

On subjecting the compound to distillation, a white viscous liquid with some silvery tinge was obtained at 128° (0.9 mm). The analysis of the distillate corresponded to that of aluminum isopropoxide. *Anal.* Calcd for Al(*i*-PrO)<sub>3</sub>: Al, 13.2; *i*-PrO, 86.8. Found: Al, 13.2; *i*-PrO, 86.8.

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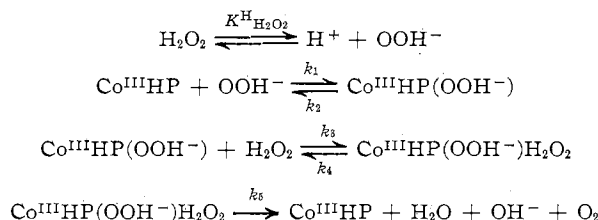
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## Metal Ions and Hydrogen Peroxide. XXVI.<sup>1</sup> On the Kinetics and Mechanism of the Catalase-Like Activity of Cobalt(III) Hematoporphyrin

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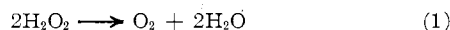
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The disproportionation of H<sub>2</sub>O<sub>2</sub>, catalyzed by the Co(III) complex of hematoporphyrin IX (Co<sup>III</sup>HP), was investigated in the pH range 5.5–10 by measuring the initial rate, *v*<sub>0</sub>, of the increasing concentration of O<sub>2</sub> (25°, *I* = 0.1). In contrast to the usual inertness of Co(III) complexes the fifth and sixth coordination positions in Co<sup>III</sup>HP are sufficiently labile toward substitution to make Co<sup>III</sup>HP a usable catalyst. In the pH range 5.5–6.5 *v*<sub>0</sub> is proportional to 1/[H<sup>+</sup>], in the pH range 8–10 *v*<sub>0</sub> is independent of the pH. At pH 6.15 *v*<sub>0</sub> is proportional to [H<sub>2</sub>O<sub>2</sub>]<sup>2</sup> and at pH 9.20 to [H<sub>2</sub>O<sub>2</sub>]. This is evidence that in the higher pH range 8–10 the catalyst is present as a peroxo complex, CoHP(OOH<sup>-</sup>). In the whole pH range *v*<sub>0</sub> is proportional to [Co<sup>III</sup>HP]. Based on these experimental results the following reaction scheme was postulated



By using the steady-state approximation a rate law was derived which is in accord with the above mechanism. From experiments with [H<sub>2</sub>O<sub>2</sub>]<sub>tot(t=0)</sub> > [Co<sup>III</sup>HP]<sub>tot</sub> the kinetic parameters were determined: *k*<sub>1</sub> = 5.01 × 10<sup>6</sup> M<sup>-1</sup> sec<sup>-1</sup>, *k*<sub>2</sub> = 7.2 × 10<sup>-2</sup> sec<sup>-1</sup>, (*k*<sub>4</sub> + *k*<sub>5</sub>)/*k*<sub>3</sub> = 1.95 × 10<sup>-3</sup> M, and *k*<sub>5</sub> = 6.76 × 10<sup>-2</sup> sec<sup>-1</sup>. The stability constants of the peroxo adducts are log *K*<sup>CoHP</sup><sub>CoHP(OOH)</sub> = 7.84 and log *K*<sup>CoHP(OOH)</sup><sub>CoHP(OOH)(H<sub>2</sub>O<sub>2</sub>)</sub> ≥ 2.7. From these results log *v*<sub>0</sub> could be calculated with dependence on pH; the obtained curve is in excellent agreement with the experimental one. Hence, the postulated mechanism is in accord with all experimental facts. The structure of the active species is discussed; as the two peroxo ligands, OOH<sup>-</sup> and H<sub>2</sub>O<sub>2</sub>, must be bound in a trans arrangement, it is suggested that the electron transfer occurs through the metal ion. In general Co<sup>III</sup>HP is significantly more active than is usual for Co(III) complexes. However, the catalase-like activity of Co<sup>III</sup>HP is of comparable order to the one due to other metal ion complexes.

The disproportionation of hydrogen peroxide in a homogenous phase is catalyzed by metal ions and their complexes. A suitable catalyst for reaction 1 has to



have at least the following three distinct qualities. (i) The metal ion has to be redox active, *i.e.*, there must be two or more different oxidation states of reasonable stability.<sup>2,3</sup> (ii) "Free" coordination positions must be available, because the reaction proceeds within the coordination sphere of the metal ion; *i.e.*, H<sub>2</sub>O<sub>2</sub> or derivatives thereof must be able to coordinate at the metal ion.<sup>4</sup> (iii) The coordination sphere of the metal ion must be "labile"; *i.e.*, sufficiently high exchange rates are necessary that a catalyst may be effective.

Among the metal ions with a pronounced catalase-like activity, iron(III) and copper(II) are probably most well known. Both metal ions fulfill the mentioned conditions i and iii; ii is easily achieved by selecting suitable ligands, *e.g.*, hematoporphyrin<sup>5</sup> or 4,4',4'',4'''-tetrasulfophthalocyanine<sup>6</sup> with Fe<sup>3+</sup>, or 2,2'-bipyridyl<sup>7</sup> with Cu<sup>2+</sup>.

Due to the usual inert behavior of cobalt(III) complexes, these were so far not considered as very active catalysts. However, recently Fleischer, *et al.*,<sup>8</sup> have demonstrated that cobalt(III)-hematoporphyrin is rather labile with respect to substitution reactions. This report stimulated us to study the kinetics of the catalase-like activity of the Co(III) complex of hematoporphyrin IX,<sup>9</sup> which is indeed significantly more

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(8) E. B. Fleischer, S. Jacobs, and L. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).

(9) For the formula of the ligand *cf.*, *e.g.*, ref 8.

active than Co<sup>III</sup>Cyclam or Co<sup>III</sup>HDT.<sup>10</sup> The planar geometry of Co<sup>III</sup>HP makes this complex further appealing for such an investigation, because no cis-trans isomerism may occur, a fact which favors the interpretation of the results.

The catalase-like activity of Co<sup>III</sup>HP was studied in the pH range 5.5–10 and the reaction parameters were determined. The activity of Co<sup>III</sup>HP and, for reasons of comparison, that of Co<sup>III</sup>Cyclam or Co<sup>III</sup>HDT were measured with an oxygen-sensitive electrode and characterized by the initial rate of the O<sub>2</sub> formation ( $v_0 = d[O_2]/dt$ ; mol l.<sup>-1</sup> sec<sup>-1</sup>).

### Experimental Section

**Materials and Apparatus.**—Hematoporphyrin IX dihydrochloride and Co(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O were obtained from Fluka AG, Buchs, Switzerland. Cyclam was a gift from Dr. A. Portmann.<sup>11</sup> This ligand had been prepared according to Bosnich, *et al.*,<sup>12</sup> and was recrystallized four times from dioxane; mp 184–185°.<sup>13</sup>

Carbonato-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienecobalt(III) perchlorate was synthesized according to Sadasivan and Endicott.<sup>14</sup> To remove the carbonate, a solution of the complex was adjusted to a pH of 2.5 and for 2 hr nitrogen was passed through the solution.

