OXIDATION STUDIES

II. Oxidation of Water and Tertiary Alcohols by Cobaltic Ions

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Abstract

Studies on oxidation of water by cobaltic ions in perchloric, nitric and sulfuric acid media in the temperature range 20–30° C. at constant ionic strength of 2·2 M were carried out. An overall order of 3/2 for cobaltic ion concentration was observed in perchloric, nitric acid media and at low $[Co^{3+}] < 4 \times 10^{-3}$ M in sulfuric acid medium. At high $[Co^{3+}]$ in sulfuric acid medium an order 2 was observed. In all the three acid media an inverse dependence of the rates on $[H^+]$ was noticed. From the experimental results, an acid-independent reaction path was inferred in perchloric and nitric acid media. The effect of ionic strength, HSO_4^- and initially added cobaltous ions as well as temperature was studied. Suitable reaction schemes were suggested to explain the experimental results and activation energy values for some of the rate parameters were evaluated. Kinetic studies on oxidation of tertiary amyl and tertiary butyl alcohols in sulfuric acid medium and that of the former in perchloric acid medium were carried out. The reaction rates were found to vary linearly with $[Co^{3+}]$ and $[Alcohol]$. From the effect of acidity and of $[HSO_4^-]$ in H_2SO_4 medium on the reaction rates it was concluded that in $HClO_4$ medium $CoOH^{2+}$ species were the active entities while in H_2SO_4 medium Co^{3+} as well as $CoOH^{2+}$ species were the active entities. The influence of ionic strength, temperature, etc., on the raction rates were studied and activation energy values for some rate constants were evaluated.

Introduction

Studies on oxidation of water by trivalent cobalt in nitric acid medium by Noyes and Deahl[1] did not lead to satisfactory explanation of the mechanism and effect of $[H^+]$ on the reaction rate was also not studied. Bawn and White[2] in their studies in $HClO_4$ and H_2SO_4 reported first as well as second order with reference to $[Co^{3+}]$ along with a variable order for $[H^+]$ (1 to 2) and their mechanism did not very well explain their results. On the other hand Baxendale and Wells[3] reported a 3/2 order for $[Co^{3+}]$ and an inverse square

dependence of $[H^+]$ on the rate law for cobaltic ion disappearance. All the previous investigations were confined to low acidities (< 0.1 N) only. We present in this paper our results on oxidation of water by Co^{3+} in perchloric, nitric and sulfuric acid media at $[H^+] = 0.4$ M $- 2.0$ M at constant ionic strength of 2.2 M. Hoare and Waters[4, 5] have reported results on oxidation of tertiary butyl alchohol in $HClO_4$ medium at $10°$ C. at $[H^+] = 0.325$ M– 3.25 M and of other tertiary alcohols in methylcyanide-water mixture at $15°$ C. at $[HClO_4] = 1.57$ M. The results on oxidation of tertiary butyl (T.B.A.) and amyl alcohols (T.A.A.) in sulphuric acid medium and tertiary amyl alcohol in $HClO_4$ medium are presented and discussed in this paper.

EXPERIMENTAL

Reagents.—The perchlorate[6] and sulfate[2] of Co^{3+} were prepared by methods already described. Cobaltic nitrate was prepared along the same lines as for the perchlorate. Tertiary butyl alcohol (T.B.A.) and tertiary amyl alcohol (T.A.A.) (B.D.H.A.R. reagents) were distilled and the middle fractions used for all experiments. Other reagents, sodium or potassium bisulfate, sulfuric acid, perchloric acid, nitric acid, sodium nitrate, ceric ammonium nitrate, ferrous ammonium sulfate, etc., were of A.R. grade. Sodium perchlorate used for adjustment of ionic strength was prepared by neutralization of A.R. sodium carbonate with A.R. perchloric acid. Water doubly distilled over permanganate and passed through a column of " Bioderminrolit " mixed bed ion exchange resin was used for the preparation of all reagents.

Estimations and rate measurements.—Methods of estimation of $[Co^{3+}]$, total cobalt content, free acid, etc., in solution were as already described.[6] Experiments were conducted in long pyrex tubes fitted with B-24 joints. Solutions containing requisite amount of free acid and appropriate sodium salt of the free acid (and alcohol in the case of oxidation of alcohol experiments) were thermostated at the required temperature and deaerated with oxygen-free nitrogen. The cobaltic salt was added at the end of the deaeration period. The reaction was arrested by the addition of excess standard Fe^{2+} and rates of cobaltic ion disappearance, $- R_{co}$, were computed as described.[6]

RESULTS AND DISCUSSION

A. Oxidation of Water

Studies on oxidation of water were carried out in the temperature range 20–$30°$ C. At the acidities ($[H^+] = 0.4$–2.0 M) employed in this work

appreciable decomposition of water by Co^{3+} was observed. Rates in sulfuric acid medium were usually greater than in perchloric or nitric acid media.

(i) *$HClO_4$ medium.*—A 3/2 order with reference to $[Co^{3+}]$ (Fig. 1, A, B) and an inverse dependence of $[H^+]$ (Fig. 1, lines C–G) on $- R_{co}$ were observed. Plots of $- R_{co}$ *vs.* $1/[H^+]$ at various initial $[Co^{3+}]$ were devoid of intercepts on the ordinates indicating that cobaltic ions (hydrated) as such were not important as the active species. Baxendale *et al.*[3] also found a 3/2 order for $[Co^{3+}]$ but with an inverse square dependence of $[H^+]$ on $- R_{co}$. They employed low acidity, $[H^+] < 0.1$ M.
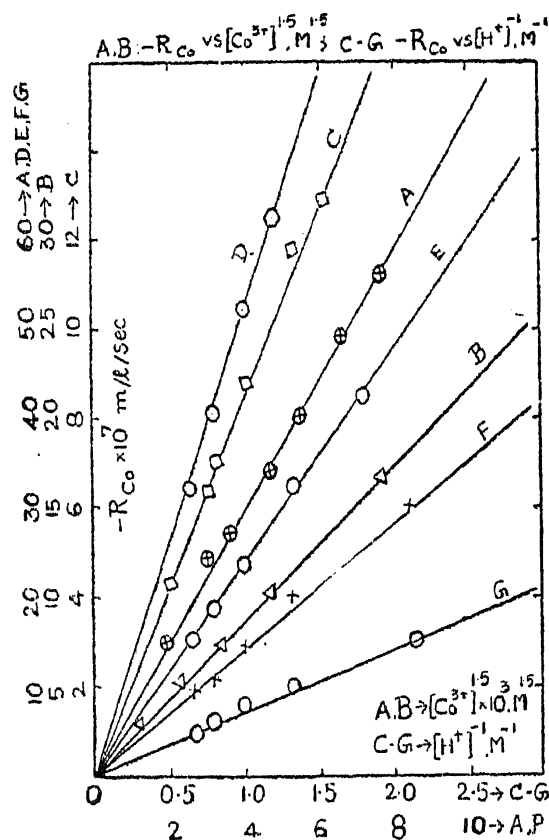

