Metal Ions and Hydrogen Peroxide. XXV. ¹

On the Kinetics of the Catalase-Like Activity of the Cobalt(II) Complex of 4,4',4'',4'''-Tetrasulfophthalocyanine

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The decomposition of H_2O_2 , catalyzed by the Co^{2+} complex of 4,4',4'',4'''-tetrasulfophthalocyanine ($\text{Co}^{\text{II}}\text{PTS}$), was investigated in the pH range 3.8 through 10 by measuring the initial rate, $v_0 = d(\text{O}_2)/dt$, of the increasing formation of O_2 (25°; $I=0.1$). In this pH range v_0 is proportional to the initial concentration of H_2O_2 (determined at pH 5.0 and 9.2). Due to the dimerization ($\log K_D = 5.47 \pm 0.09$ at natural ionic strength and about 7.63 ± 0.16 in 0.1 M NaClO_4 ; 25°) and polymerization of $\text{Co}^{\text{II}}\text{PTS}$ the catalyst and its reaction order are difficult to establish: Based on the experimental evidence it is suggested that v_0 is proportional to the concentration of monomer $\text{Co}^{\text{II}}\text{PTS}$. Additionally, there is evidence that the experimentally determined v_0 contains the contributions of a pH-independent and a pH-dependent reaction course. These results are analog to those obtained earlier with $\text{Fe}^{\text{III}}\text{PTS}$ as catalyst. A mechanism for the catalyzed disproportionation of H_2O_2 by $\text{Co}^{\text{II}}\text{PTS}$ is proposed. The catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}(\text{OH})$ is smaller than that of $\text{Co}^{\text{II}}\text{PTS}$ and the pH-dependence is different.

The decomposition of hydrogen peroxide according to equation (1)

is catalyzed by metal ions and metal ion complexes. In the first transition series, iron¹⁻⁴ and copper⁵ ions, and complexes thereof, are especially effective catalysts. From the catalase-like activity of Cu^{2+} complexes it is known⁵ that the reaction occurs within the coordination sphere. Therefore, the kind of ligand bound to the metal ion has a strong influence on the activity. This means, the activity is dependent (beside other parameters) on the saturation degree of the coordination sphere of the metal ion. This explains why Cu^{2+} complexes formed with tetradentate ligands, like 4,4',4'',4'''-tetrasulfophthalocyanine (PTS), are catalytically inactive. Of course, this does not mean that all metal ion-PTS complexes are inactive; those formed with a metal ion having a coordination number >4 may well be active².

Among the PTS complexes formed with the metal ions of the second half of the first transition series those with Co and Fe show a catalase-like activity². The interesting feature of these complexes is their structural uniformity which is determined by the planar PTS ligand. This fact offers

the possibility to compare the kinetics and mechanism of the disproportionation of H_2O_2 , catalyzed by metal ions held under identical structural conditions. This should help to evaluate the question: Do different metal ions require different reaction mechanisms²? Recently, the kinetics of the decomposition of H_2O_2 by $\text{Fe}^{\text{III}}\text{PTS}$ were studied¹. Now we are investigating the qualities of $\text{Co}^{\text{II}}\text{PTS}$ and partly those of $\text{Co}^{\text{III}}\text{PTS}(\text{OH})$ as catalysts for reaction (1).

The catalase-like activity of these Co complexes was measured under several different conditions in the pH range 3.8 to 10 using an oxygen sensitive electrode. The activity of the catalysts was characterized by the initial rate of the O_2 formation ($v_0 = d[\text{O}_2]/dt$; mole $\text{l}^{-1} \text{sec}^{-1}$) according to reaction (1).

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Experimental Section

Materials and Apparatus

The tetrasodium salt of cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine 2-hydrate was prepared according to WEBER and BUSCH⁶. The analysis of the blue, hygroscopic powder gave: Calcd. for $\text{Na}_4[\text{Co}^{\text{II}}\text{PTS}] \times 2\text{H}_2\text{O}$: C, 37.82; H, 1.59; N, 11.03. Found: C, 37.8; H, 1.9; N, 11.1. For the experiments a fresh solution of $\text{Co}^{\text{II}}\text{PTS}$ was always prepared. Longer standing of a solution resulted in an absorption decrease at 660 nm which suggests a slow decomposition of the complex; this is also known for $\text{Fe}^{\text{III}}\text{PTS}$ ⁷.