A solution of Co<sup>III</sup>Cyclam was made as described by Portmann.<sup>11</sup>

A stock solution of Co<sup>III</sup>HP was prepared by dissolving a certain amount of cobalt perchlorate in water, adding a 5% excess of hematoporphyrin IX, and adjusting to a pH of 8. This solution was kept at 45° until no further change in the spectrum was observed (about 4 hr). One obtains the characteristic absorptions described by McConnel, *et al.*,<sup>15</sup> 559 and 525 nm. The solutions were stored in the refrigerator and used within 2 days. Different preparations gave the same catalase-like activity. HP alone was inactive. All the other reagents and the apparatus were the same as used earlier.<sup>6</sup>

**Measurements of Catalysis and Evaluation of the Data.**—These were done exactly as described recently.<sup>6</sup> The logarithms of the initial rates,  $v_0$ , of the O<sub>2</sub> formation according to reaction 1 were plotted vs. the varied concentrations of the reagent, A. From the slope of the straight-line portion of the plots the relation between the reaction rate and the concentration of the reagent, A, was taken. The concentrations and compositions of the reaction solutions can be seen from the legends to the figures ( $I = 0.1$ , 25°). The average deviation of the experiments, with regard to  $\log v_0$ , was less than  $\pm 0.1$  log unit (*cf.* the figures).

### Results and Discussion

**Parameters of the Reaction.**—The catalyst, Co<sup>III</sup>HP, is somewhat oxidized by H<sub>2</sub>O<sub>2</sub>, as may be observed spectrophotometrically at the absorption at 559 nm. This is in line with the observations made with other catalysts.<sup>1,6,16</sup> However, the amount of oxidation of Co<sup>III</sup>HP is insignificant within the time range used for the evaluation,<sup>17</sup> *i.e.*, the determination of the initial rate,  $v_0$ , of the O<sub>2</sub> formation.

First, the dependence of the reaction rate of the catalysis of the disproportionation of H<sub>2</sub>O<sub>2</sub> on pH was in-

(10) Abbreviations used: [A]<sub>tot</sub>, total concentration of the reagent A; bipy, 2,2'-bipyridyl; Cyclam, 1,4,8,11-tetraazacyclotetradecane; DMG, dimethylglyoximate; HDT, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; HP, hematoporphyrin IX; I, inhibitor; L, general ligand; PTS, 4,4',4'',4'''-tetrasulfophthalocyanine.

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(16) Y. Hohokabe and N. Yamazaki, *Bull. Chem. Soc. Jap.*, **44**, 738 (1971).

(17) For example, the first 30 sec was used for a solution at pH 6.15, with [Co<sup>III</sup>HP]<sub>tot</sub> = 10<sup>-4</sup> M and [H<sub>2</sub>O<sub>2</sub>]<sub>tot(t=0)</sub> = 10<sup>-2</sup> M, or the first 200 sec was used for the same solution but with [H<sub>2</sub>O<sub>2</sub>]<sub>tot(t=0)</sub> = 5 × 10<sup>-4</sup> M.

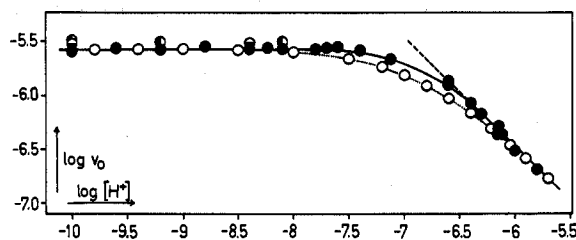


Figure 1.—Catalase-like activity of Co<sup>III</sup>HP (●, 10<sup>-4</sup> M). Dependence on pH at an initial concentration of [H<sub>2</sub>O<sub>2</sub>] = 1.25 × 10<sup>-3</sup> M, determined as the initial rate,  $v_0$  (mol l.<sup>-1</sup> sec<sup>-1</sup>), of the O<sub>2</sub> evolution. Buffers: [phosphate] = 0.05 M, pH 5.5–8.23; [borate] = 0.1 M, pH 8.1–10. In all cases [Na<sup>+</sup>]<sub>tot</sub> = 0.1 M and the temperature is 25°. Experiments without or only with little buffer: ○, pH adjusted by dotting with NaOH; ●, [borate] = 10<sup>-2</sup> M. The calculated (*cf.* eq 11) dependence on pH of the initial rate,  $v_0$  (mol l.<sup>-1</sup> sec<sup>-1</sup>), of the O<sub>2</sub> evolution is given by the dotted line and the empty points (○).

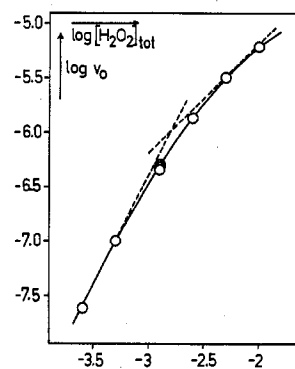


Figure 2.—Catalase-like activity of Co<sup>III</sup>HP (10<sup>-4</sup> M). Dependence on the initial concentration of H<sub>2</sub>O<sub>2</sub> at pH 6.15 ([phosphate] = 0.05 M), determined as the initial rate,  $v_0$  (mol l.<sup>-1</sup> sec<sup>-1</sup>), of the O<sub>2</sub> evolution; [Na<sup>+</sup>]<sub>tot</sub> = 0.1 M; 25°.

vestigated at a constant initial concentration of H<sub>2</sub>O<sub>2</sub> and a constant concentration of Co<sup>III</sup>HP. In Figure 1 the results are shown for the series of measurements. At pH < 6.5 the initial rate,  $v_0$ , is proportional to 1/[H<sup>+</sup>] and at pH > 8 the reaction rate is independent of the pH.

Additionally, in Figure 1 several experiments were shown with solutions that contained no or only little buffer. The concentration of Na<sup>+</sup> was kept constant (0.1 M) in these experiments by the addition of NaClO<sub>4</sub>. The rates of the reaction observed under these conditions are not significantly different from the other rates determined. Thus, it may be concluded that the anions of the buffers have no measurable influence on  $v_0$ .

