THE REACTIONS OF Co(III) WITH WATER AND WITH HYDROGEN PEROXIDE

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The absorption spectra of Co(III) perchlorate solutions at different acidities are quantitatively consistent with the presence of a species Co(III)OH⁻. The rate of reduction of Co(III) perchlorate by water is observed to be 3/2 order in Co(III) and inversely proportional to $[H^+]^2$. These kinetics are accounted for by supposing that Co(III) in aqueous solution is present predominantly in a dimeric form. The reduction of Co(III) by hydrogen peroxide is bimolecular and the rate inversely proportional to $[H^+]$.

Evidence is found for the formation of a species $Co(III)HO_2^-$ and its formation constant is obtained.

Cobaltic salts of mineral acids in aqueous solutions are spontaneously reduced to cobaltous with the simultaneous evolution of oxygen. Early work on the kinetics of the reduction has been summarized by Bawn and White,¹ who found in their investigation that the reaction was between first and second order in Co(III) and the rate decreased with increasing acidity. To conform with these kinetics it was suggested that two types of rate-determining reactions occurred, one involving a monomeric cobalt species, e.g.

 $Co^{3+} + OH^- \rightarrow Co^{2+} + HO$.

and/or

 $CoOH^{2+} + OH^{-} \rightarrow CoOH^{+} + HO$

and another involving a dimeric species of the type Co^{2+} —O— Co^{2+} . Following Oberer,² it was presumed that the hydroxyl radical leads to oxygen either directly by mutual reaction of two radicals, or via hydrogen peroxide formed by dimerization. The ability of cobaltic solutions to initiate vinyl polymerization was adduced as evidence for the production of radicals in the decomposition.

In a preliminary study ³ of the reactions of Co(III) in sulphuric acid it was indeed observed that aqueous acrylonitrile and methyl methacrylate were polymerized, and moreover the inhibition of the polymerization by oxygen indicated that it is the usual radical type of polymerization. However, increasing the acidity of the solutions sufficiently to make the reduction of Co(III) extremely slow, had little effect on the polymerization. More detailed examination of the reaction revealed that the rate of reduction of Co(III) was proportional to the monomer concentration showing that a direct reaction was occurring, probably leading to a radical, e.g.

$$H_2O + Co^{3+} + CH_2 = CHX \rightarrow Co^{2+} + H^+ + CH_2OH - CHX.$$

Hence, although these observations do not exclude it, vinyl polymerization cannot be taken as a direct proof of HO production.

In the present work we have extended Bawn and White's investigation of the reduction of Co(III) in perchloric acid solutions, examined the solutions spectroscopically for evidence of the hydrolyzed and polynuclear species mentioned above and also followed the reduction of Co(III) by hydrogen peroxide. The latter

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is of interest because of the possibility that hydrogen peroxide is an intermediate in the reduction by water, and also because it might produce more evidence for the reactions of Co(III) via polynuclear ions.

EXPERIMENTAL

MATERIALS.—Cobaltic sulphate was prepared electrolytically ⁴ and after washing the crystals with 5 M sulphuric acid they were stored at 0° C over concentrated sulphuric acid. Stock solutions of the perchlorate *ca*. 0.02 M were prepared as required by removing the sulphate with Ba(ClO₄)₂. It was found that a slight excess of the latter was sufficient to precipitate all the sulphate in these solutions in half an hour and experience showed that no further precipitation occurred on standing overnight.

Barium, sodium and potassium perchlorate solutions were prepared by neutralization of the corresponding bases. Cobaltous perchlorate solutions were obtained from the sulphate as for the cobaltic salt, or by simply allowing cobaltic perchlorate solutions in dilute acid to stand until reduction was complete. Analytical-grade starting materials were used throughout and the absence of chloride was established before using these solutions.

The stock hydrogen peroxide was 85 % stabilizer-free supplied by Messrs. Laporte, and was used without further purification.

