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Studies on Cobaloxime Compounds. II. Catalytic Activity of Cobaloximes in the Hydrogen Peroxide Decomposition Reaction

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Various cobaloximes with the general formula $[CoX(DH)_2B]$ (X: Cl, CN, OH, or CH_3. DH: Dimethylglyoximato monoanion. B: Bases such as water, nicotinamide, pyridine, imidazole, or a low molecular weight copolymer of acrylamide and 4-vinylpyridine, *etc.*) were examined for catalytic activity in the H_2O_2 decomposition reaction. Cyanocobaloximes have less activities than other cobaloximes. The effect of changing the axial bases of cobaloximes was found to be small. When methylcobaloxime was used as a catalyst, the lag time was observed in the dark, while with the irradiation of visible light the reaction proceeded without induction period. An extensive study on chloroaquocobaloxime revealed that the rate is proportional both to the concentration of H_2O_2 and to the concentration of cobaloxime and inversely proportional to $[H^+]$. It was found that the decomposition of H_2O_2 with cobaloximes proceeds with a gradual and partial degradation of cobaloximes.

The decomposition of hydrogen peroxide catalyzed by metal ions has been widely investigated,[1] but the mechanisms have not yet been clarified. A few cobaloximes have been briefly investigated for catalytic activity in the H_2O_2 decomposition reaction by Sasaki and Matsunaga.[2] The catalytic activities decreased in the order $CoCl(DH)_2P\text{-}4VP > CoCl(DH)_2Pyr \gg Co(CN)(DH)_2P\text{-}4VP > Co(CN)(DH)_2Pyr$, where P-4VP means poly-4-vinylpyridine and Pyr pyridine. No study has been reported on the kinetics of the H_2O_2 decomposition reaction catalyzed by cobaloximes.

In this work, the H_2O_2 decomposition reactions with various cobaloximes were investigated and results similar to those of Sasaki[2] were obtained in the case of chloro- and cyano-cobaloximes. Results of other cobaloximes and kinetic studies are also described.

Experimental

Materials. *Preparation of $CoCl(DH)_2$(Copoly—AM-VPy)*: To a hot methanolic solution of 0.39 g (3.4 mmol) of dimethylglyoxime (30 m*l*), 0.40 g (1.7 mmol) of $CoCl_2 \cdot 6H_2O$ in 30 m*l* of methanol was added with stirring. After an hour, an aqueous solution of 1.00 g of a copolymer of acrylamide and 4-vinylpyridine (Copoly—AM-VPy: $\bar{M}n = 1.6 \times 10^3$, AM/VPy molar ratio = 14.3) was added with stirring for an hour. The brown filtrate transparent solution was concentrated under a reduced pressure to precipitate a small amount of unreacted dimethylglyoxime, which was removed by filtration. The brown filtrate was evaporated to dryness in a vacuum. 1.28 g of green residue was obtained. It was dissolved in 20 m*l* of water to yield a brown solution, which was applied on a Sephadex LH-20 column (3.0 × 37.5 cm). By evaporating the first fraction to dryness, 0.86 g of a polymeric cobaloxime, $CoCl(DH)_2$(Copoly—AM-VPy) free from monomeric cobaloximes was recovered. From Co analysis, the compound was found to contain 1.8 wt% of Co which corresponds to 41% of the degree of coordination of the pyridine residues in polymeric ligand. The degree of coordination indicates the mole percentage of the cobaloxime moiety per pyridine residue of Copoly—AM-VPy. The brown powder obtained became insoluble after evaporation to dryness. It shows infrared absorption bands at 1238 cm^{-1} (ν_{N-O}), 1090 cm^{-1} (ν_{N-O}), *ca.* 1070 cm^{-1}, 980 cm^{-1}, 860 cm^{-1}, and 512 cm^{-1} (ν_{Co-N}) due to cobaloxime moiety.[3]

Other Materials: The synthesis of other cobaloximes examined in this work was previously reported.[3] The stock hydrogen peroxide was 30% stabilizer-free supplied from Mitsubishi Edogawa Kagaku Co., Ltd. Analytical-grade 0.1 N potassium permanganate solution was diluted 10 times to yield 0.01 N solution for the titration of the residual hydrogen peroxide in the reaction mixture. Other reagents were obtained from commercial sources and used without further purification.

