of acetone formed was determined by using gas chromatography. The concentration of the $[Ru(bpy)_3]^{2+}$ ion was determined spectrophotometrically by using the molar absorption coefficient of 1.4×10^4 M^{-1} cm^{-1} at 452 nm. The luminescence of the photoexcited species $[Ru(bpy)_3]^{2+*}$ was measured by using a Hitachi model 850 spectrofluorometer at an excitation energy of 452 nm.

Results and Discussion

The concentration of the $[Ru(bpy)_3]^{2+}$ ion did not change during the light-induced reactions; the ion acted as a catalyst. No appreciable formation of acetone or hydrogen peroxide was found in the absence of either of light, $[Ru(bpy)_3]^{2+}$, 2-propanol, or oxygen.

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Stoichiometry

The stoichiometry was determined after removal of the $[Ru(bpy)_3]^{2+}$ ion from the reacting solution at appropriate intervals during the reaction. The concentration of H_2O_2 formed was determined polarographically. The reaction solution was distilled at 60–80 °C in order to collect acetone formed; then the concentration of acetone was determined by using a Hitachi model 063 gas chromatograph. The result was $[H_2O_2]_{formed}/[(CH_3)_2CO]_{formed} = 1.0 \pm 0.1$ in an average of ten duplicate runs. Therefore, the stoichiometry is as shown in eqn. (1).

Rate Law

Under all the conditions employed, the concentrations of both H_2O_2 and $(CH_3)_2CO$ formed increased linearly with increasing reaction time (t), which corresponds to the time of irradiation of light (see Fig. 1). Therefore, the rate law could be given by eqn. (2).

$$[H_2O_2]_{formed} = [(CH_3)_2CO]_{formed} = k_{obs}t \qquad (2)$$

When some hydrogen peroxide was added to the reaction solution before initiating the reaction, the slope of the plots $[H_2O_2]_{formed}$ *vs.* t did not change at all (see Fig. 1). Thus, the hydrogen peroxide did not participate in the light-induced chain reaction, and does not decompose during the reaction.

Effect of Light Intensity

When an acidic solution containing the $[Ru(bpy)_3]^{2+}$ ion, 2-propanol, and molecular oxygen was irradiated with visible light, the amount of hydrogen peroxide formed increased with the incident light intensity. The results are given in Table I.

Effect of Oxygen Concentration

In Table II are shown the results obtained with different pressures of oxygen gas in the reacting solution. It was found that the concentration of hydrogen peroxide formed increased with increasing oxygen pressures in the reacting solution.

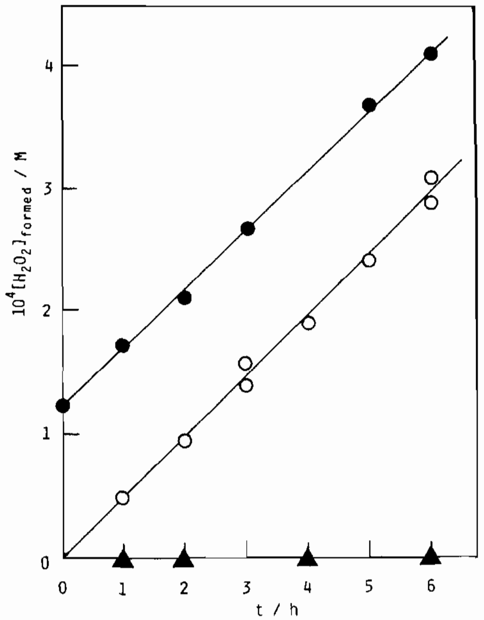

Fig. 1. Dependence of reaction time (t) on the formation of hydrogen peroxide. Conditions for plots ○ are the same as in two lamps of Table I. Hydrogen peroxide of 1.2×10^{-4} M (●) or copper(II) sulfate of 1×10^{-3} M (▲) was added to the reaction solution before initiating the photo-catalyzed reaction; the other conditions are the same as in plots ○.

Effect of Concentration of Tris(2,2'-bipyridine)-ruthenium(II)

The concentration of hydrogen peroxide formed increased with increasing concentrations of the $[Ru(bpy)_3]^{2+}$ ion in the reaction solution (Table III).

Effect of 2-Propanol

Unless 2-propanol was present in the reacting solutions, no hydrogen peroxide and acetone were formed at all. The rate of formation of hydrogen peroxide (k_{obs} in eqn. (2)) increased linearly with increasing 2-propanol concentration up to about 3 M; the rate became almost constant at the range 4–8 M (see Fig. 2).