FIG. 1. Variation of $- R_{co}$ with $[Co^{3+}]$ and $[H^+]$ in $HClO_4$ medium.

A and B: $- R_{co}$ *vs.* $[Co^{3+}]^{1.5}$ at Temp. 30°C. and 20°C. respectively and $[H^+] = 1.2$ M; μ: 2.2 M.

C, D, E, F, G: $- R_{co}$ *vs.* $1/[H^+]$; C at $[Co^{3+}]$: 26.62×10^{-3} M, Temp. 20°C.

μ: 2.2 M and D, E, F, G at $[Co^{3+}]$: 32.28×10^{-3} M, 18.81×10^{-3} M, 13.14×10^{-3} M and 7.925×10^{-3} M respectively all at μ: 2.2 M, Temp. 30°C.

(ii) *HNO_3 medium.*—In nitric acid medium results were similar to those in perchloric acid (Fig. 2, E, F). The plots of $- R_{co}$ *vs.* $1/[H^+]$ however left intercepts on the ordinates (Fig. 4, E) emphasizing the importance of the acid-independent reaction of Co^{3+} (aq.) + water. The latter aspect was studied in detail along the following lines. At a series of different initial $[Co^{3+}]$, $[H^+]$ was varied at constant ionic strength. Plots of $- R_{co}$ *vs.* $1/[H^+]$

were linear (acid-dependent reaction) leaving different intercepts for different $[Co^{3+}]$. The slopes of these plots were proportional to $[Co^{3+}]^{3/2}$ (Fig. 2, C, D) while the intercepts to $[Co^{3+}]$ (Fig. 2, A, B). The acid-dependent rate was greater than the acid-independent rate by a factor of 5, the disparity increasing with increasing $[Co^{3+}]$ and hence giving an overall order of 3/2 for $[Co^{3+}]$ in $- R_{co}$ vs. $[Co^{3+}]$ plots.
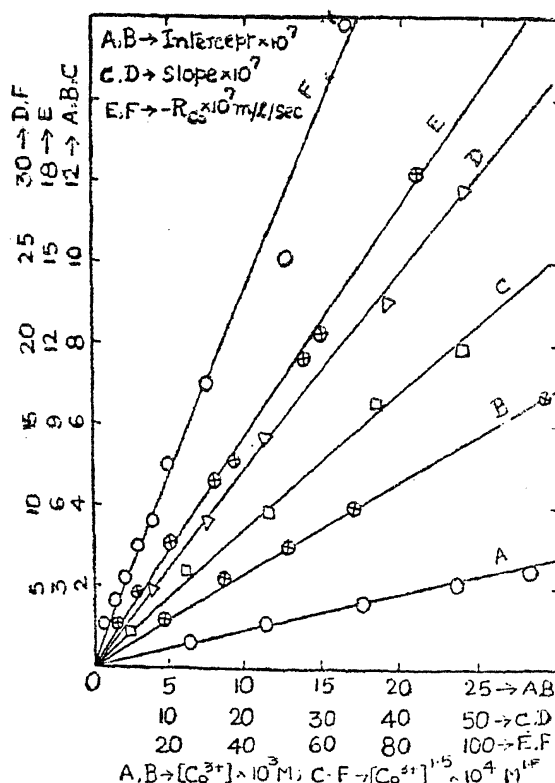

FIG. 2.   HNO$_3$ medium.

A, B: Intercept vs. $[Co^{3+}]$ at 20° C. and 30° C. respectively at μ: 2·2 M.

C, D: Slope vs. $[Co^{3+}]^{1.5}$ at 20° C. and 30° C. respectively at μ: 2·2 M; E, F: $- R_{co}$
   vs. $[Co^{3+}]^{1.5}$ at $[H^+]$: 1·2 M, μ: 2·2 M; E, at 20° C. F at 30° C.

(iii) H_2SO_4 medium.—In sulfuric acid medium the order with reference to $[Co^{3+}]$ was found to depend on the initial $[Co^{3+}]$; at $[Co^{3+}] \lesssim 4 \times 10^{-3}$ M, a 3/2 order (Fig. 3, C, D) and at $[Co^{3+}] > 4 \times 10^{-3}$ M, an order of 2 for $[Co^{3+}]$ (Fig. 3, A, B) were observed. Plots of $- R_{co}$ vs. $1/[H^+]$ at various initial $[Co^{3+}]$ ($> 4 \times 10^{-3}$ M) were linear (Fig. 4, F) with intercepts on the ordinates, the latter emphasizing the direct reaction between Co^{3+} (aq.) and water. The plots of $- R_{co}$ vs. $1/[H^+]$) at low $[Co^{3+}]$ left no intercepts on the ordinate but at lower acidities the plots were flat and almost parallel to the abscissa (Fig. 3, E). A similar behaviour was observed with high $[Co^{3+}]$ also. Probably at low acidities inert ion pair sulfate complexes of the type suggested by Sutcliffe and Weber[8] are formed which may be slowly converted to inner

