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The Decomposition of Hydrogen Peroxide with Metal Complexes. I. The Catalytic Decomposition of Hydrogen Peroxide by the Ammine-Copper(II) Complex Ions in an Aqueous Solution

Katumitu Hayakawa and Sumio Nakamura

Department of Chemistry, Faculty of Science, Kagoshima University, Kamoike-cho, Kagoshima 890

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The catalytic decomposition of hydrogen peroxide by the ammine-copper(II) complex ions has been studied using kinetic measurements, UV and visible spectroscopy, electron-spin resonance spectroscopy, and polarography. It was found that there were two reaction paths in the catalytic decomposition of hydrogen peroxide. In the first case, a linear part was observed in the plot of the amount of oxygen evolved *vs.* time. In this case, a brown intermediate was formed which was later found to be a diamagnetic peroxo-copper complex and to contain some of the stable oxygen anion radical just after the mixing of the reactants. The activation energy of the reaction was found to be 23 ± 1 kcal mol^{-1}. In the second case, no linear part was observed in the kinetic curve. In this case, the reaction had a reaction order in hydrogen peroxide varying from the first- to the second-order depending on the initial concentrations of the reactants. The nature of the brown compound and the active species of the reaction is discussed.

Since it was learned that the transition metal-ammine complexes have an enzyme-like activity in the decomposition of hydrogen peroxide,[1] many kinetic studies of the catalytic decomposition of hydrogen peroxide have been made for many transition-metal complexes.[2–10] On the other hand, electron spin resonance (ESR) studies have clarified the formation of complexed radical species in the reactions of the Ti^{III}–H_2O_2 system,[11–13] the Ce^{IV}–H_2O_2 system,[14] and the VO^{2+}–H_2O_2 system.[15] However, in the catalytic decomposition of hydrogen peroxide by the ammine-copper(II) complex ions, there is little information regarding such a radical intermediate and the rate of the reaction.[8,10]

The object of this paper is to clarify the nature and role of the brown intermediate formed in the catalytic decomposition of hydrogen peroxide by the ammine-copper(II) complex ions and to report a new reaction path without the brown intermediate. The active species of the ammine-copper(II) complex ions in the decomposition of hydrogen peroxide and the composition of the brown intermediate are discussed.

Experimental

Materials. Stabilized 30% hydrogen peroxide (GR) obtained from the Mitsubishi Gas Kagaku Co. was purified by distillation under reduced pressure. A solution of hydrogen peroxide was titrated with standard potassium permanganate just before use. The ammonia solution (28%, GR) was purified by distillation and was titrated with standard hydrochloric acid. The copper(II) sulfate (GR) was purified by recrystallization, after which the solution was titrated with standard ethylenediaminetetraacetic acid. The other chemicals (all GR) were used without further purification.

Measurements. The rates were determined by measuring the volume of oxygen evolved by the decomposition of hydrogen peroxide with a gas buret. The volume of the evolved oxygen agreed with the calculated volume from the initial concentration of hydrogen peroxide within an error of 2%. In order to clarify the composition of the brown compound formed during the reaction, the brown precipitate was prepared by the use of the reactants on a large scale without stirring and was analyzed after the decomposition of the precipitate by 3 M H_2SO_4. The absorption spectra of the reaction mixtures were recorded using a Shimadzu SV-50 Spectrophotometer. Polarograms of the reaction mixtures were recorded using a Yanagimoto PS-52 Polarograph and a PR-2 Polarorecorder. The potassium chloride was used as a supporting salt in the reaction mixtures. The ESR spectra were recorded using an X-band spectrometer with a 455 kHz field modulation. To obtain the ESR signal in the reaction mixture, a continuous-flow technique and a quenching technique were used.[13] The luminol test[16] was made using a solution of luminol (100 mg) in a 7 M ammonia solution (100 ml).