Methods. A typical procedure is as follows. To an appropriate amount of cobaloxime solution, 5 m*l* of 1 M potassium phosphate buffer, a minimal amount of PNE[4] if necessary, and distilled water were added to bring the total volume to 50.0 m*l*. Then, 1.0 m*l* of 3% hydrogen peroxide was added to the mixture. The reaction was usually conducted at 40°C. Aliquots, *e. g.*, 5 m*l*, were taken for analysis at appropriate times. Five milliliters of 9 N sulfuric acid was added to the aliquot to stop decomposition, and the residual hydrogen peroxide was titrated with a 0.01 N $KMnO_4$ solution. Since there were lag times in some cases as described below, the reaction rates were calculated from the slopes of the time conversion plots at the half-decomposition point.

Spectroscopic Measurements. An aliquot of the reaction mixture was used for the visible spectrum and was diluted 20 times for the ultraviolet spectrum, which was taken with a Shimadzu automatic recording spectrophotometer type SV-50A. Infrared spectrum was taken with a JASCO infrared spectrophotometer, model IR-G.

Results and Discussion

In order to examine the difference in catalytic activity in relation to several axial ligands of cobaloximes, the decomposition reactions of hydrogen peroxide were carried out in the presence of various cobaloximes. Typical time-conversion curves of several cobaloximes are shown in Fig. 1, which shows the presence of a lag time that differs in each case. The decomposition rates were therefore calculated from the slopes of the curves at the half-decomposition point, shown in Table 1. As can be seen in Table 1, cyanocobaloximes have less activities than other cobaloximes in the decomposition

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[1] J. H. Baxendale, "Advances in Catalysis and Related Subjects," Vol. IV, Academic Press, New York (1952), pp. 31—86.

[2] T. Sasaki and F. Matsunaga, This Bulletin, **41**, 2440 (1968).

[3] N. Yamazaki and Y. Hohokabe, *ibid.*, **44**, 63 (1971).

[4] PNE is a polyoxyethylene nonylphenol ether $P = 10$, known as a non-ionic surface activating reagent.

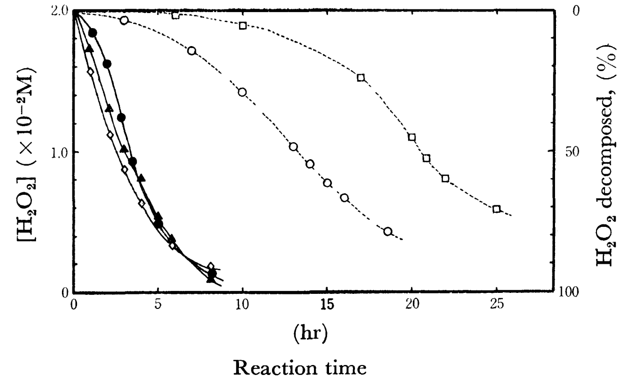

Fig. 1. H_2O_2 decomposition-time profiles catalyzed by several cobaloximes.
$[H_2O_2]_0=2.0\times10^{-2}$ M, $[CoX(DH)_2B]=3.92\times10^{-4}$ M, in 0.1 M potassium phosphate buffer (pH 7.2), 40°C.
[X, B]: —●— (Cl, pyridine); ···○··· (CN, pyridine); —▲— (Cl, H_2O); ···□··· (CN, *p*-toluidine); —◇— ($CoCl_2\cdot6H_2O$).

Table 1. H_2O_2 decomposition rates[a] with various cobaloximes

$[H_2O_2]_0=2.0\times10^{-2}$M, $[Co]=3.92\times10^{-4}$ M, in 0.1M potassium phosphate buffer (pH 7.2), 40°C

$CoX(DH)_2B$ X——B	Decomposition rate ($\times 10^{-3}$M/hr)
Cl——pyridine[b]	3.9
Cl——nicotinamide[b]	3.5
Cl——H_2O[b]	3.4
Cl——γ-picoline[b]	3.4
Cl——*p*-toluidine[b]	3.2
Cl——imidazole[b]	3.1
Cl——Copoly—AM-VPy[b]	3.0
OH——H_2O	3.3
OH——Copoly—AM-VPy[b]	3.2
CH_3——γ-picoline[b]	3.3
CH_3——H_2O	3.5(Light[c]), 3.3(Dark)
CN——*p*-toluidine[b]	1.5
CN——pyridine[b]	1.3
$CoCl_2\cdot6H_2O$	3.3

a) At the half-decomposition point, *i. e.*, at the H_2O_2 concentration of 1.0×10^{-2}M.
b) A minimal amount of PNE was added.
c) Irradiated during the course of reaction.

reaction of H_2O_2. Among chlorocobaloximes, the difference in catalytic activity was rather small, and the activity was not in the reasonable order of the axial base such as that of the strength of basicity. The polymeric ligand, Copoly-AM-VPy, *i. e.*, a low molecular weight copolymer of acrylamide and 4-vinylpyridine, exerted little change in the catalytic activity compared with other monomeric bases.