sphere complexes.[9] The formation of these inert complexes (ion pair as well as inner sphere) results in constancy of rates $(- R_{co})$ with variation in $[H^+]$. For high $[Co^{3+}]$, intercepts varied as $[Co^{3+}]$ (Fig. 4, A, B) while the slopes varied as $[Co^{3+}]^2$ (Fig. 4, C, D). The magnitude of acid-independent
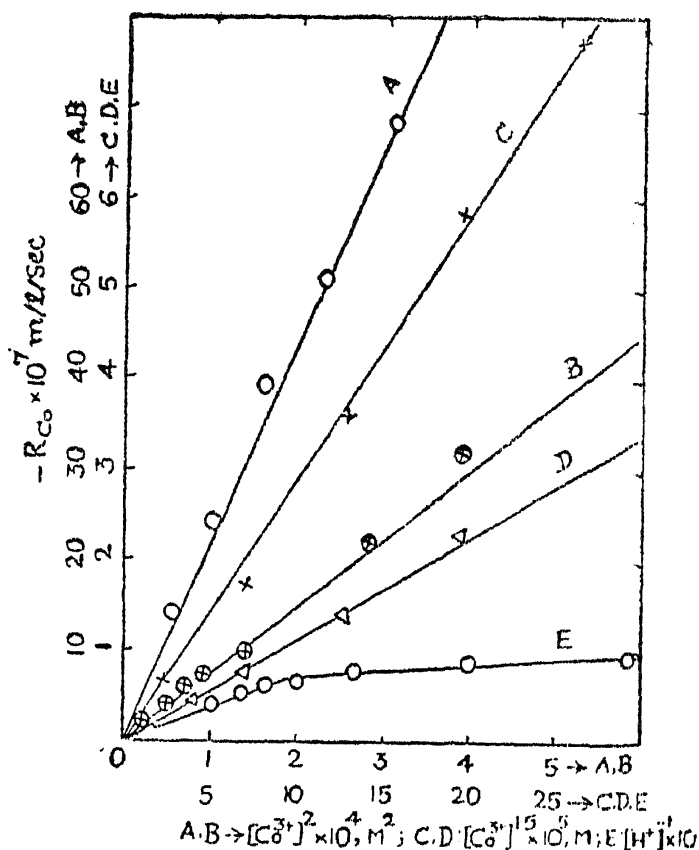

Fig. 3. Variation of $- R_{Co}$ with $[Co^{3+}]$ and $[H^+]$ in H_2SO_4 medium; all at μ: 2·2 M.

A, B: $- R_{Co}$ *vs.* $[Co^{3+}]^2$ at $[H^+]$: 1·0 M and Temp. 30° C. and 20° C. respectively.

C and D: $- R_{Co}$ *vs.* $[Co^{3+}]^{1.5}$ at $[H^+]$ 1·0 M and Temp. 30° C. and 20° C. respectively.

E: $- R_{Co}$ *vs.* $1/[H^+]$ at $[Co^{3+}]$: 2·324 × 10^{-2} M, Temp. 20° C.

rate constant being less than the acid-dependent rate constant by a factor of 100, it was understandable that an overall order of two for $[Co^{3+}]$ was obtained from plots of $- R_{co}$ *vs.* $[Co^{3+}]$. From the foregoing experimental results the summary of the rate laws in various acid media is as follows:

$$HClO_4 \text{ medium:} \quad - R_{co} = \frac{a_1 [Co^{3+}]^{3/2}}{[H^+]} \quad \text{at} \quad \mu: 2·2 \text{ M}$$

$$(a_1 = 2·242 \times 10^{-4} \text{ at } 20° \text{ C.}; \quad 9·084 \times 10^{-4} \text{ at } 30° \text{ C.}$$

$$E_{a1} = 24·69 \text{ K. cals. mole}^{-1}.)$$

HNO$_3$ medium: $\quad - R_{co} = a [Co^{3+}] + \dfrac{b [Co^{3+}]^{3/2}}{[H^+]} \quad$ at $\quad \mu: 2 \cdot 2$ M

$a = 8 \cdot 8 \times 10^{-6}$ at $20° C.; \quad 11 \cdot 53 \times 10^{-6}$ at $30° C.;$

$E_a = 4 \cdot 773$ K. cals. mole^{-1}.

$b = 2 \cdot 05 \times 10^{-4}$ at $20° C.; \quad 6 \cdot 519 \times 10^{-4}$ at $30° C.;$

$E_b = 20 \cdot 44$ K. cals. mole^{-1}.

H$_2$SO$_4$ medium : $\quad$ at $[Co^{3+}] < 4 \times 10^{-3}$ M

$- R_{co} = \dfrac{a_2 [Co^{3+}]^{3/2}}{[H^+]} \quad$ at $\quad \mu: 2 \cdot 2$ M.

$(a = 2 \cdot 889 \times 10^{-3}$ at $30° C.; \quad 1 \cdot 131 \times 10^{-3}$ at $20° C.;$

$E_a = 16 \cdot 58$ K. cals. mole$^{-1})$

and at

$[Co^{3+}] > 4 \times 10^{-3}$ M

$- R_{c_a} = a' [Co^{3+}] + \dfrac{b' [Co^{3+}]^2}{[H^+]} \quad$ at $\quad \mu: 2 \cdot 2$ M

$a' = 11 \cdot 19 \times 10^{-5}$ at $30° C.; \quad 2 \cdot 083 \times 10^{-5}$ at $20° C.;$

$E_{a'} = 29 \cdot 7$ K. cals. mole$^{-1};$

$b' = 19 \cdot 33 \times 10^{-3}$ at $30° C.; \quad 6 \cdot 183 \times 10^{-3}$ at $20° C.;$

$E_{b'} = 20 \cdot 15$ K. cals. mole^{-1}.