TABLE I. Effect of Light Intensity[a]

t (h)	$10^4\ [H_2O_2]_{formed}$ (M)				
	Dark[b]	Room light	Two lamps	Three lamps	Four lamps
0	0	0	0	0	0
1		0.4	0.47	0.3	0.75
2	0	0.79	0.95	1.0	1.0
3		1.25	1.4		2.0
4	0		1.9	2.1	2.5
5			2.4		2.9
6	0	2.3	3.1	3.1	3.6

[a] Conditions: 5×10^{-5} M in $[Ru(bpy)_3]Cl_2$, 0.5 M in H_2SO_4, and 4 M $(CH_3)_2CHOH$; 25 °C; air-saturated; with varied intensities of light. [b] The reaction vessel was covered with a black plastic adhesive tape.

TABLE II. Effect of the Oxygen Pressure[a]

t (h)	10^4 $[H_2O_2]_{formed}$ (M)					
	N_2-saturated	N_2/Air = 1	Air-saturated	O_2/N_2 = 1	O_2/Air = 1	O_2-saturated
0	0	0	0	0	0	0
1		0.32	0.47		0.58	0.67
2	0	0.62	0.95	1.05	1.3	1.4
3		0.89	1.4	1.6	1.9	1.95
4	0	1.02	1.9	2.3	2.5	2.6
5	0		2.4	2.6	3.2	3.1

[a] Conditions as in Table I; except for irradiation with two lamps and varied pressures of oxygen, *i.e.*, varied concentrations of oxygen dissolved in the reacting solution.

TABLE III. Effect of Concentration of $[Ru(bpy)_3]^{2+}$ [a]

t (h)	10^4 $[H_2O_2]_{formed}$ (M) at concentration 10^5 $[Ru(bpy)_3]^{2+}$ (M)						
	0	0.056	0.12	0.59	1.1	5.3	11
0	0	0	0	0	0	0	0
1		0.13	0.21	0.36	0.24	0.47	0.25
2	0	0.3	0.27	0.62	0.72	0.95	1.2
3		0.46	0.63	0.91	0.92	1.4	1.9
4	0	0.72	1.05	1.1	1.1	1.9	2.5
5		0.9	1.1			2.4	2.9
6	0		1.3	2.0	1.8	3.1	3.6

[a] Conditions as in Table I; except for the various concentrations of the $[Ru(bpy)_3]^{2+}$ ion and for irradiation with two lamps.

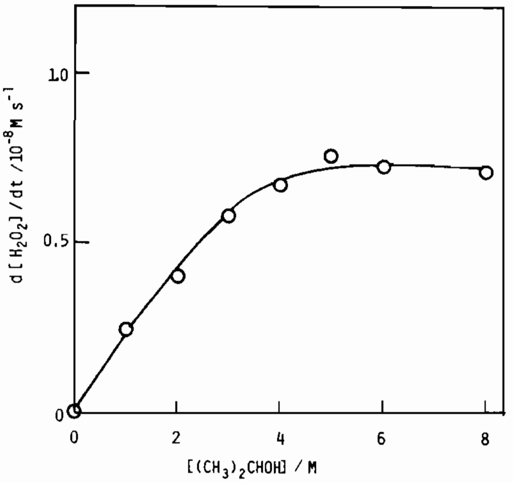

Fig. 2. Effect of concentrations of 2-propanol on the rate of formation of hydrogen peroxide. Conditions as in two lamps of Table I, except for various concentrations of $(CH_3)_2$-CHOH.

Effect of Acidity

When the concentration of sulfuric acid was varied, the rate of formation of hydrogen peroxide increased greatly with increasing acid concentration. Results are given in Fig. 3.

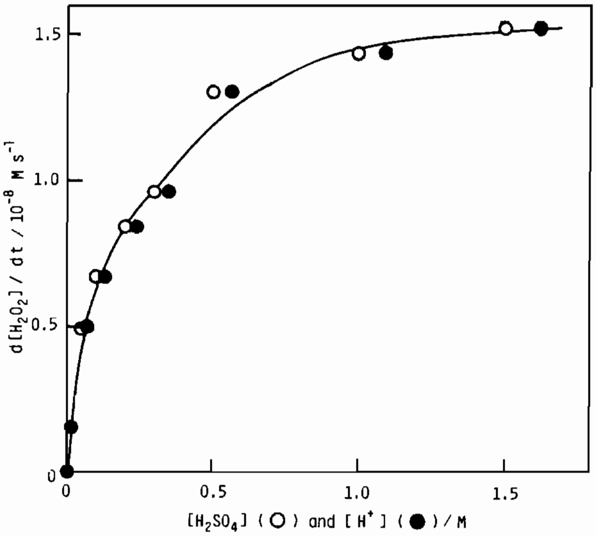

Fig. 3. Effect of hydrogen-ion concentration on the rate of formation of hydrogen peroxide. Conditions as in two lamps of Table I, except for various concentrations of hydrogen ion. We calculated the hydrogen ion concentrations using the equilibria $H_2SO_4 \rightleftarrows H^+ + HSO_4^-$ and $HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ ($pK_1 = 1.99$).