ANALYSES.—The Co(III) in solutions ca. 10^{-2} M was determined by adding to excess Fe²⁺ and back titrating with Ce⁴⁺. In 10^{-3} to 10^{-4} M solutions reduction by Fe²⁺ was again used but here the Fe³⁺ produced was measured by its absorption at 270 m μ . For less than 10^{-4} M direct absorption of the solutions at 250 m μ or 230 m μ was used. The extinction coefficient at 250 m μ was found to be 2900 in solutions with a total [ClO₄⁻] = 0·10 and is constant from 0·8 to 5×10^{-4} M Co(III), and from ca. 0·04 to 0·08 M HClO₄. At 230 m μ the coefficient is 7000 with total [ClO₄⁻] = 1·96 and is constant from ca. 10^{-4} M to 10^{-5} M Co(III) and 0·5 M to 1·96 M HClO₄. These were the wavelengths and concentration ranges used in the investigation of the reductions by water and hydrogen peroxide respectively. A small correction for the absorption of the peroxide ($\epsilon = 46$ at 230 m μ) is necessary at the higher concentrations used.

Cobaltous ion concentrations were measured by the thiocyanate method.⁵ Acid concentrations were measured by titration of the actual reaction mixtures, since it was found that variable amounts of sulphuric acid were present in different batches of the solid $Co_2(SO_4)_3$.

PROCEDURE.—Reactions were usually begun by adding a few ml of a concentrated Co(III) solution to a large amount of the reaction medium held at constant temperature. All reaction mixtures were contained in black vessels from which samples were taken for analysis at appropriate times.

RESULTS AND DISCUSSION

ABSORPTION SPECTRA

The species CoOH²⁺ formed in the equilibrium

$$Co^{3+} + H_2O \rightleftharpoons CoOH^{2+} + H^+ = K_1$$

has been suggested as a reactant, and by analogy with the corresponding Fe^{3+} compound, FeOH²⁺, it seemed likely that it would reveal itself by changes in the absorption spectrum of cobaltic solutions at different acidities. Cobaltic sulphate solutions are quite green compared with the blue of the perchlorate and since this seems to indicate the presence of a sulphate ion complex ⁶ we have used perchlorate throughout.

Spectra have been obtained from $350 \text{ m}\mu$ to $700 \text{ m}\mu$ for Co(III) solutions containing 0.10, 0.50 and 1.82 N perchloric acid in which the total ClO₄⁻ content was kept constant at 1.82 M. The concentrations of Co(III) were *ca*. 10^{-2} M and in 0.10 N acid the reduction to the cobaltous state is so rapid that concentrations had to be measured immediately after the absorption at each wavelength had been obtained. It will be seen from fig. 1 that new absorbing species do in fact appear as the acidity is decreased as might be expected from the above equilibrium. The main changes occur below 500 m μ . The maximum at 401 m μ

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and minimum at 480 m μ which are present in the stronger acidities, disappear in 0.1 N. Other observations (table 1) show that there is no change with acidity in the absorption at 250 m μ .



FIG. 1.—Spectra of cobaltic perchlorate in aqueous perchloric acid with constant $[ClO_4^-] = 1.82$ M. A, 1.82 N HClO₄; B, 0.50 N HClO₄; C, 0.10 N HClO₄.

TABLE 1.---ABSORPTION COEFFICIENTS OF CO(III) IN DIFFERENT CONDITIONS

104 [Co(III)]	[H+]	[ClO4-]	£250	\$ ₂₃₀
1.25	1.96	2.00	2900	
0.408	1.00	1.00	2890	
2.23	1.00	1.00	3040	
5.33	1.00	1.00	3040	
1.72	0.083	0.10	2840	
2.59	0.083	0.10	2850	
0.824	0.010	0.10	2920	
5.04	0.070	0.10	2950	
1.03	0.057	0.10	2950	
2.05	0.057	0.10	2820	
1.40	0.042	0.10	2700	
4.74	0.042	0.10	2780	
1.14	1.02	2.00		6950
1.13	0.52	2.00		7000
			e ₄₀₁	€605
8·73	1.82	1.82	39.0	32.6
229.0	1.82	1.82	39.7	32.8
0.69	0.10	1.82	62.5	
88·4	0.10	1.82	78.1	
1.79	0.10	1.82		44.6
103.7	0.10	1.82		47.6

If we assume that these changes are due to the formation of CoOH²⁺ from Co³⁺ and that these species have extinction coefficients ϵ_2 and ϵ_1 respectively at the same wavelength, then the following equation for the measured extinction coefficient ϵ_m is readily derived :

$$(\epsilon_m - \epsilon_1)(K_1 + [\mathbf{H}^+]) = K_1(\epsilon_2 - \epsilon_1).$$