Results and Discussion

Kinetics. The effect of the concentration of ammonia is shown in Fig. 1. In the cases of 1, 2, and

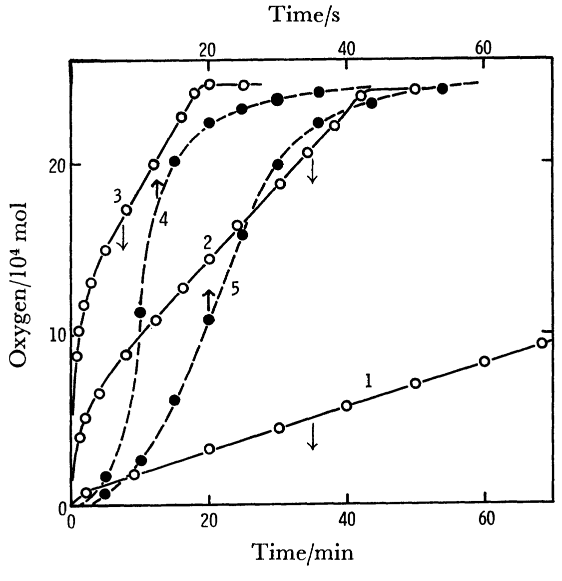

Fig. 1. Kinetic curves. The effect of the concentration of ammonia: 1. 0.04 M, 2. 0.08 M, 3. 0.10 M, 4. 0.20 M, 5. 0.50 M NH_3; 0.87×10^{-4}M $CuSO_4$; 0.125 M H_2O_2. The solid line indicates Path A and the broken line indicates Path B.

Table 1. Rate constants
Temperature 30 °C

The initial concentration of				Rate constant[a]	Order in H_2O_2	Reaction path
H_2O_2 (10^3M)	NH_3 (10^2M)	$CuSO_4$ (10^4M)	$(NH_4)_2SO_4$ (M)			
37	3.0	4.4	—	0.93	linear	A
75	3.0	4.4	—	0.73	linear	A
151	3.0	4.4	—	0.68	linear	A
34	4.0	4.4	—	1.75	linear	A
71	4.0	4.4	—	1.14	linear	A
145	4.0	4.4	—	0.85	linear	A
34	5.0	4.4	—	2.80	linear	A
49	5.0	4.4	—	1.84	linear	A
71	5.0	4.4	—	1.26	linear	A
141	5.0	4.4	—	1.08	linear	A
32	6.0	4.4	—	5.50	linear	A
67	6.0	4.4	—	1.70	linear	A
137	6.0	4.4	—	1.35	linear	A
125	4.0	0.9	—	0.62	linear	A
125	6.0	0.9	—	1.11	linear	A
125	8.0	0.9	—	2.2	linear	A
125	10	0.9	—	3.5	linear	A
20—142	2.0	2.2	0.2	0.51±0.03	1.4	B
21—141	1.0	2.2	0.3	0.31±0.02	1.5	B
71—159	3.0	16	0.5	6.54±0.40	1.6	B
33—137	1.0	8.0	0.5	2.70±0.19	1.7	B
81	0.5	9.1	1.5	1.1	1.8	B
81	1.0	9.1	1.5	2.3	1.7	B
81	1.2	9.1	1.5	1.7	1.7	B
81	2.0	9.1	1.5	1.6	1.7	B
81	3.9	9.1	1.5	0.77	1.6	B
44	0.5	9.1	0.11	9.3	1.7	B
44	0.5	9.1	0.13	11.3	1.7	B
44	0.5	9.1	0.20	7.1	1.7	B
44	0.5	9.1	0.40	1.3	1.7	B
44	0.5	9.1	0.53	0.51	1.7	B

a) 10^3 M min^{-1} for the reaction through Path A and M^{1-n} min^{-1} for the n-th-order reaction.

