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

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By

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The catalytic decomposition reaction of hydrogen peroxide was studied by using the mixture of nickel(II) salt, ammonia, and ammonium salt as catalyst. The order of reaction in hydrogen peroxide varied from the first-order to the half-order. On the basis of the effects of each component in the reaction mixture on the rate, the hydroxotetraammine complex of nickel(II) ion was concluded to have the largest activity among the various ammine-nickel(II) complex ions. The reaction was found to be a catalytic reaction with slow activation and the active species was found to be a peroxo-nickel complex ion. A possible reaction scheme was discussed.

In the previous paper[1] dealing with the decomposition of hydrogen peroxide catalyzed by the ammine-copper(II) complex ions, attention has been drawn to the change of the catalyst during reaction. This work was undertaken to determine the effects of the composition of the ammine-nickel(II) complex ions on the reaction rate of the catalytic decomposition of hydrogen peroxide by using the mixture of the nickel(II) salt, ammonia, and ammonium salt as catalyst. The reaction by the ammine-nickel(II) complex was so far studied by using a solid of hexaamminenickel(II) complex salt as catalyst.[2,3] The active species of the ammine-nickel(II) complex ions in the reaction and the reaction path 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 nickel(II) salts (GR) were purified by recrystallization, after which the concentration of the stock solution was determined by the gravimetric analysis by use of dimethylglyoxime. The effect of the nickel(II) chloride on the reaction rate was identical with those of sulfate and nitrate of nickel(II) ion. The other chemicals (all GR) were used

GAS BURET

O_2 GAS
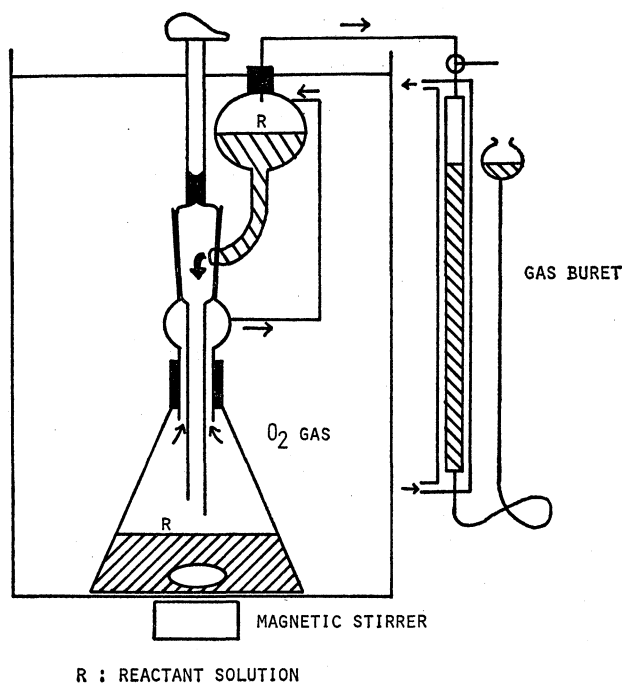
MAGNETIC STIRRER

R : REACTANT SOLUTION

Fig. 1. Reaction vessel.

without further purification.

Kinetic Measurements. The rates were determined by measuring the volume of oxygen evolved by the decomposition of hydrogen peroxide with a gas buret. The reaction vessel used is shown in Fig. 1. This reaction vessel had three seconds for the mixing of the reactants of 35 cm³. 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 precipitate formed during the reaction, the amount of nickel, peroxide, and ammonia in the solid was determined after the decomposition of the solid by 3 M H_2SO_4. The luminol test[4] was done using a solution of luminol (100 mg) in a 7 M ammonia solution (100 cm³).

Results and Discussions

The aqueous solution of the nickel(II) sulfate, the ammonium sulfate, and the mixture of those did not catalyze the decomposition reaction of hydrogen peroxide for several hours. The ammonia solution catalyzed the reaction. The catalytic action of ammonia, however, was small as compared with that of the mixture of the nickel(II) sulfate and ammonia. This result indicated that the ammine-nickel(II) complex ions catalyzed the reaction.