Hydroxocobalt(III) 4,4',4'',4'''-tetrasulfophthalocyanine was made by oxidation of a blue $\text{Co}^{\text{II}}\text{PTS}$ solution as described by WEBER and BUSCH⁸. The green colored $\text{Co}^{\text{III}}\text{PTS}(\text{OH})$ complex was not isolated, instead the solution was directly used for the experiments.

The other reagents and the apparatus were the same as used earlier¹.

Measurements of Catalysis and Evaluation of the Data

These were done exactly as described recently¹. Again, the logarithms of the initial velocities of reaction (1) plotted against the logarithms of the varied concentration of X resulted usually in straight lines. From the slope of the straight line portion the relation between the reaction rate and the concentration of X was taken.

Results

The catalyst, $\text{Co}^{\text{II}}\text{PTS}$, is somewhat oxydized by H_2O_2 ; however, this oxidation proceeds much slower than that with $\text{Fe}^{\text{III}}\text{PTS}$ ¹. The extent of the decomposition of the ligand in $\text{Co}^{\text{II}}\text{PTS}$ was followed by the absorption band at 660 nm: Within the first 5 min at $\text{pH} > 6$ no significant decrease of the absorption was observed. In the lower pH range some decomposition occurs which was estimated to be at $\text{pH} 4.6$ approximately 10 to 15% after 10 minutes. This slight degradation could have only an insignificant effect on the kinetic experiments, but this possibility was completely excluded by using only the first 4 min of the reaction for the evaluation and by extrapolating to the initial velocity¹.

First, the dependence of the reaction rate of the catalysis of the disproportionation of H_2O_2 on the concentration of H^+ was investigated at a constant initial concentration of H_2O_2 and a constant concentration of $\text{Co}^{\text{II}}\text{PTS}$. In Fig. 1 the results are shown for two series of measurements. Obviously, the relation between the initial rate, v_0 , and pH is

not a simple one. In this connection, it has to be mentioned that for solutions containing no or only little buffer the rate of the reaction is not different from the other rates determined. The concentration of Na^+ was kept constant (0.1 M) in these experiments by the addition of NaClO_4 . Thus it can be concluded that the anions of the buffers have no measurable influence on v_0 .

Fig. 1. Catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}$ (○, 10^{-4} M; ●, 2×10^{-4} M). Dependence on pH at an initial concentration of $[\text{H}_2\text{O}_2] = 10^{-2}$ M (○) or 5×10^{-3} M (●), determined as the initial rate, v_0 , (mole $\text{l}^{-1} \text{sec}^{-1}$) of the O_2 evolution. For comparison the catalase-like activity of $\text{Co}^{\text{III}}\text{PTS}(\text{OH})$ (●) is also given ($[\text{Co}^{\text{III}}\text{PTS}(\text{OH})] = 4 \times 10^{-4}$ M, $[\text{H}_2\text{O}_2]_{\text{tot}}(t=0) = 8 \times 10^{-3}$ M). Buffers: [acetate] = 0.1 M, pH 3.8 through 5.8; [phosphate] = 0.05 M, pH 5.8 through 8.2; [borate] = 0.1 M, pH 8 through 10. In all cases was $[\text{Na}^+]_{\text{tot}} = 0.1$ M and the temperature 25° .