3 in Fig. 1, the reaction solution became brown and a linear part was observed in the kinetic curves (the plot of the amount of oxygen evolved *vs.* time). This is termed Path A (the solid line). In the cases of 4 and 5 in Fig. 1, no linear part is observed (termed Path B, the broken line). As the concentration of ammonia or the ammonium salt increases to some extent, the rate increases. The reaction path changes from Path A to Path B with the increase in the ammonia. With a further increase in the concentration of ammonia or the ammonium salt, the rate decreases and the reaction has an induction period. Path A appears at a high concentration of hydrogen peroxide and at low concentrations of the ammonia and the ammonium salt.

Table 2. The rates of linear part, k_0, *versus* the optical density at 360 nm
Temperature 30 °C

The initial concentrations of			$D_{360\ nm}$	k_0 (10^3M min^{-1})
H_2O_2 (10^3M)	NH_3 (10^2M)	$CuSO_4$ (10M)		
45	5.8	3.0	0.52	2.6
45	5.8	4.4	0.74	3.4
45	5.8	5.9	1.00	4.0
20	4.8	4.6	0.47	3.6
31	4.8	4.6	0.49	2.4
42	4.8	4.6	0.51	1.8
46	4.9	3.0	0.52	1.6
46	5.9	3.0	0.52	2.0
46	7.4	3.0	0.53	3.4

In Path A, the rate in the linear part, k_0, increased with an increase in the initial concentration of ammonia or the copper(II) ion and decreased with an increase in the initial concentration of hydrogen peroxide (Table 2). However, no simple relationship between the rate and the initial concentrations of three components was found. The rate was independent of the concentration of the brown intermediate, which was estimated by the optical density at 360 nm (Table 2). The activation energy, which was obtained from the dependence of k_0 on the temperature (15—45 °C) at $[H_2O_2]_0$=0.04—0.09 M, $[CuSO_4]_0$=0.25—0.44 mM, and $[NH_3]_0$=0.13—0.045 M, was found to be 23±1 kcal mol^{-1}.

Path B had an order of reaction in hydrogen per-

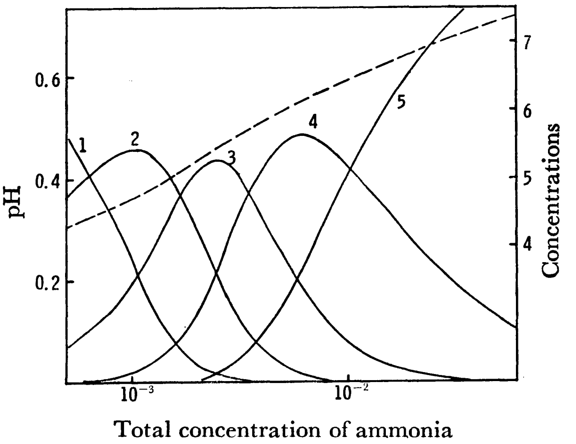

Fig. 2. The distribution of the ammine-copper(II) complex ions at the concentrations of 0.49 mM $CuSO_4$ and 1.5 M $(NH_4)_2SO_4$; 1. aquo-complex ion, 2. monoammine-, 3. diammine-, 4. triammine-, 5. tetraammine-complex ion. The broken line indicates the pH. This distribution was calculated by use of the formation constants of the ammine-copper(II) complex ions (L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964), p. 152).

oxide varying from the first- to the second-order, depending on the initial concentrations of the four components (Table 1). The order was determined by adjusting *n* to get an optimum linear plot of $[H_2O_2]^{-n+1}$ *vs.* time. The latter fourteen runs, given in Table 1, had a linear part in the plot of $[H_2O_2]^{-n+1}$ *vs.* time, at least in the region of an extent of reaction between 15 and 90% for each kinetic run.