Effect of ionic strength.—Increase of ionic strength in HClO$_4$ and HNO$_3$ ($\mu = 0 \cdot 4$–4 M) increased the rate while in H$_2$SO$_4$ the opposite effect was observed (*cf.* Table I, *a*). This is probably due to the effect of μ on the various equilibria involved in the different acid media in the presence of Co^{3+} ions.

Initial addition of Co^{2+}.—Initial addition of Co^{2+}, ([Co^{2+}]/[Co^{3+}] = 0·5 - 20) in HClO$_4$ and HNO$_3$ had no effect on the rates while in H$_2$SO$_4$ the rates were slightly retarded probably due to complexing of Co^{3+} (aq.) + SO$_4^-$ (the latter from CoSO$_4$ added) which decreased the effective concentration of reactive cobaltic species, CoSO$_4^+$ or Co^{3+} (aq.), etc. This was further supported by the fact that addition of Co (ClO$_4$)$_2$ in H$_2$SO$_4$ medium at constant ionic strength had no influence on the rates. These results further

indicate that exchange reactions between Co^{2+} (aq.) and Co^{3+} (aq.)[10,11] as well as the various species of Co^{3+} (aq.) in the various acid media, are not of any mechanistic significance.
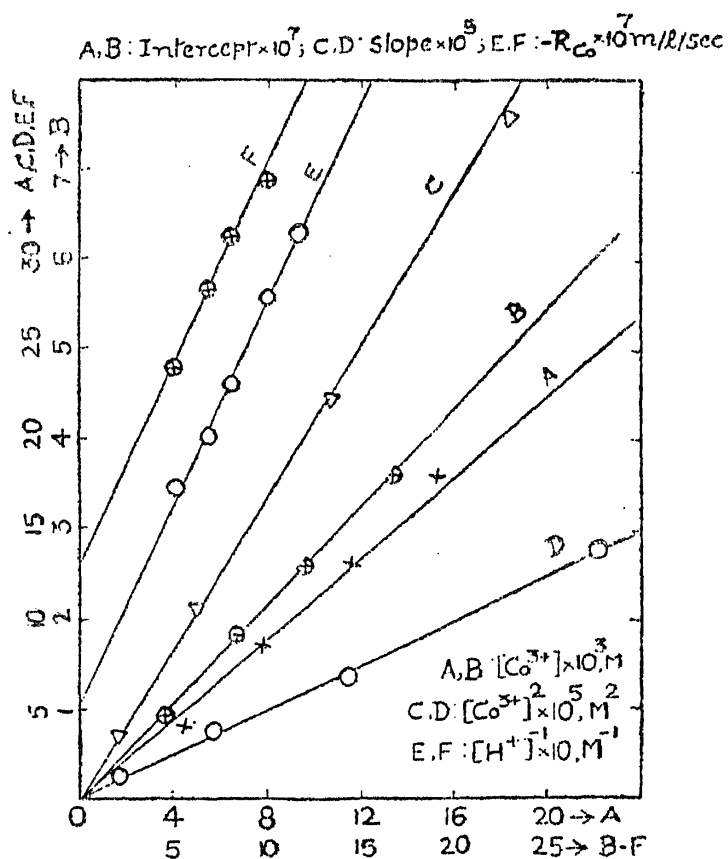

FIG. 4. H_2SO_4 medium, all at μ: 2·2 M.

A, B: Intercept *vs.* [Co^{3+}] at Temp. 30° C. and 20° C. respectively;
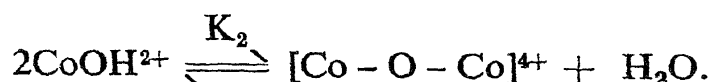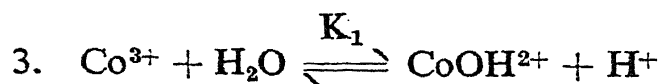
C and D: Slope *vs.* [Co^{3+}]³ at Temp. 30° C. and 20° C. respectively;

E and F: $- R_{Co}$ *vs.* 1/[H^+]; E: HNO_3 medium, [Co^{3+}]: 24·55×10⁻³ M, Temp. 30° C.

 F: H_2SO_4 medium, [Co^{3+}]: 11·55×10⁻³ M., Temp. 30° C.

Mechanism.—Bawn and White[2] as extension to studies of Oberer[7] and Noyes and Deahl[1] indicated the variable nature of the order of Co^{3+}, being unity at low [Co^{3+}] and 2 at high [Co^{3+}] and an inverse variable order for [H^+]. A mechanism based on the reactions (i) Co^{3+} + OH^- and (ii) $CoOH^{2+}$ + OH^-, both producing $OH^\cdot$ which dimerised to H_2O_2 and the latter decomposing and liberating O_2 was suggested. The higher order 2 was explaind on the basis of probable dimers like $(Co-SO_4-Co)^{+4}$ in H_2SO_4 and $(Co-O-Co)^{+4}$ in $HClO_4$ being the active species. On the other hand, studies by Baxendale and Wells[3] have shown three halves order for [Co^{3+}] and an inverse second order for [H^+] and a suitable mechanism involving interaction of monomeric and dimeric species from the hydrolysis of Co^{3+} (aq.) was suggested. It is to be noted however that Baxendale *et al.* have used [H^+] < 0·1 N in $HClO_4$ and H_2SO_4 media in which region extensive hydrolysis of Co^{3+} (aq.) and the

formation of dimeric species was quite probable. In our studies, while the 3/2 order for $[Co^{3+}]$ in $HClO_4$, HNO_3 and H_2SO_4 at low $[Co^{3+}]$ is in agreement with the results of Baxendale *et al.*, a strict $[H^+]^{-1}$ dependence in contradistinction to $[H^+]^{-2}$ dependence reported by the latter workers, was observed. Our results, however, may be explained on the basis of a mechanism slightly different (Step 4 below) from that proposed by Baxendale *et al.*:

1. $CoOH^{2+} + (HO - Co - O - Co)^{3+} \xrightarrow[\text{slow}]{k_1} 3Co^{2+} + OH^- + HO^{\circ}{}_2.$