Potentiometric titrations of solutions containing $\text{Co}^{\text{II}}\text{PTS}$ showed that at $\text{pH} \gtrsim 8$ considerable amounts of NaOH are consumed. This suggests that $\text{Co}^{\text{II}}\text{PTS}$ hydrolyzes. The reaction is slow (titration time between 2 and 4 hours) and also dependent on the concentration of the complex. The latter fact can be explained by the known dimerization and polymerization tendency of $\text{Co}^{\text{II}}\text{PTS}$ ⁹. The whole hydrolysis behavior of $\text{Co}^{\text{II}}\text{PTS}$ is completely analog to that of $\text{Fe}^{\text{III}}\text{PTS}$ ⁷. Additionally, as with $\text{Fe}^{\text{III}}\text{PTS}$ ¹ it is difficult to interpret the kinetic results of Fig. 1 in the pH range > 8 .

In order to compare the catalytic properties of Co^{II} and Co^{III} the complex, $\text{Co}^{\text{III}}\text{PTS}(\text{OH})$, was also used as a catalyst for reaction (1). In Fig. 1, the dependence on the concentration of H^+ of the initial rate, v_0 , is given for the pH range 7.4 to 10. The dependence on $[\text{H}^+]$ of the reaction rate is quite different for the two catalysts. Furthermore, taking into account the different experimental conditions (cf. Fig. 1), at pH 7.4 $\text{Co}^{\text{II}}\text{PTS}$ is, at least, by a factor of 10 the more effective catalyst.

The dependence of v_0 on the initial concentration of H_2O_2 was studied at pH 5.0 under the condition, $[\text{H}_2\text{O}_2]_{\text{tot}}(t=0) > [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}$, in two series at constant concentrations of $[\text{Co}^{\text{II}}\text{PTS}] = 4 \times 10^{-5}$ and

10^{-4} M (Fig. 2). The plots of $\log v_0$ versus $\log [H_2O_2]_{tot(t=0)}$ result in straight lines with a slope of 1, i.e. the initial rate, v_0 , is proportional to the concentration of H_2O_2 . The same result is still obtained if $[Co^{II}PTS]_{tot} (= 2 \times 10^{-3}$ M) is greater than the initial concentration of H_2O_2 . This shows that at the rate determining step at least one molecule of H_2O_2 participates. Nevertheless, the participation of a second molecule of H_2O_2 before the rate determining step cannot be excluded with certainty (though it is quite improbable) in spite of the investigations at $[Co^{II}PTS]_{tot} > [H_2O_2]_{tot(t=0)}$, as $Co^{II}PTS$ dimerizes and polymerizes, and the catalyst is probably the monomer complex (as will be discussed later in this study) which is present only at small concentrations. However, no experimental hint for a square dependence between v_0 and $[H_2O_2]$ could be observed.

Fig. 2. Catalase-like activity of $Co^{II}PTS$ ($\bullet$, 2×10^{-3} M; $\bullet$, 10^{-4} M; $\circ$, 4×10^{-5} M) at pH 5.0 ([acetate] = 0.1 M). Dependence on the initial concentration of H_2O_2 at $[Co^{II}PTS]_{tot} \geq [H_2O_2]_{tot(t=0)}$ ($\bullet$) and at $[Co^{II}PTS]_{tot(t=0)} < [H_2O_2]_{tot(t=0)}$ ($\bullet$, $\circ$), determined as the initial rate, v_0 (mole l^{-1} sec $^{-1}$) of the O_2 evolution; $[Na^+]_{tot} = 0.1$ M; 25° .

Despite the uncertainties due to hydrolysis in the pH range > 8 the dependence of v_0 on the initial concentration of H_2O_2 was also determined at pH 9.2 (Fig. 3). Surprisingly, exactly the same results were obtained as those at pH 5.0, with the exception that the curves show saturation at high concentrations of H_2O_2 . Hence, in the whole pH range studied v_0 is proportional to $[H_2O_2]$.