The green precipitate was formed after the mixing of hydrogen peroxide and the catalyst mixture and the precipitate increased with the reaction time at the initial step of the reaction. The kinetic curve, the plot of the oxygen gas evolved *versus* time, was a S-curve at the presence of ammonium sulfate, which is the characteristic of the catalytic

reaction with slow activation. The rate of the evolution of oxygen was seemed to increase with the increase of the precipitate at the initial step of reaction. This reaction, therefore, was seemed to accelerated by a product of the ammine-nickel(II) complex ions with hydrogen peroxide.

The Effects of the Initial Concentration of Hydrogen Peroxide. The order of reaction in hydrogen peroxide is shown in Table 1 at the various initial concentration of hydrogen peroxide. It was determined by using the plot of $[H_2O_2]^{1-n}$ *versus* time. At the low concentration of hydrogen peroxide below 0.02 M, there were some reaction runs in which a linear plot of $[H_2O_2]^{1-n}$ *versus* time was not obtained with a constant order of reaction. The rate constant, k_n, is plotted as a function of the initial concentration of hydrogen peroxide in Fig. 2. The rate constant depended on the initial concentration of hydrogen peroxide, but

TABLE 1. THE ORDER OF REACTION IN HYDROGEN PEROXIDE AT THE VARIOUS INITIAL
CONCENTRATION OF HYDROGEN PEROXIDE AT 30°C

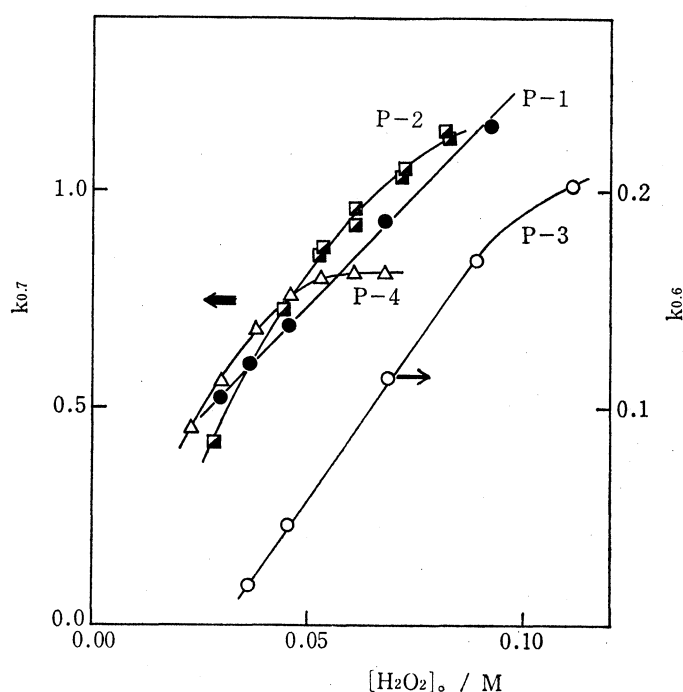| Run No.	$[H_2O_2]_0$ (M)	$[NiSO_4]_0$ (mM)	$[NH_3]_0$ (M)	$[(NH_4)_2SO_4]_0$ (M)	Order in H_2O_2
p-1	0.092-0.032	5.7	0.19	0.010	0.7
p-2	0.082-0.028	5.7	0.057	0.010	0.7
p-3	0.11 -0.036	5.7	0.21	0.020	0.6
p-4	0.068-0.023	5.5	0.060	0.0057	0.8