For the 1.5 M ammonium sulfate, the maximum rate was observed (the 23rd row in Table 1) when the concentrations of the triammine- and tetraammine-copper(II) complex ions were much larger than those of the other ammine-copper(II) complex ions (Fig. 2). When the concentration of ammonia increases further, the concentration of $[Cu(NH_3)_4]^{2+}$ increases and the rate decreases. The maximum rate is observed when the pH is higher than that at which the concentration of the triammine-copper(II) complex ion is at its maximum (the broken line in Fig. 2). Therefore, it may be supposed that the active species is the hydroxo-triammine-copper(II) complex ion. It has been reported that the hydroxo-type complex is the active species in the catalytic decomposition of hydrogen peroxide by the triethylenetetramineiron(III) complex ion,[3,17] the citrato-copper(II) complex ion,[18] and the ammine-copper(II) complex ion.[10] The activation energy was found to be 15±1 kcal mol^{-1} in one of the reactions through Path B (1.4-order rate constant), in which $[H_2O_2]_0$ is 0.04 M, $[CuSO_4]_0$ is 0.3 mM, and $[NH_3]_0$ is 0.27 M.

The Brown Compound. The brown solution has a broad absorption band in the region from 500 nm to UV (1 and 2 in Fig. 3-a), and the optical density at 360 nm was constant until the final period of the reaction (Fig. 3-b). The band with a peak at 267 nm after the termination of the reaction (4 in Fig. 3-a) is considered to be caused by the hydroxo-copper(II) complex because of the agreement with the absorption band of the supernatant solution of the mixture between the copper(II) ion and the dilute ammonia solution (the broken line). At high concentrations of the ammonium salt or ammonia, the brown compound was not observed. From the easy formation of the brown compound at a high pH and/or at a low concentration of ammonia and ammonium ion, and from the appearance of the hydroxo-copper(II) complex ion after the decomposition of the brown compound, it is supposed that the brown compound is formed from a hydroxo-copper(II) complex.

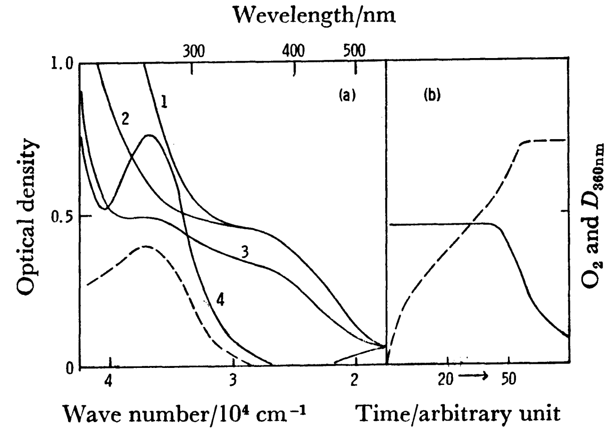

Fig. 3. (a) Spectra of the reaction mixtures: 1. 1 min, 2. 35 min, 3. 48 min, 4. 217 min. The broken line indicates a spectrum of the supernatant solution of the copper(II) sulfate-dilute ammonia mixture. (b) Schematic diagram of the relationship between the optical density at 360 nm (solid line) and the kinetic curve in the case of Path A (broken line).

To characterize the brown compound formed in the reaction mixture, the brown precipitate was prepared by the use of the reactants on a large scale without stirring and was then separated from the reaction mixture. We could not obtain the spectrum of the solid because it was bulky like the hydroxide. The visible spectrum of the aqueous solution of the solid agreed with that of the brown intermediate. The

TABLE 3. ANALYSIS OF THE BROWN PRECIPITATE

Time of reaction	Ratio of moles		
	H_2O_2/Cu	O_2/Cu	$(H_2O_2+2O_2)/Cu$
0 day	0.59	0.05	0.69
	(0)	(0.33)	(0.66)
1 day	0.16	0.02	0.20
	(0)	(0.09)	(0.18)
2 days	0.01	0.04	0.09
	(0)	(0.04)	(0.08)
10 days	0.00	0.02	0.04
	(0)	(0.02)	(0.04)
2 min[a)]	0.83	0.00	0.83
30 min[a)]	0.70	0.04	0.78
120 min[a)]	0.81	0.00	0.81

a) The sample was separated from the solution in which the reaction was undergoing. b) ( ) self-decomposition.