If $[H^+] \gg K_1$ then ϵ_m will be linear with $1/[H^+]$. Fig. 2 shows this to hold for several wavelengths and enables values of ϵ_1 and $K_1\epsilon_2$ to be obtained. Unfortunately accurate observations at lower acidities $([H^+] \sim K_1)$ which would be



FIG. 2.—Variation of molar extinction coefficient of cobaltic perchlorate with hydrogen ion concentration. \bigcirc 401 m μ ; \boxdot 350 m μ ; \times 370 m μ .

required to determine K_1 are difficult to make because of the rapid reduction reaction. However, we would have observed deviations from linearity in fig. 2 if K_1 had been 5 % of the lowest [H⁺] used, i.e. $K_1 < 5 \times 10^{-3}$ at 18° C.* At the maxima, 401 m μ and 605 m μ , ϵ_1 is 36.7 and 33.1 respectively, and is 3.2 for the minimum at 476 m μ .

The presence of an equilibrium between monomeric ions and polynuclear ions of the type Co^{2+} —O— Co^{2+} (which are also possible reactants), is likely to lead to changes in extinction coefficients with concentration and, in common with other systems showing this behaviour,⁷ lower acidity will favour the formation of polymers. The extinction coefficients at various wavelengths, acid concentrations and [Co(III)] are given in table 1. They are independent of concentration except perhaps in 0.1 N acid at 401 m μ , but here the possible errors arising from the reduction of Co(III) and the measurement of low optical densities (*ca.* 0.05)

* This is less than the value recently obtained by Sutcliffe and Weber, Trans. Faraday Soc., 1956, 52, 1232.

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are such as to make the observed difference of doubtful significance. Hence there is no evidence in these observations for the existence of an equilibrium, but the Co(III) could exist entirely in either a monomeric or polymeric form. As will be seen subsequently the kinetics indicate the presence of a dimer.

KINETICS OF REDUCTION OF CO(III) BY WATER

In less than 0.1 N acid cobaltic perchlorate is reduced by water quite rapidly. For example, at 25° C the half-life of a 2×10^{-3} M solution in 0.08 N acid is about 20 min and it decreases to about 8 min in 0.04 N acid. In agreement with previous investigations we found that the reaction order in Co(III) was between one and two. This may be the true order of reaction or it may be the result of other factors. One possibility is that reaction products such as Co²⁺ may be



Time (min)

FIG. 3.—Rates of reduction of 5×10^{-4} M Co(III) by water at 25° C in 0.07 N HClO₄ in which various [Co(III)] have previously decomposed completely. [Co(III)] decomposed: \odot none; $\Box \sim 4 \times 10^{-4}$ M; $\bigtriangleup \sim 8 \times 10^{-4}$ M; $\times \sim 12 \times 10^{-4}$ M; $\nabla \sim 16 \times 10^{-4}$ M.

participating. To confirm previous observations ¹ on this point the effect of having 5×10^{-3} M cobaltous perchlorate present initially, i.e. a tenfold excess over the Co(III), was examined. When the Co²⁺ was prepared by the double decomposition method the rate of reduction of Co(III) was appreciably increased. However, if the Co²⁺ was obtained from a Co(III) solution by allowing the latter to reduce completely in dilute acid, then no effect on the rate was observed. In all these reactions the acidities were accurately adjusted to be the same and the ionic strengths were made up to 0.10 with KClO₄.

It seems unlikely that intermediates resulting from the reduction of Co(III) can account for the difference between the Co^{2+} prepared from Co(III) and by double decomposition. Hydrogen peroxide is a possibility but is ruled out since the observations on the Co(III) + H₂O₂ reaction described below show that it would be removed extremely quickly at this acidity. A possible explanation of the difference is that small amounts of material oxidizable by Co(III) are being introduced with the Co²⁺ prepared by double decomposition, but such extraneous matter will be absent in the other solution, having been oxidized by the Co(III).

If this is the case we must also consider the possibility that oxidizable impurities might lead to spurious kinetics in the more dilute Co(III) solutions. To

check this, the reduction of 4×10^{-4} M Co(III) was followed in solutions in which various amounts of Co(III) had been allowed to decompose. The observations are given in fig. 3. It will be seen that the reaction rates decrease as the amount of Co(III) previously decomposed increases, but the rates appear to



FIG. 4.—Rates of reduction of Co(III) by water at 25° C with [H⁺] ~ 0.07 N HClO₄. \triangle and $\bigcirc -[Co(III)]_0 \sim 3 \times 10^{-3}$ M; \times and $\bigcirc -[Co(III)]_0 \sim 4 \times 10^{-4}$ M; $\bigtriangledown -[Co(III)]_0 \sim 4 \times 10^{-4}$ M, but 16 $\times 10^{-4}$ M Co(III) allowed to decompose before adding this.