Effect of Copper(II) ion

In the presence of 0.001 M copper(II) sulfate under the same conditions as in Table II, no hydrogen peroxide was formed at any time during the reaction (see plots ▲ in Fig. 1). Thus the copper(II) ion is a strong retarder of this reaction.

Luminescence of [Ru(bpy)$_3$]$^{2+*}$

For clarification of the electron-transfer step in the initial reaction, the luminescence of the [Ru(bpy)$_3$]$^{2+*}$ ion was measured in pure water and in solutions of various constituents in the presence and in the absence of oxygen. The luminescence was quenched greatly by the presence of oxygen and also by the presence of the copper(II) ion. However, it was not appreciably affected by the presence of 2-propanol and hydrogen peroxide. Thus, the initial reaction could be only a quenching reaction of the [Ru(bpy)$_3$]$^{2+*}$ ion with molecular oxygen O_2 (eqn. (5)).

Mechanisms of Reaction

The photoexcited species [Ru(bpy)$_3$]$^{2+*}$ did not react with 2-propanol or with hydrogen peroxide, but it did react with the molecular oxygen dissolved in solutions. No appreciable formation of hydrogen peroxide and acetone was found in the absence of either light, oxygen, tris(2,2′-bipyridine)ruthenium(II), or 2-propanol. Further, the $[H_2O_2]_{formed}$ and $[(CH_3)_2CO]_{formed}$ in eqn. (2) increased with increasing incident light intensity, oxygen pressure, [Ru(bpy)$_3$]$^{2+}$, 2-propanol, and acidity. Consequently, we could assume the following mechanism of reaction (eqns. (3)–(10)) to account for the results obtained. The overall reaction is thus written by eqn. (11) which is essentially the same as in the stoichiometric eqn. (1).

$$[Ru(bpy)_3]^{2+} + h\nu \xrightarrow{I_a} [Ru(bpy)_3]^{2+*} \tag{3}$$

$$[Ru(bpy)_3]^{2+*} \xrightarrow{k_0} \begin{cases} [Ru(bpy)_3]^{2+} + h\nu' \text{ (emission)} \\ [Ru(bpy)_3]^{2+} + \Delta \text{ (thermal energy)} \end{cases} \tag{4}$$

$$[Ru(bpy)_3]^{2+*} + O_2 + H^+ \xrightarrow{k_q} [Ru(bpy)_3]^{3+} + HO_2 \tag{5}$$

$$(CH_3)_2CHOH + [Ru(bpy)_3]^{3+} \xrightarrow{k_6} (CH_3)_2\dot{C}OH + H^+ + [Ru(bpy)_3]^{2+} \tag{6}$$

$$(CH_3)_2\dot{C}OH + [Ru(bpy)_3]^{3+} \xrightarrow{k_7} (CH_3)_2CO + H^+ + [Ru(bpy)_3]^{2+} \tag{7}$$

$$(CH_3)_2\dot{C}OH + O_2 \xrightarrow{k_8} (CH_3)_2CO + HO_2 \tag{8}$$

$$HO_2 + H^+ + [Ru(bpy)_3]^{2+} \xrightarrow{k_9} H_2O_2 + [Ru(bpy)_3]^{3+} \tag{9}$$

$$HO_2 + (CH_3)_2CHOH \xrightarrow{k_{10}} H_2O_2 + (CH_3)_2\dot{C}OH \tag{10}$$

Overall reaction:

$$(CH_3)_2CHOH + O_2 \xrightarrow[([Ru(bpy)_3]^{2+})]{h\nu} H_2O_2 + (CH_3)_2CO \tag{11}$$