The influence of the concentration of the catalyst on v_0 was determined in several series: The concentration of $Co^{II}PTS$ was varied at constant pH and constant initial concentrations of H_2O_2 (Fig. 4). The slopes of the straight lines in Fig. 4 are 0.87

Fig. 3. Catalase-like activity of $Co^{II}PTS$ ($\bullet$, 2×10^{-3} M; $\bullet$, 10^{-3} M; $\bullet$, 10^{-4} M; $\circ$, 4×10^{-5} M) at pH 9.2 ([borate] = 0.1 M). Dependence on the initial concentration of H_2O_2 at $[Co^{II}PTS]_{tot} \geq [H_2O_2]_{tot(t=0)}$ ($\bullet$) and at $[Co^{II}PTS]_{tot} < [H_2O_2]_{tot(t=0)}$ ($\bullet$, $\bullet$, $\circ$), determined as the initial rate, v_0 (mole l^{-1} sec $^{-1}$) of the O_2 evolution; $[Na^+]_{tot} = 0.1$ M; 25° .

and 0.91 at pH 5.0, and 0.62 and 0.87 at pH 9.2. There is no significant difference between the results at pH 5.0 and 9.2 which is again surprising with regard to the mentioned hydrolysis occurring at $pH \approx 8$.

Fig. 4. Catalase-like activity of the $Co^{II}PTS$ system at pH 5.0 ($\circ$, $\bullet$; [acetate] = 0.1 M) and pH 9.2 ($\otimes$, $\otimes$; [borate] = 0.1 M). Dependence on the total concentration of $Co^{II}PTS$ at $[H_2O_2]_{tot(t=0)} = 5 \times 10^{-3}$ M ($\bullet$, $\otimes$) or 5×10^{-2} M ($\circ$, $\otimes$), determined as the initial rate, v_0 (mole l^{-1} sec $^{-1}$) of the O_2 evolution; $[Na^+]_{tot} = 0.1$ M; 25° . Slopes of the straight lines (least squares) $m = 0.62$ ($\otimes$), 0.87 ($\circ$, $\otimes$), and 0.91 ($\bullet$).

The results of Fig. 4 are quite similar to those obtained with $Fe^{III}PTS$ as a catalyst¹; but again, the interpretation is complicated by the known dimerization^{7,9} of $Co^{II}PTS$ according to equation (2).

We determined the dimerization constant, $\log K_D = 5.47 \pm 0.09$, at 25° and natural ionic strength in a way similar to that described^{7,10}. However, the

main problem is the polymerization occurring at concentrations higher than approximately 5×10^{-4} M (cf. also l. c.¹⁰). Even worse, the presence of $\text{Na}^{\oplus}$, necessary to keep the ionic strength constant, favors the polymerization (and dimerization) very strongly. For this reason the dimerization constant, $\log K_D = 7.63 \pm 0.16$, at 25° and $I = 0.1$ (NaClO_4) can only be considered as a rough estimation. The difference of more than 2 log units between the two constants confirms the extreme influence of $\text{Na}^{\oplus}$ on equation (2). This is probably due to the decreasing negative charge of the complexes as a result of ion pair formation with the sulfo groups^{7, 10}.

Under the described circumstances it seemed inappropriate to do any calculations with $\log K_D$ and the results given in Fig. 4, as no safe conclusions could be drawn. However, it seems reasonable to note that under the assumption of having only a monomer-dimer equilibrium (eq. 2) the following proportionalities hold. If equilibrium (2) is far on its left side, i.e., the concentration of the dimer is very small, then $[\text{dimer}] \sim [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}^2$ and $[\text{monomer}] \sim [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}$. Hence, if the dimer $\text{Co}^{\text{II}}\text{PTS}$ would be the active catalyst the slope of the plot, $\log v_0$ versus $\log [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}$, should be two, while for the monomer as the catalyst it should be one. On the contrary, if equilibrium (2) is far on its right side, i.e., the concentration of the monomer is very small, then $[\text{monomer}] \sim [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}^{0.5}$ and $[\text{dimer}] \sim [\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}}$. Hence, for the monomer as the catalyst, the expected slope is 0.5 and for the dimer one. Of course, if both, the monomer and dimer $\text{Co}^{\text{II}}\text{PTS}$, are assumed to be catalyst of equal activity (per Co^{II}), the expected slope is one, and independent of the position of equilibrium (2).