FIG. 5.—First-order plot of the reduction by water with $[H^+] = 0.0724$ N HClO₄ and I = 0.10.

approach a limiting value. A 5 % change in acidity occurs over the range examined, but from the subsequent measurements of the rates at different acidities it is estimated that this has a negligible effect. Similarly the slight increase in ionic strength of the solution is too small to account for the changes. Again the observations are readily explained in terms of the removal of extraneous oxidizable matter.

The effect of beginning with a high initial Co(III) concentration is obvious

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when an attempt is made to fit rate curves obtained beginning with a 3×10^{-3} M solution to those obtained beginning with 4×10^{-4} M. In the absence of longlived intermediates, or any effects of products, these should be superposable. Fig. 4 shows that this is the case only when a high concentration of Co(III) has been allowed to reduce previously in the same solution. This last observation, as well as confirming the above effect, shows that there is no build-up of shortlived intermediates which affect the rate, and confirms that Co²⁺ has no effect.

ORDER OF REACTION

It is clear that if our interpretation of the above phenomenon is correct a kinetic analysis of the Co(III) reduction is only significant if made on observations



FIG. 6.—Plots for reaction order of 3/2 for the reduction of Co(III) perchlorate and sulphate by water; initial [Co(III)] $\sim 2 \times 10^{-3}$ M for perchlorates and $\sim 10^{-3}$ M for sulphates.

taken after any oxidizable matter has been removed, e.g. in the later stages of the decomposition of a solution initially 3×10^{-3} M in Co(III). Plots of such a run are given in fig. 4 and 5. Even then, neither first- nor second-order equations fit over a substantial concentration range and that the reaction order is still between one and two. Bawn and White ¹ found that the equation

$$- d[Co(III)]/dt = k_1[Co(III)] + k_2[Co(III)]^2$$

fitted their observations and we have applied it to ours by plotting (1/[Co(III)])(d[Co(III)]/dt) against [Co(III)] which should be linear and should give values of k_1 and k_2 . Since the determination of slopes to give d[Co(III)]/dt is subject to some inaccuracy these plots are not very good, but we used them only as an indication of the magnitude of k_1 and k_2 and then adjusted these in attempts to make the observations fit the integrated form of the above equation, i.e.,

$$\log \frac{(k_1 + k_2[\text{Co(III)}])}{[\text{Co(III)}]} = k_1 t + \text{constant.}$$

No values of k_1 and k_2 could be found to give reasonable agreement with this over a significant concentration range.

The kinetic expression which best fits our observations was found to be

 $- d[Co(III)]/dt = k'[Co(III)]^{3/2},$

and examples of $1/[Co(III)]^{\frac{1}{2}}$ against time plots are given in fig. 6. Except for a short initial period the linear relationship required by the above equation is good. In each case the linearity covers a 30-fold change in concentration, and in view of the effect described above it seems reasonable to suppose that the initial deviations occur during the removal of extraneous oxidizable material by Co(III). Examination of data previously obtained ³ using sulphates showed that runs with high initial Co(III) concentrations gave the same kinetics although the concentration range covered was not so great. Examples are shown in fig. 6.

The above constant k'

table 2. The inverse relationship with $[H^+]^2$ shown here does not hold for the sulphate data and no detailed analysis has been of these in view of the plications arising from incomplete ionization of sul-

varies inversely as [H+]² in TABLE 2.-REACTION OF Co(III) WITH WATER. VARIperchloric acid at constant ATION OF RATE CONSTANT WITH THE SQUARE OF THE ionic strength, as shown in HYDROGEN ION CONCENTRATION AT 25° C AND I = 0.10k' $k'[\mathrm{H^+}]^2 \times 10^3$ [H+] 0.369 0.08272.5

made	0.0724	0.202	2.6
com-	0.0567	0.875	2.8
m the	0.0419	1.33	2.3
of aul			

phuric acid, the variation in ionic strength and the existence of sulphate complexes.