Since chloroaquocobaloxime has greater solubility than other chloro derivatives in aqueous medium, an extensive study on the kinetic behavior of the decomposition reaction was performed in the presence of chloroaquocobaloxime.

First, the dependence on pH (6.0—8.1) was investigated at a constant initial H_2O_2 concentration and a constant cobaloxime concentration. As shown in Fig. 2, the rate was inversely proportional to $[H^+]$, and the reaction order was observed to be -0.98 in $[H^+]$. This suggests that hydrogen peroxide reacts through the ion HO_2^-.

Dependence on the concentration of cobaloxime was then investigated at pH 6.8 and 7.2. The rate was proportional to the concentration of cobaloxime and the reaction order was 0.98 in it at pH 6.8 and 0.88 at pH 7.2 (Fig. 3).

Finally, a study of the dependence on the concentration of H_2O_2 revealed that the rate was 1.28 order in $[H_2O_2]$ at pH 7.2 (Fig. 4).

In another series, the activation energy was determined between 30°C and 45°C, and found to be 17.9 kcal/mol at pH 7.2.

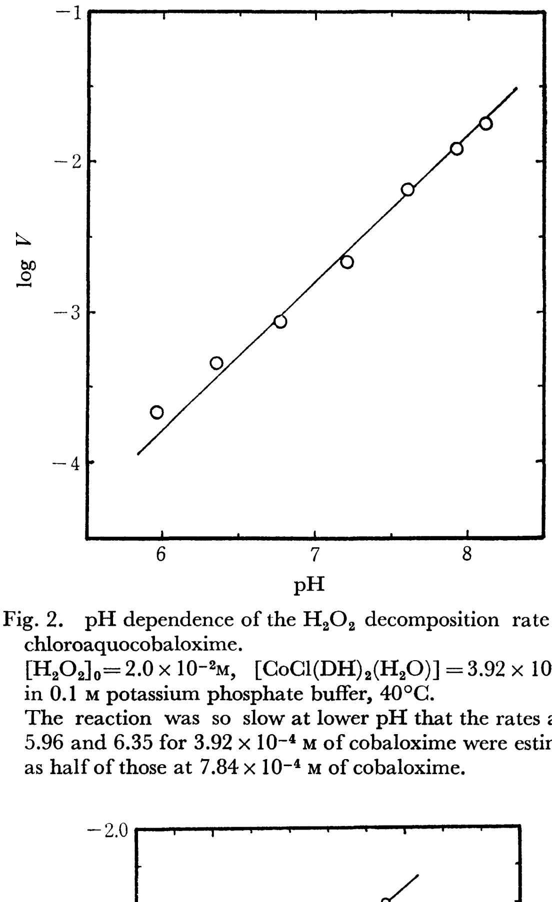

Fig. 2. pH dependence of the H_2O_2 decomposition rate with chloroaquocobaloxime.
$[H_2O_2]_0=2.0\times10^{-2}$M, $[CoCl(DH)_2(H_2O)]=3.92\times10^{-4}$ M, in 0.1 M potassium phosphate buffer, 40°C.
The reaction was so slow at lower pH that the rates at pH 5.96 and 6.35 for 3.92×10^{-4} M of cobaloxime were estimated as half of those at 7.84×10^{-4} M of cobaloxime.

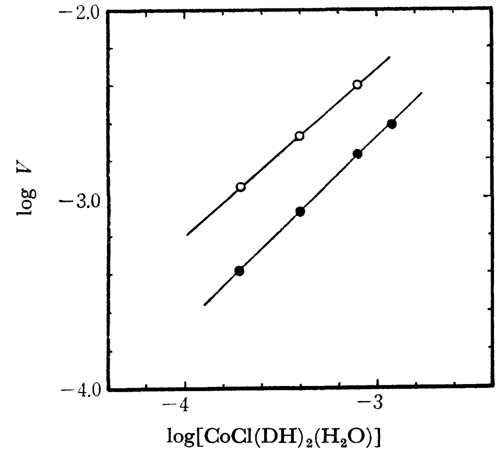

Fig. 3. Dependence of the H_2O_2 decomposition rate upon the concentration of chloroaquocobaloxime.
$[H_2O_2]_0=2.0\times10^{-2}$ M, in 0.1 M potassium phosphate buffer (—○—, pH 7.2; —●—, pH 6.8), 40°C.