Fig. 2. Dependence of the rate constant of the n-th order reaction in hydrogen peroxide, k_n, on the initial concentration of hydrogen peroxide at 30°C. P-1. 5.7 mM NiSO₄, 0.019 M NH₃, 0.010 M (NH₄)₂SO₄; P-2. 5.7 mM NiSO₄, 0.057 M NH₃, 0.010 M (NH₄)₂SO₄; P-3. 5.7 mM NiSO₄, 0.21 M NH₃, 0.020 M (NH₄)₂SO₄; P-4. 5.5mM NiSO₄, 0.060 M NH₃, 0.006 M (NH₄)₂SO₄.
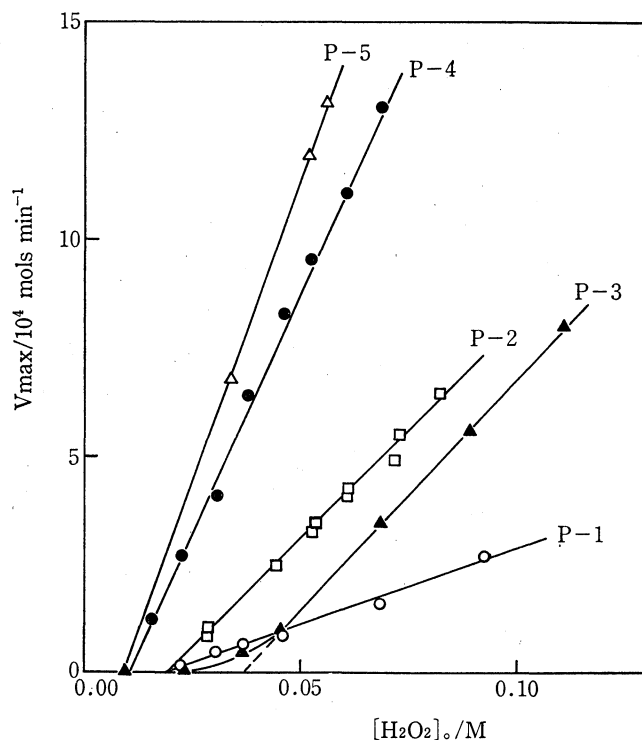
Fig. 3. Dependence of the maximum rate, V_{max}, on the initial concentration of hydrogen peroxide at 30°C. P-1–P-4 are the same condition as Fig. 2. P-5. 5.7 mM $NiSO_4$, 0.47 M NH_3, 0.0 M $(NH_4)_2SO_4$.

the relationship could not be expressed by any equation.

The maximum rate, $V_{max}=(do_2/dt)_{max}$, is plotted as ordinate and the initial concentration of hydrogen peroxide as abscissa in Fig. 3. The linear plots were obtained at the high concentration of hydrogen peroxide. The slope increased with the increase in ammonia and decreased with the increase in ammonium sulfate. The intercept of abscissa increased with the increase in ammonium sulfate. At the low concentration of hydrogen peroxide, a nonlinear part is observed (p-3 in Fig. 3).

These results suggest that the reaction rate was proportional to the concentration of hydrogen peroxide and to the active catalyst which was a product of an ammine-nickel (II) complex ion with hydrogen peroxide in the reaction mixture. At the high concentration of hydrogen peroxide, a constant amount of the active catalyst was formed, so that the rate was proportional only to the concentration of hydrogen peroxide. At the low concentration of hydrogen peroxide, the amount of the active catalyst depended on the concentration of hydrogen peroxide, so that the rate was not proportional to the concentration of hydrogen peroxide.

Effects of Ammonia. The order of reaction in hydrogen peroxide is given in Table 2 at the various concentration of ammonia. The data indicate that the order is independent on the concentration of ammonia. It was in contrast with the effect in the reaction system using a mixture of copper(II) sulfate, ammonia, and ammonium sulfate, in which