The estimated value of K_D shows that under the experimental conditions (cf. Fig. 4) equilibrium (2) is more on the side of the dimer. As the observed slopes in Fig. 4 are < 1 , we assume that in the present system the monomer $\text{Co}^{\text{II}}\text{PTS}$ is the catalyst, i.e., it is suggested that v_0 is linearly dependent on the concentration of monomer $\text{Co}^{\text{II}}\text{PTS}$. This view is further supported by the results described below, and in agreement with the evidence given in the case of $\text{Fe}^{\text{III}}\text{PTS}$ ¹, and the recent results of BROWN et al.⁴ that the catalase-like activities of ferrihems are also determined by the proportion of monomer present.

The influence of the concentration of $\text{Li}^{\oplus}$, $\text{Na}^{\oplus}$, and $\text{K}^{\oplus}$ on the initial rate, v_0 , of the decomposi-

tion of H_2O_2 is presented in the upper part of Fig. 5. The results show no real significant differences among the influence of these three ions. At $[\text{Me}^{\oplus}] > 2$ M $\text{Co}^{\text{II}}\text{PTS}$ precipitates.

Fig. 5. Catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}$ (2×10^{-4} M). Dependence on the ionic strength ($\circ$, LiClO_4 ; $\bullet$, NaClO_4 ; $\bullet$, KNO_3) at $[\text{H}_2\text{O}_2]_{\text{tot}}(t=0) = 5 \times 10^{-3}$ M and pH 9.2 ($[\text{borate}] = 0.01$ M), determined as the initial rate, v_0 (mole $\text{l}^{-1} \text{sec}^{-1}$) of the O_2 evolution (25°).

For comparison the percentage of the extinction decrease at 660 nm ($\% E_{660}$; at this wave length monomer $\text{Co}^{\text{II}}\text{PTS}$ absorbs) with increasing ionic strength ($\otimes$, $\bullet$, NaClO_4) is given for solutions with $[\text{Co}^{\text{II}}\text{PTS}]_{\text{tot}} = 10^{-5}$ M and pH ≈ 5 ($\otimes$, natural pH) or pH = 9.2 ($\bullet$, $[\text{borate}] = 0.01$ M); 25° .

The strong decrease of the catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}$ by increasing ionic strength (up to $I \cong 0.2$) supports the postulation that the monomer $\text{Co}^{\text{II}}\text{PTS}$ is the catalyst. As mentioned and shown by $\log K_D$, dimerization and polymerization is favored by increasing I . However, it is not clear why v_0 is increasing again at $I \geq 0.5$. The same behavior was observed with $\text{Fe}^{\text{III}}\text{PTS}$ as catalyst¹. One explanation could be that the negative charge of the sulfo groups (including the monomer $\text{Co}^{\text{II}}\text{PTS}$) is compensated by ion pair formation with the alkali ions, this would facilitate the formation of a peroxo adduct with $\text{HOO}^{\ominus}$.

The catalase-like activity is approximately paralleled by the extinction measured at 660 nm which is due to monomer $\text{Co}^{\text{II}}\text{PTS}$ ¹⁰ (cf. the lower part of Fig. 5). This parallelism is especially evident in solutions without buffer¹¹.

It is of interest to note that, analogous to $\text{Fe}^{\text{III}}\text{PTS}$ ¹, the catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}$ may be inhibited by the presence of imidazole. This is in agreement with the known⁸ complex formation between $\text{Co}^{\text{II}}\text{PTS}$ and imidazole, suggesting a competition between this ligand and the substrate for the "free" coordination positions at the catalyst.

Discussion

The results obtained give evidence that the initial rate, v_0 , of the disproportionation of H_2O_2 is linearly proportional to the concentration of H_2O_2 and probably also to the concentration of monomer $\text{Co}^{\text{II}}\text{PTS}$. Because these dependencies are the same as obtained with $\text{Fe}^{\text{III}}\text{PTS}$ as a catalyst, and because additionally, the shape of the curve obtained for the dependence between $\log v_0$ and pH is also the same, it is reasonable to assume that the reaction with $\text{Co}^{\text{II}}\text{PTS}$ proceeds analog to that with $\text{Fe}^{\text{III}}\text{PTS}$. For the latter case evidence was given¹ that the experimentally determined v_0 contains the contributions of a pH-independent and a pH-dependent reaction. Therefore, in analogy to $\text{Fe}^{\text{III}}\text{PTS}$ for the reaction with $\text{Co}^{\text{II}}\text{PTS}$ as catalyst the following mechanism may be postulated.