The dependence of  $v_0$  on the initial concentration of H<sub>2</sub>O<sub>2</sub> was studied in several series at constant concentrations of Co<sup>III</sup>HP. At pH 6.15, *i.e.*, in the pH region where  $v_0$  is dependent on pH, the slope of the curve obtained by plotting  $\log v_0$  vs.  $\log [H_2O_2]_{tot(t=0)}$  proceeds from 2 over 1 to <1 as can be seen in Figure 2. In Figure 3, the results obtained at pH 9.20, *i.e.*, in the pH region where  $v_0$  is independent of pH, are plotted: here the slope of the curves changes from 1 to <1. Hence, one can conclude that at pH 6.15  $v_0$  is proportional to [H<sub>2</sub>O<sub>2</sub>]<sub>tot</sub><sup>2</sup> and at pH 9.20  $v_0$  is linearly proportional to [H<sub>2</sub>O<sub>2</sub>]<sub>tot</sub>. This result combined with the observed pH dependence suggests that at pH > 8 the catalyst exists as the peroxo complex Co<sup>III</sup>HP(OOH<sup>-</sup>)

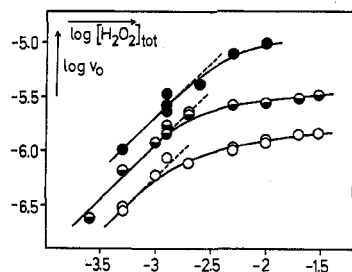


Figure 3.—Catalase-like activity of  $\text{Co}^{\text{III}}\text{HP}$  (O,  $2.5 \times 10^{-5} M$ ;  $\ominus$ ,  $5 \times 10^{-5} M$ ;  $\bullet$ ,  $10^{-4} M$ ). Dependence on the initial concentration of  $\text{H}_2\text{O}_2$  at pH 9.20 ([borate] = 0.1 M), determined as the initial rate,  $v_0$  ( $\text{mol l}^{-1} \text{sec}^{-1}$ ), of the  $\text{O}_2$  evolution;  $[\text{Na}^+]_{\text{tot}} = 0.1 M$ ;  $25^\circ$ .

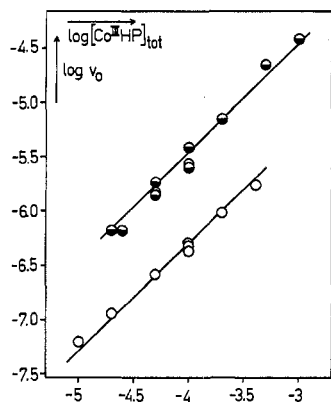


Figure 4.—Catalase-like activity of  $\text{Co}^{\text{III}}\text{HP}$ . Dependence on the total concentration of  $\text{Co}^{\text{III}}\text{HP}$  at  $[\text{H}_2\text{O}_2]_{\text{tot}}(t=0) = 1.25 \times 10^{-3} M$  and pH 6.15 (O, [phosphate] = 0.05 M) or pH 9.20 ( $\ominus$ , [borate] = 0.1 M), determined as the initial rate,  $v_0$  ( $\text{mol l}^{-1} \text{sec}^{-1}$ ), of the  $\text{O}_2$  evolution;  $[\text{Na}^+]_{\text{tot}} = 0.1 M$ ;  $25^\circ$ .

while in the lower pH region this complex is in equilibrium with  $\text{Co}^{\text{III}}\text{HP}$ .

The influence of the concentration of the catalyst,  $\text{Co}^{\text{III}}\text{HP}$ , on  $v_0$  was determined in two series. The concentration of  $\text{Co}^{\text{III}}\text{HP}$  was varied at constant pH and constant initial concentrations of  $\text{H}_2\text{O}_2$ . The results given in Figure 4 show that at pH 6.15, as well as at pH 9.20,  $v_0$  is proportional to  $[\text{Co}^{\text{III}}\text{HP}]_{\text{tot}}$ .

At this point it should be noted that there is evidence in the literature that porphyrins may exist as dimers or even polymers in solution.<sup>18,19</sup> For  $\text{Co}^{\text{III}}\text{HP}$ , based on a Beer's law plot in the concentration range  $10^{-6}$  to  $5 \times 10^{-4} M$ , we could find no hint of a dimerization; this is in agreement with Loach and Calvin's deduction of the monomeric nature of manganese(III) hematoporphyrin.<sup>20</sup> Fleischer, *et al.*,<sup>8</sup> who have studied substitution reactions at the fifth and sixth coordination positions of  $\text{Co}^{\text{III}}$  in HP, concluded also "that, if dimers or aggregates do exist, they do not seem to influence the ligand reactions studied"; this is in line with our own observations. Furthermore, it must be noted that the observed linear proportionality between  $v_0$  and  $[\text{Co}^{\text{III}}\text{HP}]_{\text{tot}}$  can be explained only by the following three principal ways. (i) All  $\text{Co}^{\text{III}}\text{HP}$  is present in the dimer form and the dimer is the catalyst. Based on the results obtained with heme,<sup>5</sup>  $\text{Co}^{\text{II}}\text{PTS}$ ,<sup>1</sup> and  $\text{Fe}^{\text{III}}$ -

(18) J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, London, and New York, N. Y., 1964.

(19) R. R. Das, R. F. Pasternack, and R. A. Plane, *J. Amer. Chem. Soc.*, **92**, 3312 (1970).

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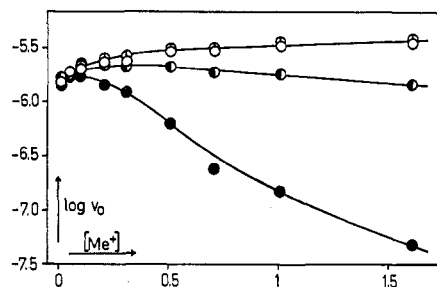


Figure 5.—Catalase-like activity of  $\text{Co}^{\text{III}}\text{HP}$  ( $5 \times 10^{-5} M$ ). Dependence on the ionic strength ( $\bullet$ ,  $\text{LiClO}_4$ ; O,  $\text{NaClO}_4$ ;  $\ominus$ ,  $\text{KNO}_3$ ) at  $[\text{H}_2\text{O}_2]_{\text{tot}}(t=0) = 1.25 \times 10^{-3} M$  and pH 9.20 ([borate] = 0.0025, 0.005, or 0.01 M), determined as the initial rate,  $v_0$  ( $\text{mol l}^{-1} \text{sec}^{-1}$ ), of the  $\text{O}_2$  evolution;  $25^\circ$ .

$\text{PTS}^6$  such an assumption appears completely unjustified. (ii) The monomer and the dimer are catalysts of equal activity (per  $\text{Co}^{\text{III}}$ ); such an equality is highly improbable. (iii)  $\text{Co}^{\text{III}}\text{HP}$  exists under the experimental conditions in the monomer form.<sup>21-23</sup> As already stated above this appears to be the case.<sup>24,25</sup>

**Influence of the Ionic Strength.**—The influence of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  on the initial rate,  $v_0$ , of the decomposition of  $\text{H}_2\text{O}_2$  is shown in Figure 5. At low ionic strength (up to 0.1) all three alkali ions have the same influence; *i.e.*,  $v_0$  increases. This observation could be explained by ion-pair formation between the alkali ions and the two carboxylate groups of  $\text{Co}^{\text{III}}\text{HP}$ . This would compensate the negative charge of the carboxylate groups and thus facilitate the reaction between  $\text{OOH}^-$  and  $\text{Co}^{\text{III}}\text{HP}$ . In any case, this experimental result is in agreement with the assumption of the monomeric nature of  $\text{Co}^{\text{III}}\text{HP}$ . In contrast herewith, the catalase-like activity of  $\text{Co}^{\text{II}}\text{PTS}$  and  $\text{Fe}^{\text{III}}\text{PTS}$ , for which the monomer-dimer equilibria are well established,<sup>23</sup> decreases with increasing ionic strength,<sup>1,6</sup> and the latter is known to favor the formation of the (less active or inactive) dimers.