TABLE 2. THE ORDER OF REACTION IN HYDROGEN PEROXIDE AT THE VARIOUS
CONCENTRATION OF AMMONIA AT 30°C

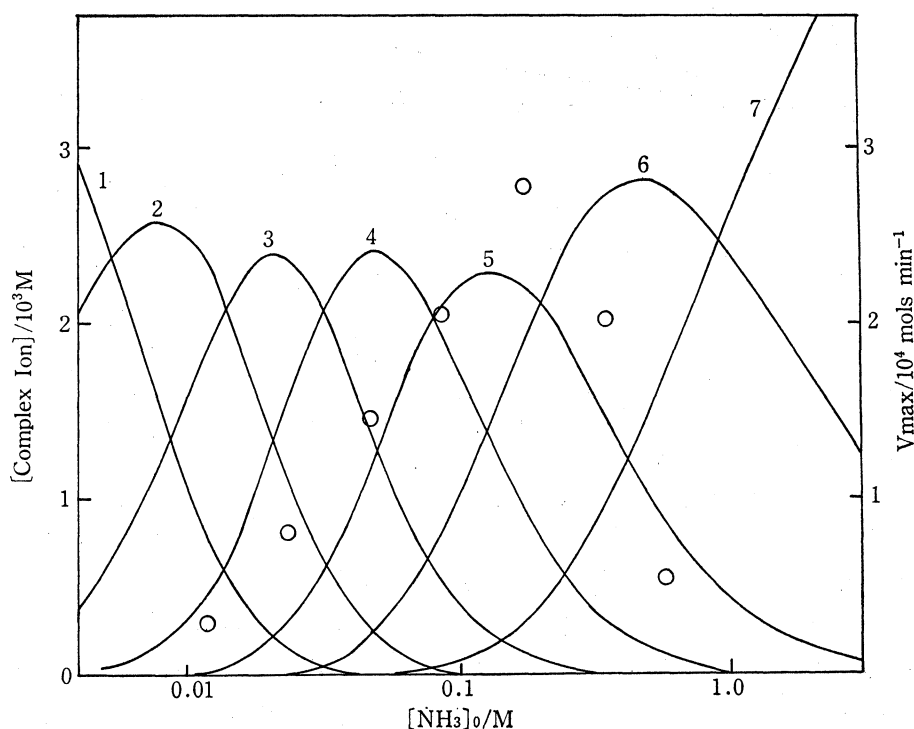| Run No.	$[NH_3]_0$ (M)	$[H_2O_2]_0$ (M)	$[NiSO_4]_0$ (mM)	$[(NH_4)_2SO_4]_0$ (M)	Order in H_2O_2
A-1	0.087-0.66	0.09	5.7	0.010	0.7-0.8
A-2	0.006-0.60	0.043	5.5	0.0	0.8-0.9
A-3	0.011-0.57	0.037	5.7	0.0057	0.8
A-4	0.012-0.60	0.043	5.5	0.011	0.8
A-5	0.005-0.52	0.051	5.2	0.016	0.6

Fig. 4. Equilibrium distribution of the ammine-nickel (II) complex ions at 5.5 mM $NiSO_4$ and 0.011 M $(NH_4)_2SO_4$ and the dependence of the maximum rate, V_{max}, on the concentration of ammonia (0, see the right scall). 1. aquo-complex ion, 2. mono-, 3. di-, 4. tri-, 5. tetra-, 6. penta-, 7. hexa-amminenickel(II) complex ion (See the left scall).

the order depended on the concentration of ammonia.[1]   At the large excess ammonia, the constant order could not be determined. It seemed to be due to the addition of the catalytic effect of the free ammonia.

The maximum rate and the distribution of the ammine-nickel(II) complex ions are shown in Fig. 4. The distribution of the ammine-nickel(II) complex ions was calculated by using the formation constants of the ammine-nickel(II) complex ions.[5]   In the calculation, the presence of hydroxo-ammine complexes of nickel(II) ion was neglected. Although the distribution calculated was different from that in the reaction mixture through the coexistence of hydrogen peroxide and the neglect of the hydroxo-ammine complexes of nickel(II) ion, the difference probably is not so much in the initial step of the
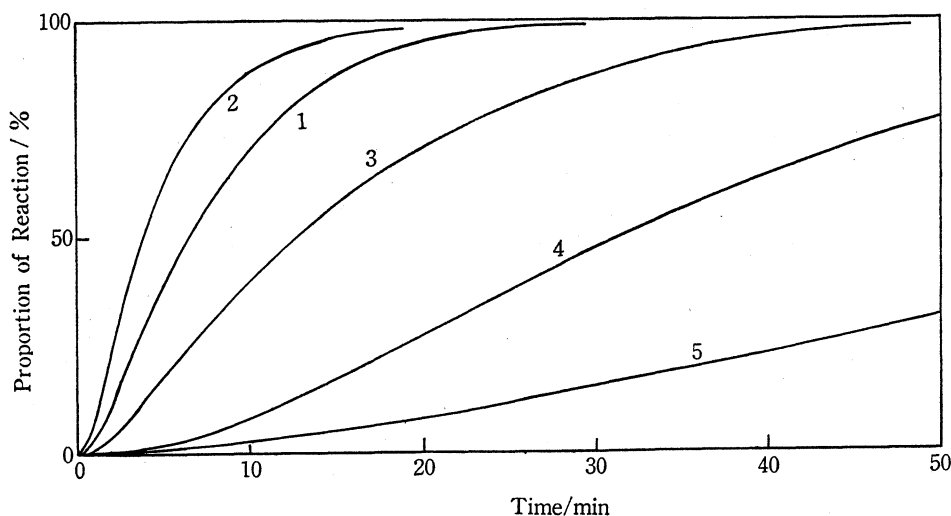
Fig. 5.   Dependence of the kinetic curve on the concentration of ammonium sulfate. $NiSO_4$ 5.2 mM,
   NH_3 0.026 M, $(NH_4)_2SO_4$ 1. 0.0 M, 2. 0.0026 M, 3. 0.0052 M, 4. 0.021 M, 5. 0.031 M, 6. 0.041 M.

reaction.