2. $HO^{\circ}{}_2 + CoOH^{2+} \xrightarrow{\text{fast}} Co^{2+} + H_2O + O_2.$

3. $Co^{3+} + H_2O \underset{\longleftarrow}{\overset{K_1}{\rightleftharpoons}} CoOH^{2+} + H^+$

     $2CoOH^{2+} \underset{\longleftarrow}{\overset{K_2}{\rightleftharpoons}} [Co - O - Co]^{4+} + H_2O.$
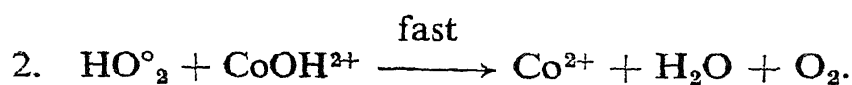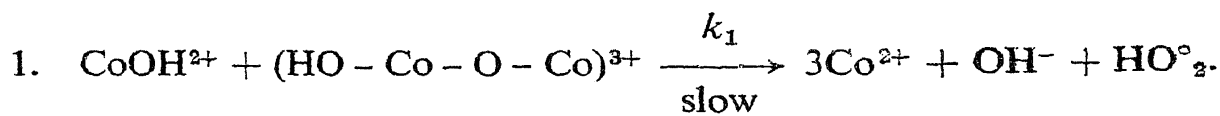
The new equilibrium now assumed is

4. $[Co - O - Co]^{4+} + H_2O \underset{\longleftarrow}{\overset{K_3}{\rightleftharpoons}} (HO - Co - O - Co)^{3+} + H^+.$

On the basis of this mechanism the rate is given by

$$- R_{co} = \frac{K_3 k_1}{K_2^{\frac{1}{2}}} \frac{[(Co - O - Co)^{4+}]^{3/2}}{[H^+]} \approx \frac{K [Co^{3+}]^{3/2}}{[H^+]}.$$

In HNO_3 medium it is assumed that the same type of equilibria are involved since addition of NO_3^- in $HClO_4$ medium at constant μ had no effect on the rates which suggested that probably no nitrate ion pairs were formed. In H_2SO_4 medium however addition of HSO_4^- at constant μ enhanced the rates with increasing $[HSO_4^-]$, but at higher $[HSO_4^-]$, a slight retardation was observed (*ref.* Table I, *b*) the latter phenomenon occurring probably due to formation of stable inert poly-sulfato complexes of Co^{3+} (monomeric, dimeric, etc.). The initial increase in rates with increasing $[HSO_4^-]$ evidently indicates the involvement of sulfate ion pair (or inner sphere) complexes in the reaction sequence. Our results in H_2SO_4 medium at $[Co^{3+}] < 4 \times 10^{-3}$ M may be explained on the basis of a similar mechanism assuming $CoSO_4^+$ species instead of $CoOH^{2+}$ as the active species. Our results in H_2SO_4 medium at

TABLE I

(a) *Effect of ionic strength on the rates of oxidation of water by cobaltic ions*

HNO_3 medium: $[H^+] = 0 \cdot 362$ M; Temp. $= 20°$ C., $[Co^{3+}] = 8 \cdot 358 \times 10^{-3}$ M

μ, M ($HNO_3 + NaNO_3$)	0·4125	0·8124	1·346	2·401	2·945	3·478	4·011
$- R_{co} \times 10^7$ m/1/sec.	3·210	3·505	4·005	4·406	5·005	5·805	6·209

H_2SO_4 medium; $[H^+] = 0 \cdot 5026$ M; Temp. $= 20°$ C.; (Co^{3+}): $2 \cdot 2 \times 10^{-2}$ M

μ, M ($H_2SO_4 + KHSO_4$)	0·8	1·4	2·0	2·6	3·2
$- R_{co} \times 10^6$ m/1/sec.	5·937	5·104	4·583	4·429	4·271

(b) *Effect of [HSO_4^-] on the rates of water oxidation in H_2SO_4 medium by cobaltic ions*

$[H^+]$: $0 \cdot 3981$ M, Temp. $20°$ C.; μ: $2 \cdot 2$ M; $[Co^{3+}]$: $3 \cdot 684 \times 10^{-3}$ M

($H_2SO_4 + NaHSO_4$), M	0·398	0·695	0·945	1·345	1·745	2·145
$- R_{co} \times 10^7$ m/1/sec.	4·783	6·327	7·360	7·790	7·582	7·218

$[H^+]$: $0 \cdot 618$ M; Temp. $20°$ C.; μ: $2 \cdot 4$ M; $[Co^{3+}]$: $15 \cdot 25 \times 10^{-3}$ M

($H_2SO_4 + NaHSO_4$), M	0·618	0·971	1·271	1·571	1·871	2·171
$- R_{co} \times 10^6$ m/1/sec.	3·591	3·869	3·994	3·987	3·885	3·766

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high $[Co^{3+}]$, second order for $[Co^{3+}]$ together with the $1/[H^+]$ dependence can be satisfactorily explained as follows:

$$Co^{3+} + HSO_4^- \overset{K_4}{\rightleftharpoons} CoSO_4^+ + H^+$$

$$CoSO_4^+ + Co^{3+} + H_2O \overset{K_5}{\rightleftharpoons} (Co - O - CoSO_4)^{2+} + 2H^+$$

$$(Co - O - CoSO_4)^{2+} + H_2O \xrightarrow[\text{slow}]{k_2} 2Co^{2+} + SO_4^- + 2OH°$$