At ionic strength  $>0.1$  the influence of the three alkali ions on  $v_0$  is very different. This is in contrast to the observations made with  $\text{Co}^{\text{II}}\text{PTS}$  and  $\text{Fe}^{\text{III}}\text{PTS}$  where all three alkali ions had the same influence over the whole investigated range of ionic strength.<sup>1,6</sup> It is not possible to give a simple explanation for the present case, as neither the ionic radii nor the radii of the hydrated ions<sup>26</sup> of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  can be ordered in a way analogous to the curves of activity shown in Figure 5. Finally, it should be noted that increasing concentrations of  $\text{NaNO}_3$  or  $\text{NaClO}_4$  influence the catalase-

(21) One may ask which order the dimerization constant,  $K_D = [(\text{Co}^{\text{III}}\text{HP})_2]/[\text{Co}^{\text{III}}\text{HP}]^2$ , could have under the present experimental conditions that no significant amounts of (inactive) dimer exist; *i.e.*, no significant deviation from a slope of 1 is observed. Based on the experiments of Figure 4 one estimates  $\log K_D \lesssim 3.5$ . For an ethylenediamine-substituted metal-free porphyrin,  $\log K_D = 5.85$  was determined.<sup>19</sup> It is interesting to compare these values with those due to  $\text{H}_2\text{PTS}$  and  $\text{Co}^{\text{II}}\text{PTS}$ :  $\log K_D = 7.8$ <sup>22</sup> and 5.5,<sup>23</sup> respectively.

(22) K. Bernauer and S. Fallab, *Helv. Chim. Acta*, **45**, 2487 (1962).

(23) H. Sigel, P. Waldmeier, and B. Priejs, *Inorg. Nucl. Chem. Lett.*, **7**, 161 (1971).

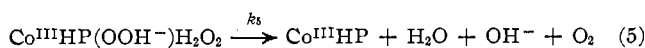
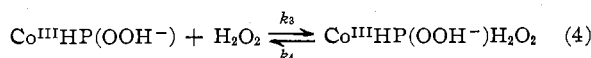
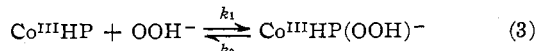
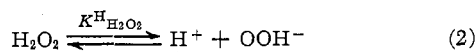
(24) In this connection the following statement of Falk<sup>18</sup> is of interest: "... while both ferrous and ferric porphyrins tend to polymerize in aqueous solution, particularly in the alkaline media... no evidence of polymerisation of  $\text{Mn}(\text{II})$ ,  $\text{Mn}(\text{III})$ ,  $\text{Co}(\text{II})$  or  $\text{Co}(\text{III})$  mesoporphyrins in aqueous solution has been found." Maybe the key to these differences is the fact that the dimerization of ferrihemes occurs *via* hydroxo-oxo bridges.<sup>25</sup>

(25) S. B. Brown, T. C. Dean, and P. Jones, *Biochem. J.*, **117**, 733 (1970).

(26) F. A. Cotton and G. Wilkinson, "Anorganische Chemie," translated by H. P. Fritz, Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1967, p 395.

like activity of Co<sup>III</sup>HP in the same way; *i.e.*, the anions are without influence.

**Mechanism of the Catalysis.**—The results obtained at pH 6.15 and an ionic strength of 0.1 (Na<sup>+</sup>, 25°) give evidence that the initial rate,  $v_0$ , of the disproportionation of H<sub>2</sub>O<sub>2</sub> is linearly proportional to the concentration of the catalyst, Co<sup>III</sup>HP, and also proportional to 1/[H<sup>+</sup>] and [H<sub>2</sub>O<sub>2</sub>]<sup>2</sup> (*cf.* Figures 1, 2, and 4). In the pH range 5.5–10 Co<sup>III</sup>HP is not hydrolyzed ( $pK_A = 10.5$ );<sup>8</sup> therefore, taking into account the mentioned proportionalities the following reaction scheme can be written



Obviously, on the basis of data obtained by studies of the kinetics it is not possible to distinguish between the coordination of H<sub>2</sub>O<sub>2</sub> to Co<sup>III</sup>HP and subsequent deprotonation or the coordination of OOH<sup>-</sup> as described by equilibria 2 and 3. However, the latter formulation is more convenient for considerations which are to follow and was therefore used. If equilibrium 3 is completely on its right side,  $v_0$  becomes independent of the pH and is only linearly proportional to the concentration of H<sub>2</sub>O<sub>2</sub>; in other words, this describes the situation as observed in the pH range 8–10 (*cf.* Figures 1, 3, and 4). The rate-determining step of the catalysis is reaction 5.

At the end of the cycle of a catalytic reaction the catalyst is restored; therefore, it is reasonable to treat such a system according to the steady-state method.<sup>27</sup> Then in accord with the reaction scheme (2)–(5) for the change of the concentrations of Co<sup>III</sup>HP(OOH)<sup>-</sup>H<sub>2</sub>O<sub>2</sub> and Co<sup>III</sup>HP it holds that

$$\frac{d[\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2]}{dt} = k_3[\text{CoHP}(\text{OOH})][\text{H}_2\text{O}_2] - k_4[\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] - k_5[\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] = 0 \quad (6)$$

$$\frac{d[\text{CoHP}]}{dt} = k_2[\text{CoHP}(\text{OOH})] - k_1[\text{CoHP}][\text{OOH}^-] + k_5[\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] = 0 \quad (7)$$

If eq 6 is solved for [CoHP(OOH)], eq 7 for [CoHP], [OOH<sup>-</sup>] replaced by  $K^{\text{H}}_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]/[\text{H}^+]$ , and the resulting expressions substituted in the equation

$$[\text{CoHP}]_{\text{tot}} = [\text{CoHP}] + [\text{CoHP}(\text{OOH})] + [\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] \quad (8)$$

one obtains<sup>28</sup> eq 9.

(27) H. R. Mahler and E. H. Cordes, "Biological Chemistry," Harper and Row, New York, N. Y., Evanston, Ill., and London, and John Weatherhill, Inc., Tokyo, 1966.

(28) In principle, instead of [H<sub>2</sub>O<sub>2</sub>] the equation [H<sub>2</sub>O<sub>2</sub>]<sub>tot</sub> = [H<sub>2</sub>O<sub>2</sub>] + [CoHP(OOH)] + 2[CoHP(OOH)H<sub>2</sub>O<sub>2</sub>] should be used. However, in the experiments used for the evaluations (Figures 2 and 3) [H<sub>2</sub>O<sub>2</sub>]<sub>tot(t-Δt)</sub> > [Co<sup>III</sup>HP]<sub>tot</sub> always holds and, therefore, in good approximation [H<sub>2</sub>O<sub>2</sub>]<sub>tot</sub> = [H<sub>2</sub>O<sub>2</sub>].