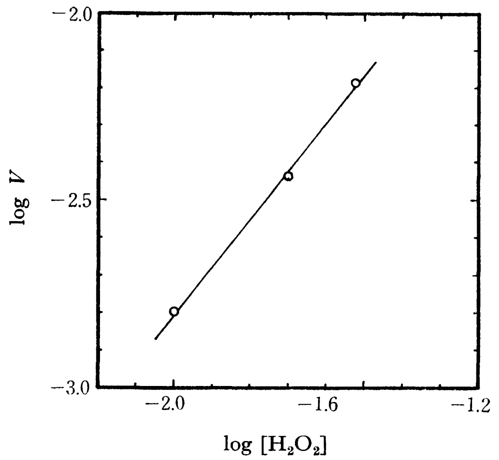

Fig. 4. Dependence of the H_2O_2 decomposition rate upon the concentration of H_2O_2.
$[CoCl(DH)_2(H_2O)]=3.92\times10^{-4}$ M, in 0.1 M potassium phosphate buffer (pH7.2), 40°C.

The results can be summarized in the following equation for the decomposition rate of H_2O_2:

$$V = -\frac{d[H_2O_2]}{dt} = k\cdot\frac{[\text{Cobaloxime}][H_2O_2]}{[H^+]}.$$

A similar rate law was obtained in the reaction of cobaltic ion and H_2O_2 by Baxendale and Wells.[5] Since in our experiments cobaltous chloride which is considered to be oxidized to cobaltic ion in this experimental condition yielded the same rate without lag time as the cobaloximes, the active intermediates in the reaction with cobaloximes are estimated to have more than one free coordination site. Thus the presence of a lag time whose length differs in each case can be explained as follows: The hydroxide or chloride ligand is readily displaced by H_2O_2 or presumably HO_2^-, and hence hydroxo- or chloro-cobaloximes show little lag time, while a strongly coordinated cyano ligand is not readily displaced, resulting in the appearance of lag time.

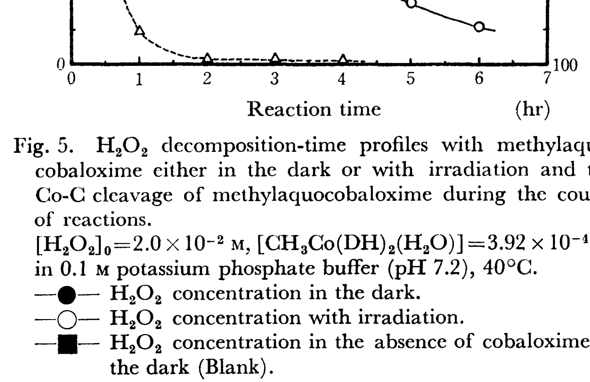

Fig. 5. H_2O_2 decomposition-time profiles with methylaquocobaloxime either in the dark or with irradiation and the Co-C cleavage of methylaquocobaloxime during the course of reactions.
$[H_2O_2]_0=2.0\times10^{-2}$ M, $[CH_3Co(DH)_2(H_2O)]=3.92\times10^{-4}$ M, in 0.1 M potassium phosphate buffer (pH 7.2), 40°C.

—●— H_2O_2 concentration in the dark.
—○— H_2O_2 concentration with irradiation.
—■— H_2O_2 concentration in the absence of cobaloxime in the dark (Blank).
—□— H_2O_2 concentration in the absence of cobaloxime with irradiation (Blank).
…▲… Co-C cleavage in the dark.
…△… Co-C cleavage with irradiation.

Methylaquocobaloxime yielded the same rate in the dark as that with the irradiation of visible light, which was performed at a distance of 15 cm with a 100 W tungsten lamp. The decomposition-time profile, however, was distinctly different as shown in Fig. 5. The lag time was observed in the dark, while with irradiation the reaction proceeded without induction period. The degree of the Co–C bond fission at the same time which was determined spectrophotometrically from the decrease in absorption at 443 mμ[6] is also given in Fig. 5. 78% of methyl-Co bond was cleaved by the decomposition reaction of H_2O_2 in the dark. However, the Co–C cleavage step is not considered to be the rate determining step, since the solution of methylaquocobaloxime irradiated prior to the addition of H_2O_2, which exhibits the absorption maximum at 246 mμ due to dimethylglyoximato ligand and is considered to contain hydroxoaquocobaloxime,[6] exerted the same rate in the H_2O_2 decomposition reaction as methylaquocobaloxime in the dark. As the reaction proceeds, the gradual decrease in absorption occurs at a wavelength longer than 230 mμ up to the visible region.