$$2OH° \longrightarrow H_2O + \tfrac{1}{2} O_2$$
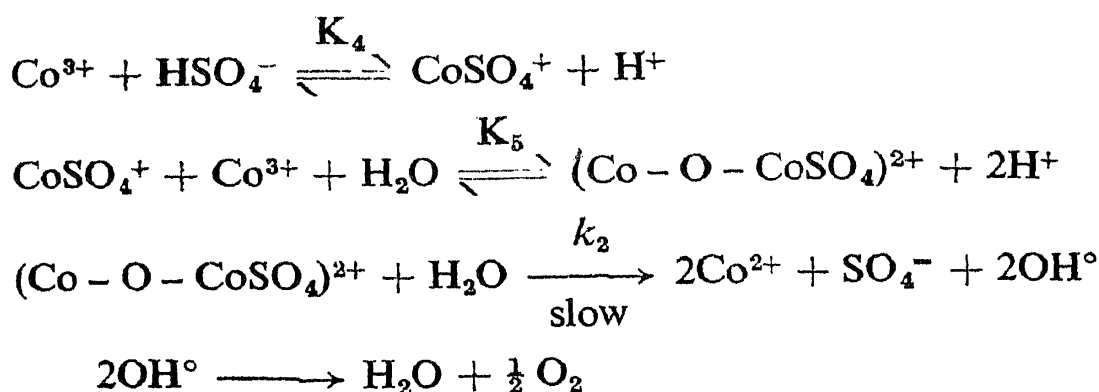
on the basis of this mechanism, the rate is given by

$$- R_{co} = k_2 (Co - O - CoSO_4)^{2+}$$

$$= k_2 K_5 \frac{[CoSO_4^+] [Co^{3+}]}{[H^+]^2} = \frac{K [Co^{3+}]^2}{[HSO_4^-] [H^+]}$$

if

$$[CoSO_4^+] \approx [Co^{3+}] \text{ Total} \quad \text{and} \quad K = k_2 K_5/K_4.$$

For acid-independent reaction in HNO_3 and H_2SO_4 media

$$Co^{3+} \text{ (aq.)} + 2H_2O \xrightarrow{k_3} Co^{2+} \text{ (aq.)} + O_2 + 4H^+.$$
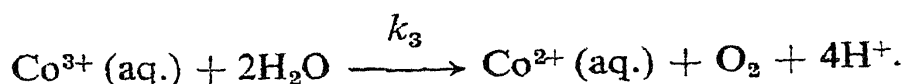
The above reaction schemes fit in with our experimental observations very well. However the question of formation of dimeric species leading to $Co - O - Co$ bridging and that of the nature of active species being inner or outer sphere complexes, in our system, must be considered as unsettled.

B. Oxidation of Alcohols

Studies on oxidation of T.B.A. and T.A.A. in aqueous solution by Co^{3+} in $HClO_4$ and H_2SO_4 in the temperature range 10–25°C. were carried out. It was found that oxygen had no effect on the reaction rate. In the range of cobaltic concentrations $(10^{-3} - 10^{-2} M)$ and acidities $(0.5–2.0 M)$ used, a certain amount of decomposition of water was unavoidable but the overall rate, $- R_{co}$, was strictly proportional to the first power of $[Co^{3+}]$; log $a/a-x$ vs. Time plots were linear in both acids, with small constant intercepts corresponding to water oxidation rate. The pseudo first-order rate constants $(k, \text{ sec.}^{-1})$ were strictly proportional to the first power of alcohol concentration (Fig. 5, A, B, C) for both alcohols. A linear variation of k, sec.$^{-1}$ with $1/[H^+]$ was observed (Fig. 5, D-I) with no intercepts on the ordinates in $HClO_4$ medium and with intercepts on the ordinates for H_2SO_4 medium (Fig. 5, F-I) for both alcohols. An oxidation route involving free cobaltic (aq.) ions also was evident in the latter case, while the hydrolysis product $CoOH^{2+}$ alone was probably the active species in $HClO_4$ medium. In their studies on oxidation of T.B.A. in $HClO_4$ medium (at $[H^+] = 0.325$, $- 3.25 M$, Temp. $= 10°$ C., μ: $3.25 M$) Hoare and Waters[4] reported that $CoOH^{2+}$ was the stronger oxidant. Our results with respect to T.B.A. are in accordance with those of Hoare and Waters. We find that for T.A.A. also, $CoOH^{2+}$ is the active species in $HClO_4$ medium. In H_2SO_4 medium, however, the inverse dependence of k, sec.$^{-1}$ on $[H^+]$ may arise from $CoOH^{2+}$ and/or $CoSO_4^+$ being the active species. A direct variation of k, sec.$^{-1}$ with $[HSO_4^-]$ would be noticed if $CoSO_4^+$ is the active species. Increase of total ionic strength using HSO_4^-, resulted only in less than 16% variation in the k, sec.$^{-1}$ values, the values actually decreasing at first with increasing $[HSO_4^-]$ and then practically becoming constant (ref. Table II, a). This is probably due to the formation of

stable inert sulfato complexes of Co^{3+} (aq.) being formed and the consequent depletion of active Co^{3+} species. The above results indicated that in H_2SO_4 medium $CoSO_4^+$ were not the active entities. Our results with reference to k, sec.$^{-1}$ with increase of μ in $HClO_4$ medium for both alcohols cannot be explained and the observed salt effect is therefore anomalous (*cf.* Table II, *a*). The inverse dependence of rate on $[H^+]$ in H_2SO_4 medium may be satisfactorily explained on the basis of $CoOH^{2+}$ being the active species though present in smaller concentrations. Further support for this conclusion is adduced from the effect of $[HSO_4^-]$ at constant μ (maintained with $NaClO_4$) when no direct variation of k, sec.$^{-1}$ with $[HSO_4^-]$ was observed. On the contrary,
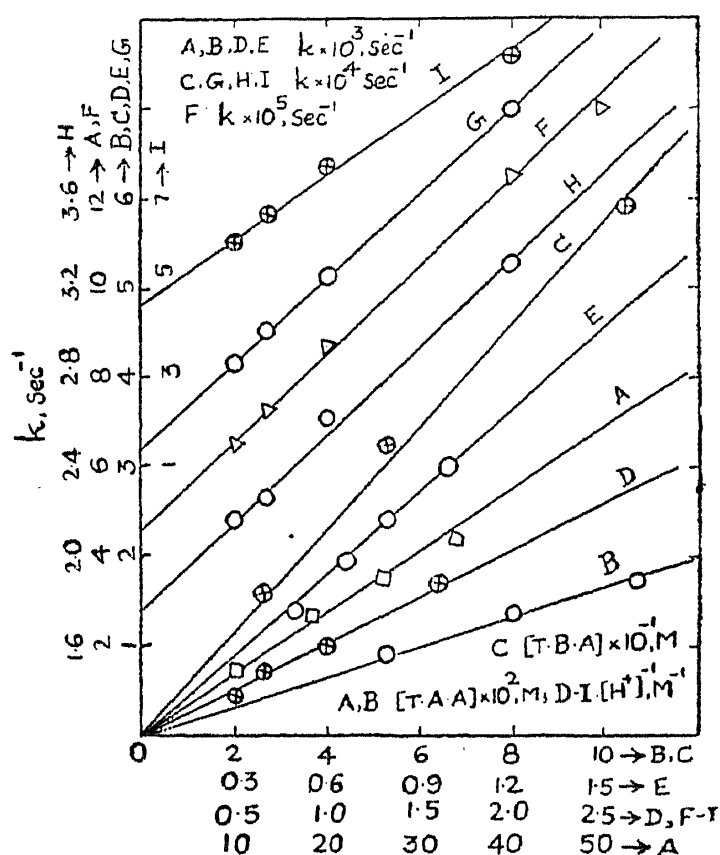