The results shown in Fig. 4 indicated that the dependence of the maximum rate on the concentration of ammonia accords with that of the tetraamminenickel(II) complex ion on the concentration of ammonia.

At large excess of ammonia, little amount of the solid was formed and a blue color of the ammine-nickel(II) complex ions was observed in the supernatant solution of the reaction mixture.

Effects of Ammonium Sulfate.   By the addition of a much amount of ammonium sulfate, the reaction was greately retarded and the kinetic curve became the marked S-curve as shown in Fig. 5.   The solid in the reaction mixture was not observed at large excess of ammonium sulfate.   The reaction rate, however, was small at the absence of ammonium salt and increased with the addition of a slight amount of ammonium salt.   This effect of ammonium salt was observed also in the case of the decomposition of hydrogen peroxide catalyzed by the ammine-copper(II) complex ions.[1]   The effect may be seemed to concern to the formation of hydroxo-ammine complexes of nickel(II) ion.

At the low concentration of ammonium salt, a much amount of nickel(II) hydroxide which had a little catalytic activity was formed and the reaction rate, accordingly, was small.   At the high concentration of ammonium salt, the hydroxo-ammine complex ions of the nickel(II) ion are not formed.   On the basis of the fact that the reaction was retarded at the high concentration of ammonium salt, it seemed reasonable to propose that the precursor of the active species was not the tetraamminenickel(II) complex ion but the hydroxo-tetraammine complex ion of the nickel(II) ion.

The hydroxo ligand is labile in the substitution reaction.   For example, the substitution reaction of the monohydroxopentaaquoiron(III) ion by chloride ion was faster than that of the hexaaquoiron(III) ion by a factor of about 1000.[6]   It was reported

that the dihydroxotriethylenetetramineiron(III) complex ion[7], hydroxoammine-copper (II) complex ion,[1,8] and hydroxocitratocopper(II) ion[9] were the active species in the decomposition of hydrogen peroxide. These facts support the proposal that the hydroxo-tetraammine complex of the nickel(II) ion was the precursor of the active species in the decomposition of hydrogen peroxide.

It could be considered that the hydroxo ion coordinated to nickel(II) ion promotes the formation of the univalent anion of hydrogen peroxide, HO_2^-, in the coordination sphere of nickel(II) ion following to the equilibrium, $Ni(II)-OH^- + H_2O_2 \rightleftarrows H_2O + Ni(II)-O_2H^-$, so that the decomposition of hydrogen peroxide is promoted by the hydroxocomplex.

The Precipitate Formed in the Reaction Mixture. When the ammoniacal luminol reagent was added to the precipitate formed in the reaction mixture, chemiluminescence was observed. The chemiluminescence of luminol was observed in many peroxo-compounds by Gillard and Spencer.[4] The observation of the chemiluminescence by the solid, therefore, suggests that the solid contained a peroxo-compound.

The composition of the solid was determined by the chemical analysis after the decomposition of the solid by 3 M H_2SO_4. The molar ratio of oxygen, peroxide (as hydrogen peroxide), and ammonia to nickel is given in Table 3. The data given in Table 3 support the presence of peroxo-compound in the solid and show that the peroxo-compound decomposed slowly. That the ratio of peroxide to nickel is smaller than 0.5 (for the μ-peroxo binuclear complex) or 1.0 (for the peroxo-nickel complex) suggests that the solid is a mixture of peroxo complex and hydroxide of nickel.

TABLE 3. THE MOLAR RATIO OF THE COMPONENT IN THE SOLID DURING THE REACTION.