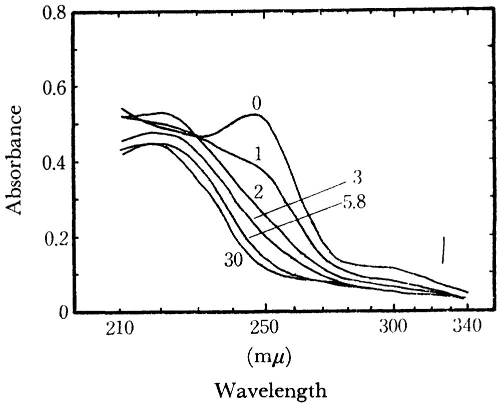

Fig. 6. UV spectral change during the course of the H_2O_2 decomposition reaction by chloroaquocobaloxime.
H_2O_2 decomposition reaction was conducted under the following conditions; $[H_2O_2]_0=2.0\times10^{-2}$ M, $[CoCl(DH)_2(H_2O)]=3.92\times10^{-4}$ M, in 0.1 M potassium phosphate buffer (pH 7.2), at 40°C.
Aliquots were taken after 1, 2, 3, 5, 5.8, and 30 hr, and diluted 20 times to obtain the spectra. At the same time, the percentages of the H_2O_2 decomposed were determined and found to be 14% (1 hr), 35% (2 hr), 49% (3 hr),81% (5.8 hr), and 100% (30 hr), respectively.

There is some indication in the UV spectra that the cobaloxime is transformed or degradated by H_2O_2. The spectral change during the course of the reaction with the preirradiated solution of methylaquocobaloxime as well as with chloroaquocobaloxime solution proceeded quite similarly (Fig. 6): The gradual decrease in ab-

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[5] J. H. Baxendale and C. F. Wells, *Trans. Faraday Soc.*, **53**, 800 (1957).

[6] N. Yamazaki and Y. Hohokabe, "Studies on Cobaloxime Compounds. VI.," submitted to this Bulletin.

sorption occurs at a wavelength longer than 230 mμ up to the visible region with the progress of reaction. The absorption maximum at 246 mμ both in chloro- and hydroxo-aquocobaloximes decreased in intensity and the maximum shifted to *ca.* 220 mμ. Thus, the spectrum of the solution immediately after the addition of H_2O_2 did not differ from that before the addition of H_2O_2, but after an hour when 14—16% of H_2O_2 was decomposed, the absorption maximum at 246 mμ decreased to 65% in intensity and the new absorption maximum appeared at *ca.* 220 mμ. As the reaction further proceeded, the maximum at 246 mμ decreased gradually, but not that at 220 mμ. This seems to show that a partial decomposition of cobaloxime occurs. In fact, by concentrating the solution after the reaction, a trace of blue precipitate was recovered. This seemed to be an inorganic compound whose infrared spectrum is quite different from that of original or typical cobaloximes. The maximum at 220 mμ shifted to 275 mμ when solid alkali was added to the solution. Since dimethylglyoxime which has an absorption maximum at 224 mμ in acidic medium is known to shift the maximum to 265 mμ in alkaline medium,[7) the spectral change in the presence of alkali suggests that the solution contains some substance like oxime which can be dissociated in alkaline medium. This may be some form of cobaloxime or some degradation product.

Thus, it is concluded that cobaloximes catalyze the decomposition of H_2O_2, and they themselves are also gradually and partially degradated during the course of the reaction. The lower activity of cyanocobaloximes than hydroxo-, chloro-, or methyl-cobaloximes can be attributed to higher stability toward the reactant H_2O_2 than other cobaloximes due to stronger interaction of cyano group with Co. A mechanism has been proposed for the decomposition reaction with ferric ion,[8) in which the peroxide concentration was higher than ferric ion concentration. This can be applied to the reactions with cobaloximes. The primary active species reacting with cobaloximes seems to be HO_2^-, but not H_2O_2 as in the case of pentacyanocobaltate(II),[9) since the rate was inversely proportional to $[H^+]$. HO_2^- may coordinate with Co(III) species forming CoOOH by electron transfer from HO_2^- to Co(III). The presence of hydroperoxocobaloxime may be supported by Schrauzer's recent observation of the relative stable mononuclear peroxocobaloxime radicals.[10)

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7) K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nucl. Chem.*, **27**, 179 (1965).

8) F. Haber and J. Weiss, *Proc. Roy. Soc. (London)*, **A147**, 332 (1934).

9) P. B. Chock, R. B. K. Dewar, J. Halpern, and L-Y. Wong, *J. Amer. Chem. Soc.*, **91**, 82 (1969).

10) G. N. Schrauzer and L. P. Lee, *ibid.*, **92**, 1551 (1970).