FIG. 5. Variation of k, sec.$^{-1}$ with [A] and $[H^+]$.

A, B: k, sec.$^{-1}$ *vs.* [T.A.A.] in H_2SO_4 and $HClO_4$ respectively.

A: $[H^+]$: 1·0 M, Temp. 14° C., $[Co^{3+}]$: 2·138×10^{-2} M.

B: $[H^+]$: 2·0 M, Temp. 10° C., $[Co^{+3}]$: 1·335×10^{-2} M.

C: k, sec.$^{-1}$ *vs.* (T.B.A.] in H_2SO_4 at $[H^+]$: 1·0 M, μ: 1·67 M, Temp. 14° C., $[Co^{3+}]$: 2·081 × 10^{-2} M.

D, E: k, sec.$^{-1}$ *vs.* $[H^+]^{-1}$ in $HClO_4$ medium.

D: [T.B.A.]: 0·2554 M, Temp. 14° C., μ: 2·1 M; $[Co^{3+}]$: 1·525×10^{-2} M;

E: [T.A.A.]: 8·001×10^{-2} M; Temp. 10° C., μ: 2·1 M, $[Co^{3+}]$: 1·572×10^{-2} M;

F-I: k, sec.$^{-1}$ *vs.* $[H^+]^{-1}$ in H_2SO_4 medium, initial $[Co^{3+}]$: 5–8×10^{-3} M, μ: 2·1 M;

F: [T.B.A.]: 0·1 M, Temp. 15° C.; G: [T.B.A.]: 0·1 M, Temp. 25° C.;

H: [T.A.A.]: 5·782×10^{-2} M, Temp. 9° C.; I: [T.A.A.]: 5·782×10^{-2} M, Temp. 14° C.

the rate constants showed a decreasing trend (*cf.* Table II, *b*). This easily follows if it is assumed that $CoOH^{2+}$ alone is the active species.

Table II

(*a*) *Effect of ionic strength on the oxidation of T.B.A. and T.A.A. by cobaltic ions*

$[HClO_4].$: $1 \cdot 0$ M; Temp: $14°$ C., (T.B.A.): $0 \cdot 2554$ M; $[Co^{3+}]$: $1 \cdot 257 \times 10^{-2}$ M

μ, M $(HClO_4 + NaClO_4)$	$1 \cdot 00$	$1 \cdot 42$	$1 \cdot 92$	$2 \cdot 42$
$k \times 10^4$ sec.$^{-1}$	$6 \cdot 2$	$7 \cdot 041$	$8 \cdot 626$	$10 \cdot 44$

$[HClO_4]$: $1 \cdot 028$ M, Temp. $10°$ C.; (T.A.A.)$= 8 \cdot 001 \times 10^{-2}$M; $[Co^{3+}]$: $1 \cdot 572 \times 10^{-2}$ M

μ, M $(HClO_4 + NaClO_4)$	$1 \cdot 12$	$1 \cdot 5$	$2 \cdot 5$	
$k \times 10^3$ sec.$^{-1}$	$1 \cdot 919$	$2 \cdot 175$	$3 \cdot 358$	

$[H_2SO_4] = 1 \cdot 026$ M; Temp. $14°$ C.; (T.B.A.]: $1 \cdot 054$ M; $[Co^{3+}]$: $2 \cdot 018 \times 10^{-2}$ M

μ, M $(H_2SO_4 + NaHSO_4)$	$1 \cdot 026$	$1 \cdot 357$	$1 \cdot 757$	$2 \cdot 357$
$k \times 10^4$ sec.$^{-1}$	$5 \cdot 279$	$4 \cdot 484$	$4 \cdot 764$	$4 \cdot 918$

$[H_2SO_4]$: $1 \cdot 0$ M; Temp. $14°$ C.; (T.A.A.)$= 0 \cdot 1835$ M; $[Co^{3+}]$: $2 \cdot 01 \times 10^{-2}$ M

μ, M $(H_2SO_4 + NaHSO_4)$	$1 \cdot 056$	$1 \cdot 485$	$1 \cdot 913$	$2 \cdot 341$
$k \times 10^3$ sec.$^{-1}$	$2 \cdot 618$	$2 \cdot 408$	$2 \cdot 550$	$2 \cdot 525$

(*b*) *Effect of* $[HSO_4^-]$ *on the oxidation of T.B.A. and T.A.A. in* H_2SO_4 *medium by* Co^{3+}

$[T.A.A.] = 5 \cdot 782 \times 10^{-2}$ M; Temp. $14°$ C.; $[Co^{3+}]$: $4 \cdot 908 \times 10^{-3}$ M; $[H^+]$: $0 \cdot 5$ M; μ: $2 \cdot 0$ M