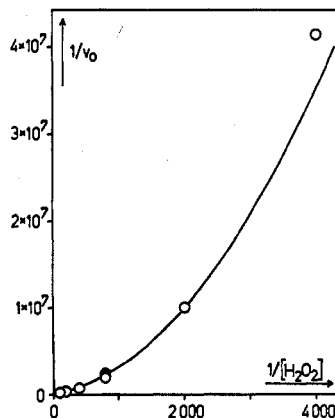


Figure 6.—Determination of the reaction parameters of the catalysis (*cf.* eq 12 and 13) by a Lineweaver–Burk-like plot of the experimental results (O) at pH 6.15 of Figure 2. The drawn curve is the result of a regression calculation<sup>29</sup> using  $v_0^2$  weight factors.<sup>30,31</sup>

$$[\text{CoHP}]_{\text{tot}} = [\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] \times \left\{ \frac{k_2 \frac{k_4 + k_5}{k_3} \frac{1}{[\text{H}_2\text{O}_2]} + k_5}{k_1 K^{\text{H}}_{\text{H}_2\text{O}_2} \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]}} + \frac{k_4 + k_5}{k_3} \frac{1}{[\text{H}_2\text{O}_2]} + 1 \right\} \quad (9)$$

Equation 10 holds for  $v_0$ , as follows from reaction 5.

$$v_0 = \frac{d[\text{O}_2]}{dt} = k_5[\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] \quad (10)$$

If eq 9 is solved for [CoHP(OOH)H<sub>2</sub>O<sub>2</sub>] and the resulting expression substituted in eq 10, one obtains the general rate law (11) which is in accord with the reaction mechanism as described by eq 2–5.

$$v_0 = \frac{k_5[\text{CoHP}]_{\text{tot}}[\text{H}_2\text{O}_2]^2}{\frac{k_2 k_4 + k_5}{k_1 k_3 K^{\text{H}}_{\text{H}_2\text{O}_2}} [\text{H}^+] + \left( \frac{k_5}{k_1 K^{\text{H}}_{\text{H}_2\text{O}_2}} [\text{H}^+] + \frac{k_4 + k_5}{k_3} \right) [\text{H}_2\text{O}_2] + [\text{H}_2\text{O}_2]^2} \quad (11)$$

For the determination of the constant parameters, eq 11 is transformed to

$$\frac{1}{v_0} = \frac{k_2 k_4 + k_5}{k_1 k_3 K^{\text{H}}_{\text{H}_2\text{O}_2}} \frac{[\text{H}^+]}{k_5[\text{CoHP}]_{\text{tot}}} \frac{1}{[\text{H}_2\text{O}_2]^2} + \frac{k_5}{k_1 K^{\text{H}}_{\text{H}_2\text{O}_2}} \frac{[\text{H}^+]}{k_5[\text{CoHP}]_{\text{tot}}} + \frac{k_4 + k_5}{k_3} \frac{1}{[\text{H}_2\text{O}_2]} + \frac{1}{k_5[\text{CoHP}]_{\text{tot}}} \quad (12)$$

This equation is of the second order and of the general form

$$y = cx^2 + bx + a \quad (13)$$

The coefficients  $a$ ,  $b$ , and  $c$  were determined from a Lineweaver–Burk-like plot of  $1/v_0$  vs.  $1/[\text{H}_2\text{O}_2]$  with the experimental data at pH 6.15 of Figure 2. In Figure 6 the best fitting curve for the experimental points is shown; this curve is the result of a regression calculation<sup>29</sup> using  $(v_0)^2$  weight factors.<sup>30,31</sup> The results ob-

(29) F. W. Küster, A. Thiel, and K. Fischbeck, "Logarithmische Rechen-tafeln für Chemiker, Pharmazeuten, Mediziner und Physiker," Walter de Gruyter & Co., Berlin, 1962, p 190, 269.

(30) G. N. Wilkinson, *Biochem. J.*, **80**, 324 (1961).

(31) With  $v_0^2$  weight factors all experiments have about the same "weight" in the regression calculation.

tained are

$$a = \frac{1}{k_5[\text{CoHP}]_{\text{tot}}} = 2114 \quad (14)$$

$$b = \frac{\frac{k_3}{k_1 K^{\text{H}}_{\text{H}_2\text{O}_2}}[\text{H}^+] + \frac{k_4 + k_5}{k_3}}{k_5[\text{CoHP}]_{\text{tot}}} = 1202 \quad (15)$$

$$c = \frac{\frac{k_2}{k_1} \frac{k_4 + k_5}{k_3 K^{\text{H}}_{\text{H}_2\text{O}_2}}[\text{H}^+]}{k_5[\text{CoHP}]_{\text{tot}}} = 1.90 \quad (16)$$

From relation 14 one could now calculate the rate constant,  $k_5$ , of the rate-determining step. However, from Figure 2 it can be seen that in these experiments the saturation rate, *i.e.*, a slope of zero, is not even nearly reached. Hence, one cannot expect to obtain an exact value for the rate constant,  $k_5$ , from eq 14; therefore, this value was determined as described below.

Figure 1 demonstrates that at  $\text{pH} > 8$   $v_0$  is independent of  $[\text{H}^+]$ . This means, under these experimental conditions equilibrium 3 is completely on its right side and eq 8 is reduced to eq 17. This is in agreement with

$$[\text{CoHP}]_{\text{tot}} = [\text{CoHP}(\text{OOH})] + [\text{CoHP}(\text{OOH})\text{H}_2\text{O}_2] \quad (17)$$

the observation of only a linear proportionality between  $v_0$  and  $[\text{H}_2\text{O}_2]$  at  $\text{pH} 9.2$  as indicated by Figure 3. Therefore, in eq 11 all terms containing  $[\text{H}^+]$  become negligible and one obtains the simpler rate law for the  $\text{pH}$  region 8–10

$$v_0 = \frac{k_5[\text{CoHP}]_{\text{tot}}[\text{H}_2\text{O}_2]}{\frac{k_4 + k_5}{k_3} + [\text{H}_2\text{O}_2]} \quad (18)$$

For the determination of the constant parameters the procedure of Eadie and Hofstee<sup>27</sup> was used, and eq 18 transformed to eq 19. A plot of  $v_0/[\text{H}_2\text{O}_2]$  vs.  $v_0$  results

$$\frac{v_0}{[\text{H}_2\text{O}_2]} = -\frac{1}{(k_4 + k_5)/k_3} v_0 + \frac{k_5[\text{CoHP}]_{\text{tot}}}{(k_4 + k_5)/k_3} \quad (19)$$

in a straight line, the intercepts with the axis are due to the terms  $k_5[\text{CoHP}]_{\text{tot}}/((k_4 + k_5)/k_3)$  ( $y$  axis) and  $k_5[\text{CoHP}]_{\text{tot}}$  ( $x$  axis). In Figure 7, as an example, the plot is shown for the experiments of Figure 3 at  $\text{pH} 9.2$  and  $[\text{CoHP}]_{\text{tot}} = 2.5 \times 10^{-5} M$ . The straight line was drawn according to a "least-squares" treatment. The average results obtained from the experiments in Figure 3<sup>32</sup> are for the rate constant of the rate-determining step,  $k_5 = 6.76 \times 10^{-2} \text{ sec}^{-1}$ , and for the term  $(k_4 + k_5)/k_3 = 1.95 \times 10^{-3}$ .