peroxide and copper in the precipitate were analyzed, and the volume of the oxygen gas, which was liberated by the decomposition of the precipitate by acid or on standing for 12 hr, was measured by means of a gas buret (Table 3). When the precipitate was decomposed by acid immediately after separation from the reaction solution and washing, *ca.* 10^{-5} mol of oxygen gas evolved. Therefore, it may be supposed that a part of the oxygen which was adsorbed on the precipitate after the self-decomposition was liberated by the acid treatment. The fact that the molar ratio of $(H_2O_2+2O_2)/Cu$ in the case of decomposition by the acid treatment agreed with the molar ratio of $2O_2/Cu$ in the case of the self-decomposition (shown in the fourth column in Table 3) indicates that the hydrogen peroxide coordinates to the copper ion with a molar ratio of 1 : 1. Ammonia was detected in the brown precipitate, but the quantity was too small for us to obtain the NH_3/Cu ratio.

Thus, the brown compound is found to be a peroxo-copper complex and to decompose with the evolution of oxygen on standing. The brown peroxo-copper complex changed to a green compound on standing for several hours and to a sky-blue compound on standing for several days.

ESR. The ESR signal obtained using a quenching technique and the ESR signal of the free O_2^- radical obtained by the UV irradiation of an alkaline hydrogen peroxide aqueous solution are shown in Figs. 4-a and 4-b respectively (measured at 77 K). The S_1 signal in Fig. 4-a is assigned to the O_2^- radical. The S_2 signal is consistent with the perpendicular component of the anisotropic signal of the tetraammine-copper(II) complex ion, as is shown in Fig. 4-c. The copper(II) complex ion is considered to be present in a very small amount because of the weak intensity of the signal as compared with the signal of the copper(II) ion of the original concentration.

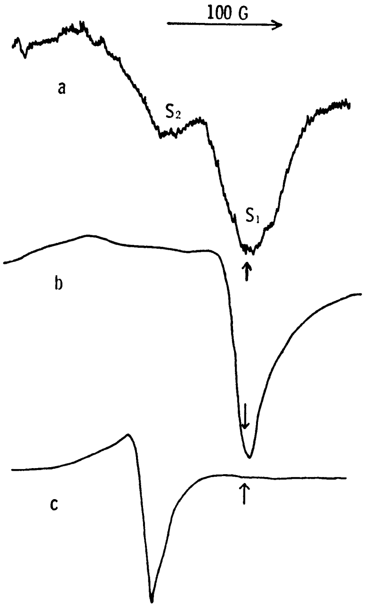

Fig. 4. ESR spectra of the quenched sample of the reaction mixture (a), the oxygen anion radical, O_2^-, (b), and the ammine-copper(II) complex ions (c) measured at 77 K.

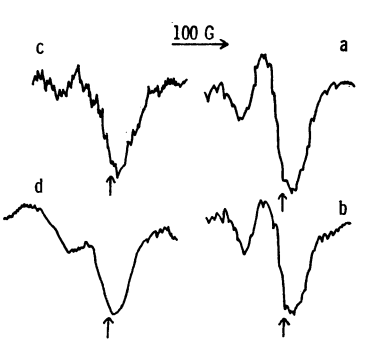

Fig. 5. Dependence of the signal of the quenched sample on the temperature: a. 108 K, b. 149 K, c. 217 K, and d. 77 K after the melting treatment for two minutes.

The dependence of the S_1 signal on the temperature is shown in Fig. 5. The S_1 signal was observed at 232 K and was also observable at 77 K after the melting treatment of the quenched sample for two minutes at *ca.* 0 °C. The signal of the free O_2^- radical obtained by the UV irradiation was not as stable as the S_1 signal; *e.g.*, it had already disappeared at 194 K.

Sometimes no signal was observed in the range of the magnetic field between 0 and 4300 gauss at 77 K in the brown quenched sample at a high concentration of hydrogen peroxide or a small rate of mixing; therefore, it may be concluded that the copper ion in the brown intermediate is a diamagnetic species.