$(H_2SO_4 + NaHSO_4)$, M	$0 \cdot 426$	$0 \cdot 926$	$1 \cdot 426$	$1 \cdot 926$
$k \times 10^3$ sec.$^{-1}$	$3 \cdot 434$	$1 \cdot 862$	$1 \cdot 382$	$1 \cdot 105$

$[T.B.A.]$: $0 \cdot 12$ M; Temp. $22°$C.; $[Co^{3+}]$: $4 \cdot 586 \times 10^{-3}$ M; $[H^+]$: $0 \cdot 3249$ M; μ: $1 \cdot 8$M

$(H_2SO_4 + NaHSO_4)$, M	$0 \cdot 68$	$1 \cdot 23$	$1 \cdot 73$	
$k \times 10^3$ sec.$^{-1}$	$1 \cdot 326$	$1 \cdot 114$	$1 \cdot 028$	

If

$$k_{obs.} [Co^{3+}] \text{ Total} = k_a [CoOH^{2+}]$$

and

$$[Co^{3+}] \text{ Total} = Co^{3+} + CoSO_4{}^+ + CoOH^{2+}$$

$$\frac{1}{k_{obs.}} = \frac{1}{k_a} + \frac{[H^+]}{k_a K_1} + \frac{K_2 [HSO_4{}^-]}{k_a K_1} \text{ if } K_1$$

is the hydrolytic equilibrium constant for Co^{3+} (aq.) and K_2 is the formation constant for $CoSO_4{}^+$. Further, the possibility of higher species, $Co (SO_4)_2{}^-$, etc., being the active entities is eliminated, since if such were the case a direct dependence of k, sec.$^{-1}$ on $[HSO_4{}^-]^2$ and $[Co^{3+}]^2$ and an inverse square dependence on $[H^+]$, should have been observed.

From the foregoing results, the rate laws for both alcohols may be summarised as follows:

$HClO_4$ medium:

$$- R_{co} = \frac{K [Co^{3+}] [A]}{[H^+]} = \frac{K_1 k_a [Co^{3+}] [A]}{[H^+]}$$

where $[A]$ = concentration of alcohol; K_1 = hydrolytic constant for Co^{3+};

$$K_1 k_a = 1 \cdot 245 \times 10^{-3} \text{ for T.B.A. at } 10° \text{ C. and } \mu: 1 \cdot 5 \text{ M.}$$

Hoare and Waters[4] have reported $1 \cdot 82 \times 10^{-3}$ at $10°$ C.; $\mu: 3 \cdot 25$ M.

For T.A.A. $K_1 k_a = 3 \cdot 53 \times 10^{-2}$ at $10°$ C. and $\mu: 2 \cdot 3$ M. Hoare and Waters[5] reported a value of $5 \cdot 01 \times 10^{-2}$ at $15°$ C. for oxidation of T.A.A. in $HClO_4$ medium, from extrapolation of their data in H_2O + Methylcyanide mixture.

H_2SO_4 medium:

$$- R_{co} = \left\{ a_3 + \frac{b_3}{[H^+]} \right\} [Co^{3+}] [A]$$

where a_3 and b_3 are constants corresponding to acid independent and dependent reactions respectively. Values of a_3 and b_3 at $\mu: 2 \cdot 3$ M are given below together with the E values.

For T.A.A. in H_2SO_4.

$$a_3 = 3 \cdot 078 \times 10^{-3} (9° \text{ C.}), 7 \cdot 956 \times 10^{-3} (14° \text{ C.});$$

$$E_{a_3} = 30 \cdot 59 \text{ K. cals. mole}^{-1}$$

$$b_3 = 1 \cdot 328 \times 10^{-3} \, (9° \, C.); \quad 4 \cdot 941 \times 10^{-3} \, (14° \, C.);$$

$$E_{b_3} = 42 \cdot 33 \, K. \, cals. \, mole^{-1}.$$

For T.B.A. in H_2SO_4:

$$a_3 = 4 \cdot 6 \times 10^{-4} \, (25° \, C.); \quad 3 \cdot 2 \times 10^{-4} \, (15° \, C.);$$

$$E_{a_3} = 6 \cdot 2 \, K. \, cals. \, mole^{-1}$$

$$b_3 = 1 \cdot 875 \times 10^{-3} \, (25° \, C.); \quad 3 \cdot 886 \times 10^{-4} \, (15° \, C.);$$

$$E_{b_3} = 26 \cdot 89 \, K. \, cals. \, mole.^{-1}$$

The overall rate constant $a_3 + b_3/[H^+]$ evaluated from k, sec.$^{-1}$ vs. [A] plots are $5 \cdot 882 \times 10^{-4}$ (14° C.) for T.B.A. and $1 \cdot 369 \times 10^{-2}$ (14° C.) for T.A.A. under indentical conditions of μ and [H$^+$]: $1 \cdot 0$ M. It is evident that there is good agreement between these values and sum of ($a_3 + b_3$) values evaluated separately.

Our results may be explained satisfactorily by the same mechanism as that proposed by Hoare and Waters[5] involving the fission of O–H bond leading to products.

$$R'CR_2OH + Co^{3+} \longrightarrow R'CR_2O° \begin{cases} R^{°\prime} + R_2C = O \\ R° + R' \, COR \end{cases}$$
$$\text{or}$$
$$CoOH^{2+}$$
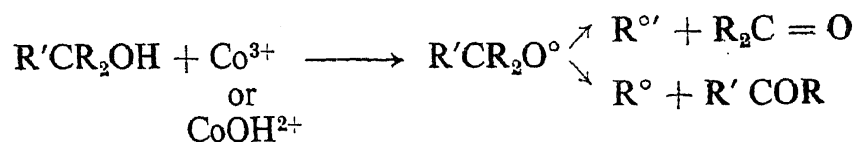
$R^{°\prime}$ or $R°$ on further reaction with Co^{3+} will lead to alcohols which will be further oxidised to aldehydes, acids, etc.

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