MECHANISM

We are unable to explain our observation that the reaction order is 3/2 in Co(III), in terms of the existence of Co(III) in the simple monomeric state in equilibrium with a small amount of dimeric species, usually assumed to be of the form (Co-O-Co)4+. However, if we assume that the ion is predominantly in the dimeric state with a small amount of monomer in equilibrium with it, e.g.

$$2\text{CoOH}^{2+} \xrightarrow{\longrightarrow} (\text{Co---Co})^{4+} + \text{H}_2\text{O},$$

then, if the slow step in the reduction is, say,

$$CoOH^{2+} + (Co-O-Co)^{4+} \rightarrow 3Co^{2+} + HO_{2^{\bullet}}$$

followed by the fast reaction,

$$CoOH^{2+} + \cdot HO_2 \rightarrow Co^{2+} + H_2O + O_2$$

the observed order of 3/2 in total Co(III) concentration would follow.

The assumption that in these conditions Co(III) is present predominantly as a dimer is contrary to the accepted view. However, other binuclear compounds of Co(III) are known and we can find no evidence which rules out this possibility here. In fact the magnetic susceptibility of Co(III) in perchloric acid solution might be interpreted in its favour for it is found to be only slightly paramagnetic.⁸ It has been suggested that this arises because the hydration water forms a penetration complex as NH_3 in the cobaltamines. On the other hand it might also result from its existence as the dimer, since in the parallel case of Fe(III) it is observed that the dimer is only slightly paramagnetic.⁹ The observations made in the present work are not inconsistent with this since the failure to observe any spectral changes with concentration could be accounted for by a sufficiently high dimer formation constant. Also the spectral changes occurring at lower acidities can be explained equally well by the ionization of the hydrated dimer as by that of the monomer assumed above.

The observed dependence of the 3/2 order velocity constant on $1/[H^+]^2$ can be accounted for in terms of hydrolysis of the dimeric form of Co(III). Thus, assuming that the species reacting in the slow step are

$$CoOH^{2+} + (HOCo-O-CoOH)^{2+} \xrightarrow{\kappa_3} 3Co^{2+} + 2OH^- + HO_2$$
,

and that in the rapid equilibria

$$2\text{CoOH}^{2+} \xleftarrow{K_2} (\text{Co-O-Co})^{4+} + \text{H}_2\text{O},$$
$$(\text{Co-O-Co})^{4+} + 2\text{H}_2\text{O} \xleftarrow{K_3} (\text{HOCo-O-CoOH})^{2+} + 2\text{H}^+$$

 K_2 is large and K_3 small, we have

$$- d[Co(III)]/dt = k_3[CoOH^{2+}][(HOCo-O-CoOH)^{2+}]$$
$$= \frac{K_3k_3[(Co-O-CO)^{4+}]^{3/2}}{K_2^{\frac{1}{2}}[H^+]^2}.$$

Since the Co(III) is, on the above assumptions, present predominantly as $(Co-O-Co)^{4+}$ this becomes

$$-\frac{\mathrm{d}[\mathrm{Co(III)}]}{\mathrm{d}t} = \frac{k[\mathrm{Co(III)}]^{3/2}}{[\mathrm{H}^+]^2}$$

as observed.

KINETICS OF REDUCTION OF CO(III) BY HYDROGEN PEROXIDE

Using the sampling technique and measuring the absorption due to Co(III) at 230 m μ convenient rates were obtained with initial Co(III) concentrations ca. 10^{-4} M, H₂O₂ concentrations 10^{-4} to 5×10^{-3} M and HClO₄ concentrations 0.5 to 2.0 M. Salt effects were minimized by adjusting the ionic strength of each solution to 2.00 with sodium perchlorate. In these high acidities the reduction of Co(III) by water is negligible.

Experiments at 25° C, examples of which are given in fig. 7, show that the reaction is accurately first order in both Co(III) and H₂O₂. The second order rate constant k_4' is inversely proportional to [H⁺] as shown in table 3. At 12.5° C and 0° C a large excess of H₂O₂ over Co(III) can be used to give first-order reactions in Co(III), and these first-order constants are proportional to [H₂O₂] as expected.