From these facts, the increased stability of the O_2^- radical, and the lack of the copper(II) ion, the O_2^- radical which coordinates to any diamagnetic copper complex ion can be tentatively proposed as the origin of S_1, even without any direct evidence such as the hyperfine structure due to the copper nucleus. It may be supposed that the observation of the resolved hyperfine structure in the sample of the polycrystalline state is fairly difficult as compared with the case of the Ti^{III}–H_2O_2 system[19] or the VO^{2+}–H_2O_2 system,[15,20] where the ESR signal was detected by means of a flow technique.

It is known that the free radical resulting from hydrogen peroxide coordinates with the oxidized form of the metal ion in the reactions of the Ti^{III}–H_2O_2 system[11–13,21] and the VO^{2+}–H_2O_2 system[15,21] and with the reduced from of the metal ion in the reaction of the Ce^{IV}–H_2O_2 system.[14,21] The free radical is stabilized by the coordination with the metal ion.

The diamagnetic copper(III) ion in the D_{4h} symmetry has a vacant $d(x^2-y^2)$ orbital which does not overlap with the π^*-orbital of the O_2^- radical. Therefore, the electron transfer from the unpaired π^*-orbital to the vacant $d(x^2-y^2)$ orbital is difficult. For this reason, it is considered that the free radical coordinated to the copper(III) ion is stabilized. The complexed radical compound has been considered to be formed in a by-path of the catalytic decomposition of hydrogen peroxide because of the increased stability of the compound compared to that of the original free radical.[12,13,21]

About the copper(III) compound, it has been reported that a colloidal copper(III) oxide is formed in the reaction between hydrogen peroxide and the ammine-copper(II) complex.[22,23]

Luminol Test. When an alkaline luminol reagent was added to a mixture of hydrogen peroxide and hemin, a chemiluminescence was observed.[24] The ammoniacal luminol reagent was here added to the brown precipitate, a mixture of hydrogen peroxide and the copper(II) ion, a hydrogen peroxide solution, and a copper(II) sulfate solution. Chemiluminescence was observed in the brown precipitate and the mixture of hydrogen peroxide and the copper(II) ion. This fact suggests that the decomposition of hydrogen peroxide by the ammine-copper(II) complex ions and that of the brown compound by the ammonia solution proceeds with the formation of a free radical, because the chemiluminescence is observed in the reaction between the luminol reagent and the free radical resulting from hydrogen peroxide.[16]

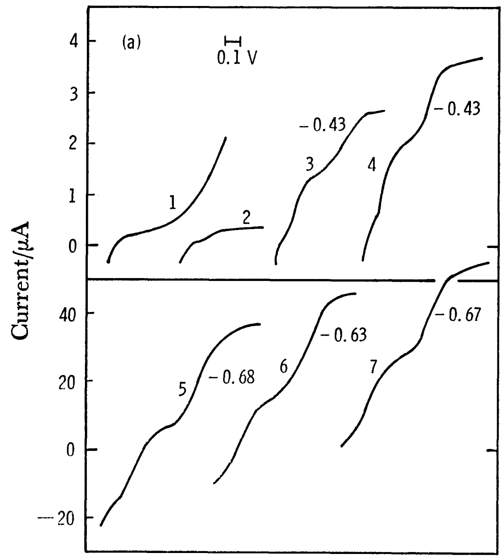

Fig. 6. Polarograms of the reaction mixture (a) and the copper(I) chloride-ammonia mixture (b); 1. 40 min, 2. 130 min, 3. 300 min, 4. 310 min after mixing of the reactants; 5. 10 min, 6. 22 min, 7. 45 min after mixing of copper(I) chloride and ammonia. The 1 M KCl and 1.5 M ammonium sulfate were used for (a) and (b) as the supporting salt respectively. The fractional values in this figure indicate a half-wave potential *vs.* SCE.