Time (hr.)	0.1	12	37	59	85	107
O_2/Ni	—	0.084	0.083	0.081	0.079	0.081
H_2O_2/Ni	0.29	0.24	0.19	0.17	0.16	0.15
NH_3/Ni	—	0.3	0.3	—	—	—

When an additional hydrogen peroxide was added to the reaction mixture containing the solid, the kinetic curve in Fig. 6 was obtained. As the latter kinetic curves did not become any S-curve, the solid was considered to containe an active species. As the solid had a larger catalytic activity than nickel(II) hydroxide and nickel(II) oxide which contained an equal amount of nickel, the peroxo-nickel compound in the solid was considered to be an active species.

Reaction Scheme. On the basis of the previous results and discussions, the reaction scheme was proposed as shown in Fig. 7. In the reaction scheme, Reaction (1) is a slow activation reaction and Compound II is a active species of catalyst. Hydrogen peroxide accelerates Reaction (1) and increases Compound II, so that the decomposition of hydrogen peroxide is accelerated. At the optimum concentration of ammonia, the concentration of Compound I becomes maximum. As ammonium ion shifts Reaction (5) to right, Compound I and the active species II decrease and the decomposition reaction of
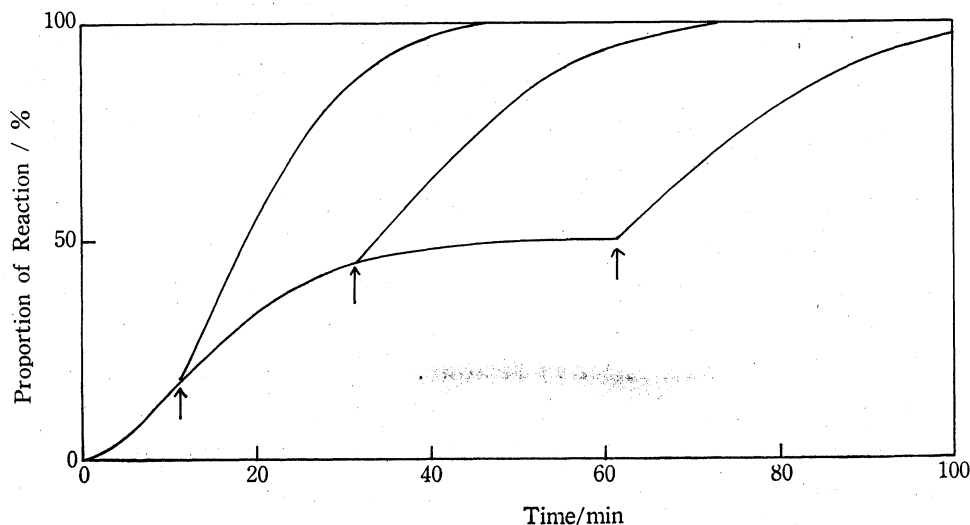
Fig. 6. Kinetic curves when the additional hydrogen peroxide was added to the reaction mixture.
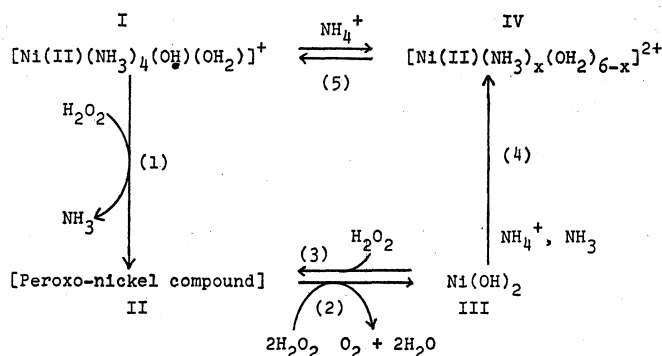↑ : the additional hydrogen peroxide was added at the time.

Fig. 7. Reaction scheme.

hydrogen peroxide is retarded. As ammonium ion also accelerates Reaction (4), the ammine-nickel(II) complex ions IV increase in the supernatant solution of reaction mixture.

Owing to the very complex system of the reaction, that the heterogeneous system (solid, solution and gas) and the complex equilibrium (5) between Compound I and Compounds IV, the quantitative realtionship between the rate of reaction and the concentration of each component of the catalyst mxiture could be not determined.

In the previous studies by using a solid of the hexaamminenickel(II) complex, the information of the active species could not been obtained. This study clarified the active species of the ammine-nickel(II) complex catalyst by using a mixture of nickel(II) sulfate, ammonia, and ammonium sulfate.

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