Table 3.—Second-order rate constants for the reaction of Co(III) with H_2O_2 ; $k_4 = k_4'[H^+]$

[H+]	25.	l° C	12.	5° C	0.0	° C
	k4'	k_4	k_4'	k_4	k4'	k_4
0.52	2930	1520	352	183	51.5	26.8
1.02	1510	1530	186	190	26.9	27.4
1.96	810	1570	107	210	13.1	25.7

However, it was observed that the first-order plots, although linear, when extrapolated to zero time gave [Co(III)] less than the known starting concentration, i.e. it appears as if some Co(III) is removed by a very rapid initial reaction. This effect becomes more marked with increase of [H₂O₂], with decrease in acidity and with decrease in temperature. Typical results are shown in fig. 8 for 0.52 M HClO₄ at 0° C. It will be seen, for example, that with 2.36×10^{-3} M H₂O₂ the



FIG. 7.—Bimolecular plots of the reaction of cobaltic ions with hydrogen peroxide at 25° C and with I = 2.00.



FIG. 8.—Rapid initial drop in apparent Co(III) concentration at 0° C with initial [Co(III)] $\sim 7 \times 10^{-5}$ M, [H⁺] = 0.517 N HClO₄, I = 2.00, and various [H₂O₂].

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extrapolated [Co(III)] at zero time is 1.8×10^{-5} M compared with 5.9×10^{-5} M actually present.

It seemed possible that this phenomenon was due to a rapid reduction of Co(III) by some oxidizable material other than H_2O_2 . However, this is unlikely since the extent of the apparent reduction was found to be unaffected by successive additions of Co(III), a procedure which could be expected to remove at least part of the impurity. These experiments also showed that Co^{2+} , at the concentrations which are produced during the reaction, has no effect on the reaction rates.



FIG. 9.—Effect of acidifying after mixing Co(III) and H₂O₂ at 0° C, $[H_2O_2] = 1.85 \times 10^{-3}$ M and initial $[Co(III)] = 7.65 \times 10^{-5}$ M; initial $[H^+] = 0.517$ N and $- \cdot \odot - \cdot$ made 1.67 N at 3.25 min.

A more likely explanation of this initial fall in [Co(III)] is that Co(III) is removed by a rapid and reversible reaction with hydrogen peroxide, e.g.,

$$Co(III) + H_2O_2 \xrightarrow{\longrightarrow} Co(III) \cdot HO_2^- + H^+ = K_4$$

Provided Co(III). HO_2^- has a smaller absorption coefficient at 230 m μ than free Co(III), the apparent decrease in Co(III) and the variation of the extent of this with acid and H_2O_2 concentrations are qualitatively explained by the above equilibrium. As will be seen below, the observations are also quantitatively consistent with this.

Evidence that the initial removal of Co(III) is reversible was obtained by making a mixture of Co(III) and H_2O_2 (initially 0.52 M in acid) 1.67 M in acid soon after mixing. The apparent [Co(III)] in the strongly acidified solution at the time of acidifying (obtained by extrapolating back) was then compared with that of a sample of the original mixture which had not been made strongly acid. The observations are shown in fig. 9. It will be seen that the apparent concentration in the stronger acidity is appreciably higher than that observed at the same time in the weaker acidity, as would be expected if the equilibrium is shifted in the direction of more free Co(III).

Formation constant of Co(III). HO_2^-

The observations similar to those in fig. 8 can be analysed quantitatively in terms of the above equilibrium. Thus it appears from fig. 8 that the optical absorption of Co(III). HO_2^- is small compared with that of Co(III), since at the

highest $[H_2O_2]$ the extrapolated [Co(III)] at t = 0 is only about 10 % of that added, i.e. at least 90 % of the Co(III) is present as Co(III) . HO₂⁻ and hence the absorption coefficient of free Co(III) is at least ten times that Co(III) . HO₂⁻. To the accuracy which the observations allow we can therefore assume that the optical absorption arises from free Co(III) only. The extrapolations to t = 0 then give the instantaneous values of [Co(III)] and [Co(III) . HO₂⁻] before any reduction of Co(III) has occurred. These are shown in table 4 for different [H⁺] and [H₂O₂]. Values of the formation constant K_4 given by

$$K_4 = \frac{[\text{Co(III)} \cdot \text{HO}_2^-][\text{H}^+]}{[\text{Co(III)}][\text{H}_2\text{O}_2]}$$

have been calculated, and although showing some variation are sufficiently con stant to lend support to the above interpretation. The experimental difficulty in getting accurate values of K_4 in this way arises from the fact that appreciable amounts of Co(III). HO₂⁻ are only present at the higher [H₂O₂] and lower [H⁺] where the extrapolations to t = 0 are liable to inaccuracy on account of the high reaction rates.