With these results and relation 15 one can calculate<sup>33,34</sup> the forward rate constant of equilibrium 3,  $k_1 = 5.01 \times 10^6 M^{-1} \text{ sec}^{-1}$ . Finally, by including eq 16 one obtains  $k_1/k_2 = 6.94 \times 10^7 M^{-1}$  and  $k_2 = 7.2 \times 10^{-2} \text{ sec}^{-1}$ .

Now all the constants appearing in the rate law (11)

(32) The results are the average of the experiments with  $[\text{CoHP}]_{\text{tot}} = 2.5 \times 10^{-5} M$  ( $k_5 = 6.00 \times 10^{-2}$ ;  $(k_4 + k_5)/k_3 = 1.97 \times 10^{-3}$ ) and  $5 \times 10^{-6} M$  ( $k_5 = 7.52 \times 10^{-2}$ ;  $(k_4 + k_5)/k_3 = 1.93 \times 10^{-3}$ ). The experiment with  $[\text{CoHP}] = 10^{-4} M$  was not evaluated, because the saturation rate is not significantly reached; hence, a less exact value would have been obtained.

(33)  $[\text{CoHP}]_{\text{tot}} = 10^{-4} M$  and  $\text{pH}$  is 6.15 (*cf.* Figure 2).

(34)  $K^{\text{H}}_{\text{H}_2\text{O}_2} = 1.55 \times 10^{-12}$ ; V. A. Kargin, *Z. Anorg. Allg. Chem.*, **183**, 77 (1929).

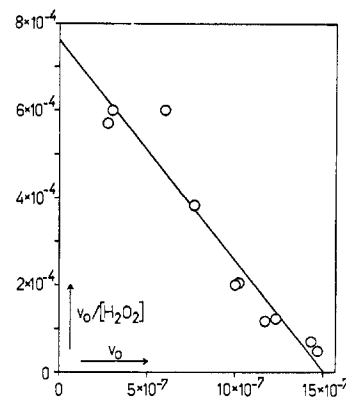
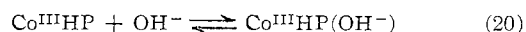


Figure 7.—Determination of the reaction parameters of the catalysis (*cf.* eq 19) by a plot according to Eadie and Hofstee and the experimental results (O) at  $\text{pH} 9.20$  and  $[\text{Co}^{\text{III}}\text{HP}]_{\text{tot}} = 2.5 \times 10^{-5} M$  of Figure 3. The straight line is drawn according to a simple regression method (least squares). Intercept with the  $y$  axis,  $7.63 \times 10^{-4}$ ; slope,  $-0.508 \times 10^3$ .

are determined. Therefore, one can use this rate law and the known constants and calculate the initial rate,  $v_0$ , of the decomposition of  $\text{H}_2\text{O}_2$  by  $\text{Co}^{\text{III}}\text{HP}$  with its dependence on  $\text{pH}$ . For  $[\text{Co}^{\text{III}}\text{HP}] = 10^{-4} M$  and  $[\text{H}_2\text{O}_2]_{\text{tot}(t=0)} = 1.25 \times 10^{-3} M$  one obtains the curve with the empty points given in Figure 1. The agreement between the experimentally determined and the calculated curves is excellent. Hence, the mechanism postulated in eq 2–5 is in agreement with the experimental observations.

**Stability of the  $\text{Co}^{\text{III}}\text{HP}$ -Peroxo Adducts.**—From the rate constants determined in the last section for equilibrium 3 one may calculate the stability constant of the complex formed between  $\text{Co}^{\text{III}}\text{HP}$  and  $\text{OOH}^-$ :  $\log K^{\text{CoHP}}_{\text{CoHP}(\text{OOH})} = \log (k_1/k_2) = 7.84$  ( $[\text{Na}^+] = 0.1, 25^\circ$ ). It is interesting to compare this equilibrium constant with the one due to the reaction between  $\text{Co}^{\text{III}}\text{HP}$  and  $\text{OH}^-$  (eq 20). The hydrolysis constant



of  $\text{Co}^{\text{III}}\text{HP}$  was determined by Fleischer, *et al.*,<sup>8</sup> at  $[\text{Na}^+] = 0.15 M$  and  $25^\circ$  as  $\text{p}K_A = 10.5$ . Using this value and  $\text{p}K_W = 13.75$ , as given by Margerum, *et al.*,<sup>35</sup> for  $[\text{NaClO}_4] = 0.1 M$  and  $25^\circ$ , one obtains  $\log K^{\text{CoHP}}_{\text{CoHP}(\text{OH}^-)} = 3.3$  for the equilibrium constant of eq 20.

A comparison of the two values shows that  $\text{Co}^{\text{III}}\text{HP}$  forms with  $\text{OOH}^-$  a complex that is significantly more stable than the one with  $\text{OH}^-$ . This result is in correlation with the known fact that  $\text{OOH}^-$  has much stronger nucleophilic qualities than  $\text{OH}^-$ , even though the latter is the stronger base.<sup>36</sup>

The second  $\text{Co}^{\text{III}}\text{HP}$ -peroxo adduct is formed according to equilibrium 4 between  $\text{Co}^{\text{III}}\text{HP}(\text{OOH}^-)$  and  $\text{H}_2\text{O}_2$ . For the stability constant the relationship  $K^{\text{CoHP}(\text{OOH})}_{\text{CoHP}(\text{OOH})(\text{H}_2\text{O}_2)} = k_3/k_4$  holds. However, this ratio is not known; we could determine only  $k_3/(k_4 + k_5)$ . Hence, for the stability constant only a lower limit can be given:  $\log K^{\text{CoHP}(\text{OOH})}_{\text{CoHP}(\text{OOH})(\text{H}_2\text{O}_2)} \geq 2.7$ . However, one may expect that the actual value due to  $\log K^{\text{CoHP}(\text{OOH})}_{\text{CoHP}(\text{OOH})(\text{H}_2\text{O}_2)}$  will be close to 2.7.

(35) H. Hauer, E. J. Billo, and D. W. Margerum, *J. Amer. Chem. Soc.*, **93**, 4173 (1971).

(36) Reference 26, p 157; J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962).