In this mechanism equations (6) and (10) represent the rate determining steps of the pH-independent and the pH-dependent reactions, respectively¹². To test the postulated mechanism given in equations (3) through (11) it would be reasonable to include the steady-state approximation and derive a rate law. This would have then exactly the same form as the one recently given for $\text{Fe}^{\text{III}}\text{PTS}$ ¹. However, this treatment would not improve the present situation with $\text{Co}^{\text{II}}\text{PTS}$, as in the lower pH range, where the pH-independent reaction dominates, no saturation of the reaction rate, by adding large excesses of H_2O_2 , could be obtained (cf. Fig. 2). This

fact precludes the determination of the reaction parameters which are necessary for a re-calculation of the pH-dependence. The comparison of such a calculated curve with one of the experimentally determined curves of Fig. 1 would give high evidence that the postulated mechanism is correct. But even so, due to the analogous experimental results, it is quite likely that the reaction course proceeds *via* the same mechanism with both catalysts, $\text{Co}^{\text{II}}\text{PTS}$ and $\text{Fe}^{\text{III}}\text{PTS}$; the latter one being somewhat more effective.

With regard to the mechanism of the catalase-like activity of $\text{Co}^{\text{II}}\text{PTS}$, especially its pH dependence, it is of interest to note that the oxidation of H_2O_2 by aquocobalt(III) ions in aqueous perchlorate media proceeds within the coordination sphere of the metal ion. More important, the decomposition of $\text{Co}^{\text{III}}(\text{HO}_2^{\ominus})$ dominates over that of $\text{Co}^{\text{III}}(\text{H}_2\text{O}_2)$ ¹³. This is analog to the results presented in Fig. 1. The results obtained for the catalase-like activity of cobaloximes — which contain Co^{III} — also resemble those found with $\text{Co}^{\text{II}}\text{PTS}$, the latter being a somewhat more effective catalyst. The rate law for the decomposition of H_2O_2 by chloroaquocobaloxime is $v = -d[\text{H}_2\text{O}_2]/dt = k \cdot [\text{cobaloxime}] [\text{H}_2\text{O}_2] / [\text{H}^{\oplus}]$ ¹⁴. In this case no hint for a pH-independent reaction course was observed.

But despite these similarities, for the reaction with $\text{Co}^{\text{II}}\text{PTS}$, there is no experimental evidence so far which would support the postulation of a Co^{III} species as an intermediate during the reaction course. Furthermore, it was shown (cf. Fig. 1) that $\text{Co}^{\text{III}}\text{PTS}(\text{OH})$ has significant different catalytic qualities than $\text{Co}^{\text{II}}\text{PTS}$. However, it should be mentioned that a blue solution of $\text{Co}^{\text{II}}\text{PTS}$ if treated with 0.5 M H_2O_2 turns to green and finally yellow or even colorless after about 1 hour. This suggests the formation of a Co^{III} species^{6,8}, as well as a degradation of the ligand. Additionally, it may be noted here that $\text{Co}^{\text{II}}\text{PTS}$ is known to form a reversible oxygen adduct at low temperature in an aqueous methanol solution¹⁵.

The mentioned degradation of the phthalocyanine system in $\text{Co}^{\text{II}}\text{PTS}$ by H_2O_2 is also known for $\text{Fe}^{\text{III}}\text{PTS}$ ¹. The dimethylglyoximate monoanion (in its Co^{III} complex) is degraded as well by H_2O_2 ¹⁴. Quite generally, it appears that the catalase-like activity is closely connected with a peroxidase-like one⁵.

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