TABLE 4.—FORMATION CONSTANTS OF CO(III). HO2-

total [Co(III)] × 10 ⁵ M	$[\rm H_2O_2] \times 10^4 M$	extrapolated [Co(III). HO_2^{-}] × 10 ⁵ M at $t = 0$	K_4	
9.3	2.42	<i>ca</i> . 0·3		
9.1	4.76	ca. 0.4		1.96 N HClO₄
8.3	11.4	1.2	300	at 0° C
7.6	21.1	1.8	300	
8.2	41.7	3.2	300	
7.8	2.37	<i>ca</i> . 0·4		
7.5	4.67	0.8	260	
7.0	11.2	1.2	190	1.02 N HClO4
6.3	20.7	1.7	180	at $0^{\circ} C$
5-4	36.2	2.9	320	
7.2	2.71	0.9	280	
7.0	5.33	1.9	360	
6.6	12.7	2.7	290	0.2 N HClO₄
5.9	23.6	3.8	400	at 0° C
4.9	41.3	4.2		
8.1	.8.34	1.1	380	1.96 N HClO ₄ at 12.5° C
7.9	8.31	2.0	420	1·02 N ,, ,,
7.75	8.38	3.1	410	0·52 N " "

The constant K_4 above is related to the constant K_c for the equilibrium

 $Co(III) + HO_2^- \xrightarrow{\longrightarrow} Co(III) \cdot HO_2^- K_c$

by the equation $K_4 = K_c K_p$, where K_p is the ionization constant of hydrogen peroxide. The mean value of K_4 from table 4 are 290 at 0° C and 12.5° C respectively. Combining these with the values of K_p at the same temperatures and ionic strength ¹⁰ gives $K_c = 1.4 \times 10^{14}$ and 9×10^{13} respectively, from which $\Delta H = -5$ kcal/mole and $\Delta S = 46$ cal/mole deg. for the formation of Co(III). HO₂⁻ from the ions.

The exact formulation of the species Co(III) . HO_2^- depends upon the state of Co(III) in solution. If as is commonly supposed Co³⁺ is the predominant form then the observations are consistent with the peroxy complex being CoHO₂²⁺ and the ΔH and ΔS of formation are of the order observed for the corresponding Fe³⁺ complex.¹¹ If on the other hand Co(III) is in the binuclear form, as suggested

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above, then the formula $CoHO_2^{2+}$ would not lead to a constant value of K₄. It would then have to be of the form (Co-O-CoHO₂)³⁺, i.e. with binuclear Co(III) in the peroxy complex.

MECHANISM OF REDUCTION OF Co(III) by H_2O_2

We have seen that the method used for following the reaction measures only free Co(III) so that the observed rate law is

$$- \mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = k_4[\mathrm{Co(III)}][\mathrm{H}_2\mathrm{O}_2]/[\mathrm{H}^+].$$

The values of k_4' in table 3 give

 $k_4 = 6 \times 10^{22} \exp(-26,000/RT) \text{ mole}^{-1} \text{ l. min}^{-1}$.

If we are concerned with the reaction of a monomeric form of Co(III) the inverse dependence on [H⁺] can arise from any or all of the following mechanisms :

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$$\begin{array}{c} \mathrm{Co^{3+} + HO_{2^{-}} \rightarrow \mathrm{Co^{2+} + HO_{2^{+}}},}\\ \mathrm{Co^{3+} + HO_{2^{-}} \xrightarrow{K_{c}} \mathrm{CoHO_{2^{+}}^{2^{+}} \rightarrow \mathrm{Co^{2+} + HC_{2^{+}}},}\\ \mathrm{CO^{3+} . H_{2}O \xleftarrow{K_{1}} \mathrm{CoOH^{2^{+}} + H^{+} + H_{2}O_{2} \rightarrow \mathrm{Co^{2+} + H_{2}O + HO_{2^{+}} + H^{+}}.} \end{array}$$

Assuming that the equilibria are established rapidly all three schemes lead to observed rate law provided $[H^+] \gg K_c K_p$, or $[H^+] \gg K_1 K_w$, both of which hold in the range of [H⁺] used.

If in fact Co(III) is present as the dimer exactly analogous reactions to the above can be written, the only difference being that the oxidation can now take place as a two-electron step giving oxygen directly.

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