This relatively high constant is in agreement with the fact that H<sub>2</sub>O<sub>2</sub> is even more suitable for solvation than H<sub>2</sub>O.<sup>37</sup>

**Comparison of the Catalase-Like Activity of Co<sup>III</sup>HP, Co<sup>III</sup>HDT, and Co<sup>III</sup>Cyclam.**—The rate constant  $k_1$  determined in this study for the reaction between Co<sup>III</sup>HP and OOH<sup>-</sup> (eq 3) confirms the observation of Fleischer, *et al.*,<sup>8</sup> *i.e.*, the great lability of Co(III) in Co<sup>III</sup>HP. It is suggested<sup>8</sup> that the delocalized orbitals of the porphyrin molecule and their interaction with those of the metal ion are responsible for the great substitution lability of Co<sup>III</sup>HP. Therefore, we felt it might be worthwhile to compare the catalase-like activity of Co<sup>III</sup>HP with Co(III) complexes formed by ligands which have no cyclic delocalized orbitals. The ligands chosen are both cyclic tetradentate amines, Cyclam is completely aliphatic, and HDT,<sup>10</sup> which is Cyclam-like, has two double bonds in its ring. In

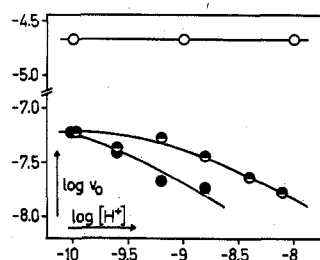


Figure 8.—Catalase-like activity of Co<sup>III</sup>Cyclam (●,  $4 \times 10^{-4}$  M) and Co<sup>III</sup>HDT<sup>10</sup> (●,  $4 \times 10^{-4}$  M). Dependence on pH at an initial concentration of  $[\text{H}_2\text{O}_2]_{\text{tot}(t=0)} = 8 \times 10^{-3}$  M, determined as the initial rate,  $v_0$  (mol l.<sup>-1</sup> sec<sup>-1</sup>), of the O<sub>2</sub> evolution; [borate] = 0.1 M;  $[\text{Na}^+]_{\text{tot}} = 0.1$  M; 25°. For comparison, the activity of Co<sup>III</sup>HP (○) was calculated for the same experimental conditions with eq 11.

Figure 8 the activity of these Co(III) complexes is shown with its dependence on pH.

Indeed, both complexes are significantly less active than Co<sup>III</sup>HP: at pH 8 the difference in activity is more than a factor of  $10^3$ . As there is no evident basic difference between the structure of Co<sup>III</sup>HP on the one hand and of Co<sup>III</sup>HDT or Co<sup>III</sup>Cyclam on the other, the difference in the catalytic activity must be due to different substitution rates. Hence, it appears indeed, as stated very recently by Fleischer and Krishnamurthy,<sup>38</sup> that "the porphyrin ligand labilizes both Cr(III) and Co(III) by some type of electronic effect which has as its origins the delocalized electronic structure of the complex in which there is very strong mixing of metal ion orbitals and ligand orbitals causing the metal ion to lose its d<sup>6</sup> (or d<sup>8</sup>) character."

One could argue that the differences in catalytic activity are due to differences in hydrolysis between these complexes. The hydrolysis constants of Co<sup>III</sup>Cyclam are  $\text{p}K_{A/1} = 5$  and  $\text{p}K_{A/2} = 7.2$ ,<sup>11</sup> while Co<sup>III</sup>HP has  $\text{p}K_A = 10.5$ .<sup>8</sup> Hence, Co<sup>III</sup>Cyclam is indeed largely hydrolyzed at pH 8 while Co<sup>III</sup>HP is not. However, as shown in the previous section, the coordination tendency of OOH<sup>-</sup> is considerably larger than the one of OH<sup>-</sup>. Therefore, one would not expect a significant inhibition of the catalysis by hydrolysis.

(37) M. Schmidt, "Anorganische Chemie I," Hochschultaschenbücher 86/86a B.I., Mannheim, 1967, p 97.

(38) E. B. Fleischer and M. Krishnamurthy, *J. Amer. Chem. Soc.*, **93**, 3784 (1971).

## Conclusions

The given results demonstrate unequivocally that certain Co(III) complexes are sufficiently labile toward substitution to be able to catalyze the disproportionation of H<sub>2</sub>O<sub>2</sub> effectively. The turnover number, *i.e.*, the number of H<sub>2</sub>O<sub>2</sub> molecules brought to reaction within 1 min by one molecule of the catalyst, is 8 for Co<sup>III</sup>HP.<sup>39</sup> As the turnover number of catalase<sup>40</sup> is in the order of  $5 \times 10^6$ , one is tempted to classify Co<sup>III</sup>HP as a poor catalyst. Indeed, compared with the enzyme this is true; however, compared with other metal ions and their simple complexes, Co<sup>III</sup>HP is a remarkably effective catalyst. This becomes evident from the data listed in Table I. Among the Co(III) complexes

TABLE I

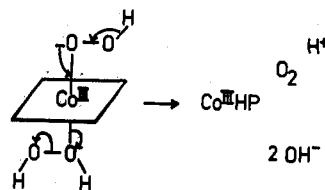
COMPARISON OF THE INITIAL RATE OF THE O<sub>2</sub> EVOLUTION,  $v_0 = d[\text{O}_2]/dt$  (MOL L.<sup>-1</sup> SEC<sup>-1</sup>), FOR SEVERAL CATALASE-LIKE SYSTEMS<sup>a</sup>

| Catalyst <sup>10</sup>                 | Normalized rates at— |         | Ref |
|--|----------------------|---------|-----|
|  | pH 5                 | pH 8    |     |
| Co <sup>III</sup> HP                   | 0.1                  | 1       | b   |
| Co <sup>III</sup> HDT                  |                      | ~0.002  | b   |
| Co <sup>III</sup> Cyclam               |                      | ≤ 0.002 | b   |
| Co <sup>III</sup> (DMG) <sub>2</sub>   |                      | 0.01    | 16  |
| Co <sup>III</sup> PTS(OH) <sup>c</sup> |                      | ≤ 0.006 | 1   |
| Co <sup>II</sup> PTS <sup>b</sup>      | 0.03                 | 0.06    | 1   |
| Fe <sup>III</sup> PTS <sup>c,d</sup>   | ~0.7                 | ~4      | 6   |
| Hemin <sup>c</sup>                     | ~0.2                 | ~1      | 6   |
| Cu(bipy) <sub>2</sub> <sup>2+</sup>    | 0.05                 | 54      | 7   |
| Ni <sub>aq</sub> <sup>2+</sup>         |                      | 0.0003  | e   |

<sup>a</sup> The data given correspond to the conditions [catalyst] =  $10^{-4}$  M,  $[\text{H}_2\text{O}_2]_{\text{tot}(t=0)} = 10^{-2}$  M,  $I = 0.1$ , and 25° and are either the result of a direct experimental determination or of a calculation from the known rate laws. All data are normalized for the catalase-like activity of Co<sup>III</sup>HP at pH 8:  $v_0 = 5.6 \times 10^{-6}$  mol l.<sup>-1</sup> sec<sup>-1</sup>. <sup>b</sup> This work. <sup>c</sup> These complexes tend to dimerize or polymerize in aqueous solution;<sup>23,25</sup> however, the most active catalyst is probably the monomer species.<sup>1,5,6</sup> The data given correspond, for example, to  $[\text{Fe}^{\text{III}}\text{PTS}]_{\text{tot}} = 10^{-4}$  M. <sup>d</sup> In a  $10^{-4}$  M solution only about 1% is present as Fe<sup>III</sup>PTS<sub>monomer</sub>.<sup>6,23</sup> <sup>e</sup> H. Sigel and K. Wyss, to be submitted for publication.

Co<sup>III</sup>HP is superior by a factor of 100 or more. Additionally, the activity of Co<sup>III</sup>HP is in the order observed for other metal ion complexes.