Polarography. Polarograms of the reaction mixture and the mixture of the copper(I) ion and ammonia are shown in Fig. 6. In the reaction mixture, the wave-height of the mixture of the ammine-copper(II) complex ions (3 and 4 in Fig. 6-a, the two-step wave) increased with the decrease in the brown intermediate after the disappearance of the wave of hydrogen peroxide (1 and 2 in Fig. 6-a). In the mixture of the copper(I) ion and ammonia, the first wave (*ca.* −0.25 volt *vs.* SCE) resulting from $Cu(II) \rightleftharpoons Cu(I)$ shifted from a negative current to a positive current with the increase in the copper(II) ion by air-oxidation (Fig. 6-b). The shift was also observed in a mixture of a reductant and an oxidant.[25] The difference in the half-wave potential between the reaction mixture and the mixture of the copper(I) ion and ammonia is a result of the difference in the concentrations of ammonia and the supporting salt (1 M KCl for the reaction mixture and 1.5 M $(NH_4)_2SO_4$ for the mixture of the copper(I) ion and ammonia). The rate of the formation of the ammine-copper(II) complex ions by the addition of concd ammonia to the brown compound was very rapid as compared with that by the addition of concd ammonia to the copper(I) chloride, which was tested by the rate of blue coloration. These facts suggest that the copper ion in the brown intermediate is not a univalent ion.

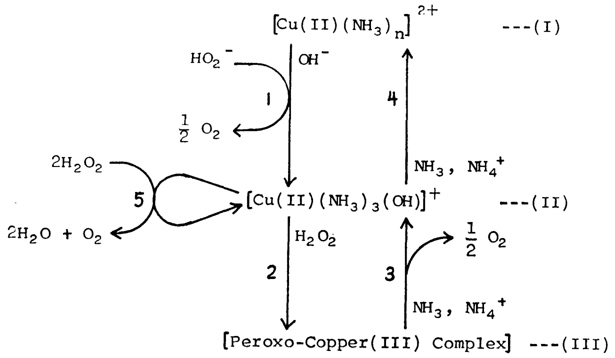

Fig. 7. Reaction scheme of the catalytic decomposition of hydrogen peroxide by the ammine-copper(II) complex ions.

Reaction Scheme. From the preceding discussions, it may be assumed that the path of the catalytic decomposition of hydrogen peroxide by the ammine-copper(II) complex ions is as is shown schematically in Fig. 7. In the reaction scheme, Reaction 1 is very slow compared with the other reactions. Reaction 2 depends on the concentrations of hydrogen peroxide and the hydroxide ion. Reaction 3 depends on the concentration of ammonia or the ammonium ion. The rate of the evolution of oxygen in Reaction 5 is much larger than that in Reaction 3.

In Path A, the rate of Reaction 2 is much larger than that of Reaction 3, so the copper compound in the reaction mixture is almost entirely Compound III (brown intermediate) during the reaction. The rate of the evolution of oxygen is the sum of the rates of Reactions 3 and 5. In the initial stage of Path A, Reaction 5 is predominant, so the rate of the evolution of oxygen is large (see the solid lines in Fig. 1). In the final stage of Path A, the concentration of Compound II increases because of the small rate of Reaction 2 resulting from the low concentration of hydrogen peroxide, so the rate of the evolution of oxygen increases because of the increase in Reaction 5 (2 and 3 in Fig. 1). The linear part can be attributed to the steady concentration of Compounds III and II. Also, the fact that the rate in the linear part is not proportional to the concentration of the brown Compound III suggests that the rate is determined by the concentrations of ammonia and Compounds II and III.

In Path B, the rate of Reaction 2 is very small compared with the rates of Reactions 3 and 4, so Compound III is not observed. The increase in the ammonia or the ammonium salt decreases the active species, II, and the rate of the decomposition of hydrogen peroxide. The induction period is caused by Reaction 1. The mechanism of Reaction 5 was not found owing to the complicated rate equation.

The difference in the activation energy between the two reaction paths, A and B, suggests that their mechanisms of the evolution of oxygen gas are different.

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