The rate constants k_0, k_q, and k_8 are 1.52×10^6 s^{-1} [2], 5.5×10^9 M^{-1} s^{-1} [3], and 4.2×10^9 M^{-1} s^{-1} [4], respectively. All the reactions except for reaction (6) will be fast. The concentration of hydrogen peroxide formed reached constant at about 4–5 M of 2-propanol (see Fig. 2). When the concentration of 2-propanol is so large that the [Ru(bpy)$_3$]$^{3+}$ ion formed could disappear rapidly by the reaction (6), and when reactions (8)–(10) occur successively, the concentration of hydrogen peroxide formed would be expressed as follows.

$$d[H_2O_2]/dt = 2k_q[[Ru(bpy)_3]^{2+*}][O_2][H^+] = \frac{2k_q I_a \Phi [O_2][H^+]}{k_0 + k_q[O_2][H^+]} \tag{12}$$

$$\frac{dt}{d[H_2O_2]} = \frac{1}{2I_a\Phi} + \frac{k_0}{2k_q I_a \Phi [O_2][H^+]} \tag{13}$$

where I_a indicates the absorbed-light intensity, and Φ indicates the efficiency of the photoexcited species; thus, the term $I_a\Phi$ is the formation rate of [Ru(bpy)$_3$]$^{2+*}$ in eqn. (3). Equation 13 indicates that the plots of $dt/d[H_2O_2]$ *vs.* $(P_{O_2})^{-1}$ or $dt/d[H_2O_2]$ *vs.* $[H^+]^{-1}$ are rectilinear, having intercept and slope. These plots are obtained by using the data in Table II and Fig. 3, and are given in Figs. 4 and 5.

The retardation effect of the copper(II) ion against the formation of hydrogen peroxide and acetone could be due to the competitive quenching of [Ru(bpy)$_3$]$^{2+*}$ with O_2 and Cu^{2+}.

$$[Ru(bpy)_3]^{2+*} + Cu^{2+} \xrightarrow{k_{14}} [Ru(bpy)_3]^{3+} + Cu^+ \tag{14}$$

($k_{14} = 6.2 \times 10^7$ M^{-1} s^{-1} [5])

Moreover, the rate of reaction between [Ru(bpy)$_3$]$^{3+}$ and Cu^+ would be so fast that it could compete with reactions (6) and (7). Accordingly, the copper(II) ion could be a strong retarder of the light-catalyzed reactions presented in eqns. (3)–(10).

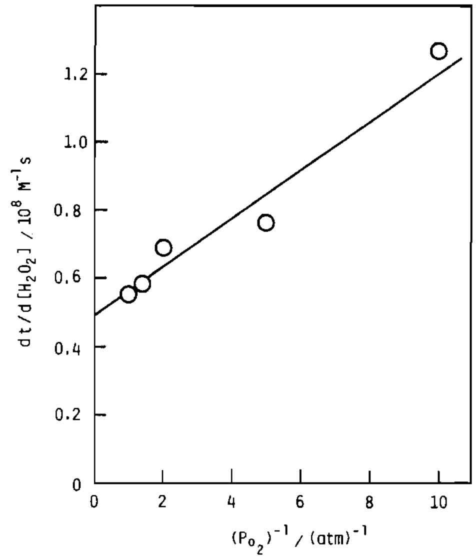

Fig. 4. Plots of dt/d[H_2O_2] *vs.* $(P_{O_2})^{-1}$ (eqn. (13)). P_{O_2} indicates the oxygen pressure (1 atm = 101 325 Pa). Conditions as in Table II.

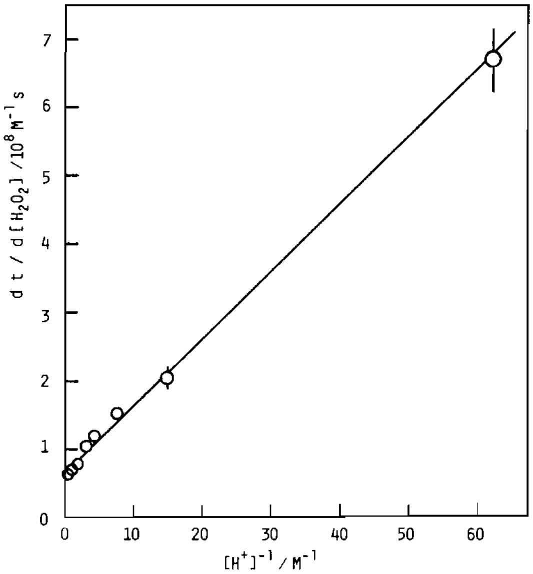

Fig. 5. Plots of dt/d[H_2O_2] *vs.* $[H^+]^{-1}$ (eqn. (13)). Conditions as in Fig. 3.

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