The catalytic process with Co<sup>III</sup>HP was described by the mechanism given in eq 2–5. In this mechanism it is assumed that the rate-determining step occurs within the complex Co<sup>III</sup>HP(OOH<sup>-</sup>)H<sub>2</sub>O<sub>2</sub>. For the structure of this active species and the disproportionation of H<sub>2</sub>O<sub>2</sub> the following scheme may be outlined



The experiments revealed that two molecules of H<sub>2</sub>O<sub>2</sub>, *i.e.*, H<sub>2</sub>O<sub>2</sub> and OOH<sup>-</sup>, participate in the reaction before the rate-determining step. Hence, the whole reaction may take place within the coordination sphere of the metal ion; there is no need to postulate the formation of *free* radicals. It is suggested that the elec-

(39) Turnover number =  $2 \times 60 \times k_5 = 120 \times 6.76 \times 10^{-2} = 8$ .

(40) P. Karlson, "Biochemie," Georg Thieme Verlag, Stuttgart, 1962, p 67.

tron transfer from the peroxo species to be oxidized occurs *through* the orbitals of the metal ion to the peroxo species to be reduced.<sup>41</sup> This mechanism is similar to the one proposed recently for systems with  $\text{Cu}(2,2'\text{-bipy})^{2+}$  as catalyst,<sup>7,42</sup> though in this system a

(41) In this connection it may be of interest to note that a cobalt(II) porphyrin is known to form a reversible  $\text{O}_2$  adduct: F. A. Walker, *J. Amer. Chem. Soc.*, **92**, 4235 (1970).

(42) H. Erlenmeyer, C. Flierl, and H. Sigel, *ibid.*, **91**, 1065 (1969).

cis arrangement of  $\text{H}_2\text{O}_2$  and  $\text{OOH}^-$  is possible, while in the present case with  $\text{Co}^{\text{II}}\text{HP}$  only a trans arrangement can occur.

**Acknowledgments.**—A part of the measurements was performed with the skillful technical assistance of Miss R. Baumbusch. This work was supported by a research grant from the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung.

CONTRIBUTION FROM THE PHILIPS RESEARCH LABORATORIES,  
EINDHOVEN, THE NETHERLANDS

## Viscosity of Molten Alkali Molybdates, Tungstates, and Sulfates<sup>1</sup>

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The viscosities of molten  $\text{M}_2\text{MoO}_4$  and  $\text{M}_2\text{WO}_4$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ) have been determined as a function of temperature up to  $1000^\circ$  by the method of the oscillating hollow cylinder. Viscosity values, ranging from 2 to 10 cP, are higher for the tungstates than for the corresponding molybdates and decrease in the order  $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ . In addition, viscosity values of  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  are reported, in order to allow a comparison with the behavior of other high-melting salts with complex anions. The relationships between viscosity and temperature can be represented satisfactorily by an Arrhenius equation. Values of the activation energy for viscous flow  $E_\eta$  are as follows (in kcal mol<sup>-1</sup>):  $\text{Li}_2\text{MoO}_4$ , 7.0;  $\text{Na}_2\text{MoO}_4$ , 6.8;  $\text{K}_2\text{MoO}_4$ , 5.1;  $\text{Li}_2\text{WO}_4$ , 12.0;  $\text{Na}_2\text{WO}_4$ , 9.2;  $\text{K}_2\text{WO}_4$ , 8.6;  $\text{Li}_2\text{SO}_4$ , 12.8;  $\text{Na}_2\text{SO}_4$ , 10.0. The  $E_\eta$  values found are predicted reasonably well by the semiempirical relation  $E_\eta = 3.7RT_m$ . The relatively low values of the ratio  $E_\eta/E_A$ , *i.e.*, activation energy of viscosity *vs.* activation energy of equivalent conductivity, in the case of molten alkali molybdates, tungstates, and sulfates would suggest that the melts have a more or less associated character.

### 1. Introduction

Although several physical properties of molten alkali molybdates and tungstates have been determined (density,<sup>2-8</sup> surface tension,<sup>2,8</sup> electrical conductivity,<sup>3-6,9-12</sup> thermal stability,<sup>13</sup> and volatility<sup>13</sup>), viscosity values have not yet been reported in the literature. The only indication has been given by van der Wielen, *et al.*,<sup>7</sup> who stated that alkali molybdate melts have viscosities of the order of  $10^{-2}$  P.

The viscosity values of molten molybdates and tungstates are interesting in view of the glass formation observed in the systems  $\text{M}_2\text{MoO}_4\text{-MoO}_3$ <sup>7</sup> and  $\text{M}_2\text{WO}_4\text{-WO}_3$ <sup>14</sup> ( $\text{M} = \text{alkali ion}$ ). Furthermore, they allow a comparison with other physical properties of the same molten salts, especially electrical conductivity, and with the properties of related salts with complex anions. Therefore, they may contribute to our knowledge of the transport properties of ionic liquids.

The present paper describes the determination of the

viscosities of  $\text{Li}_2\text{MoO}_4$ ,  $\text{Na}_2\text{MoO}_4$ , and  $\text{K}_2\text{MoO}_4$ , and also of  $\text{Li}_2\text{WO}_4$ ,  $\text{Na}_2\text{WO}_4$ , and  $\text{K}_2\text{WO}_4$  as a function of temperature up to  $1000^\circ$ .

Owing to the scarcity of viscosity data on high-melting salts with complex anions, viscosity values for  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  were also determined and are reported in this paper. The viscosity of molten  $\text{K}_2\text{SO}_4$  could not be measured with the described apparatus, because of the relatively high melting point of this salt.

### 2. Experimental Section

**Materials.**—As described earlier,<sup>8</sup> molybdate and tungstate samples were made from alkali carbonates (Merck p.a.),  $\text{MoO}_3$  (Merck p.a.), and  $\text{WO}_3$  (Merck). The carbonates were dried by heating at  $300^\circ$  for several hours. Weighed quantities of carbonate and trioxide were mixed thoroughly and melted together in a platinum dish at  $950\text{--}1000^\circ$  for 2 hr. The  $\text{Li}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  used were reagent grade chemicals (Merck).

**Method.**—The method used for the determination of viscosities was that of the oscillating hollow cylinder. The melt is contained in a cylindrical crucible, which is suspended by a torsion wire. When the crucible is oscillating, the logarithmic decrement of the oscillation forms a measure of the viscosity of the melt.

The apparatus used was almost identical with that of Janz and Saegusa,<sup>15</sup> the most important difference being that the adjustable inertia pieces were omitted.

The torsion wire was a tungsten wire having a diameter of 0.4 mm. The crucible containing the melt consisted of an 80% Au-20% Pd alloy, its height was 6.0 cm, and its diameter was 2.5 cm. It was inserted in a closely fitting Inconel cradle which was suspended in a long electric furnace. The oscillating part of the apparatus was protected against air currents by Plexiglas draught shields.

Amplitudes of oscillation were determined visually with the aid of a system consisting of a lamp, a mirror, and a scale on which the maximum torsion angles  $\alpha$  could be read.

The logarithmic decrement  $\delta$  was calculated by

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