# Reactions of the $\mu$-Peroxo Complexes of Cobalt

## Part 4.—Kinetics of the Reduction of a Single-Bridged Complex with Iodide Ions.

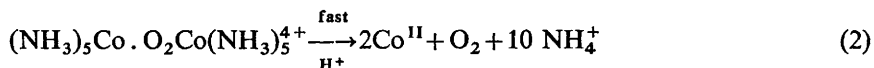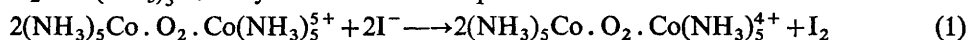By A. G. Sykes

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Kinetic studies have indicated that the $1:1$ reaction between the dicobalt peroxo complex $(NH_3)_5Co.O_2.Co(NH_3)_5^{5+}$ and $I^-$ in perchloric acid solutions, $I = 2\cdot0$ M, proceeds by two different paths. Iodide ions interact with the complex to form ion pairs in an equilibrium first step, electron transfer can then take place with or without interaction of a second iodide ion. Chloride ions inhibit the reaction and the extent of chloride ion pair association with the complex has been estimated. In reactions with the corresponding di- and tri-bridged complexes further quantities of $I^-$ are consumed and $3:1$ iodide to complex stoichiometries were observed.

Although many oxidation-reduction reactions are relatively simple one-step processes, in particular the isotopic exchange reactions between metal cations, others such as that between $Fe^{II}$ and $Tl^{III}$ are a more complex sequence of reactions involving reactive intermediates.[1] Reactions having two distinct paths are comparatively rare, a recent example being the $V^{III} + Fe^{III}$ system.[2]

The likelihood of $(NH_3)_5Co.O_2.Co(NH_3)_5^{4+}$ formation in some reactions of $(NH_3)_5Co.O_2.Co(NH_3)_5^{5+}$ has previously been considered,[3b] and in the $(NH_3)_5Co.O_2.Co(NH_3)_5^{5+}+I^-$ system a reaction sequence

$$2(NH_3)_5Co.O_2.Co(NH_3)_5^{5+}+2I^- \longrightarrow 2(NH_3)_5Co.O_2.Co(NH_3)_5^{4+}+I_2 \qquad (1)$$

$$(NH_3)_5Co.O_2Co(NH_3)_5^{4+} \underset{H^+}{\overset{fast}{\longrightarrow}} 2Co^{II}+O_2+10\ NH_4^+ \qquad (2)$$

seems likely. Kinetic measurements described here are concerned with the mechanism of (1). The oxidized and reduced forms of the complex are denoted by $M_1^{5+}$ and $M_1^{4+}$ respectively.

## EXPERIMENTAL

### MATERIALS

May and Baker sodium iodide was used, solutions were estimated using solutions of potassium iodate of known concentration. The nitrate salt of $M_1^{5+}$, NaCl, NaClO$_4$, HClO$_4$ and the dibridged complex $(NH_3)_4Co.\mu(NH_2, O_2).Co(NH_3)_4^{4+}$ were all as described previously.[3a, 3b] Some of the latter was converted into the nitrate of the tri-bridged complex $(NH_3)_3Co.\mu(NH_2, OH, O_2).Co(NH_3)_3^{3+}$, following the procedure used by Werner.[4]

### STOICHIOMETRIC DETERMINATIONS

Stoichiometries were determined by allowing a large excess of iodide to react with the complex, and titrating the iodine formed with standard sodium thiosulphate solution. By using an excess of iodide the reaction was conveniently fast, hydrolysis of iodine

$$I_2+H_2O \rightleftharpoons HI+HOI$$
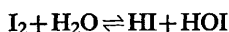
and further reaction of hypoiodous acid

$$3HOI \rightarrow 2HI+HIO_3$$

was minimized, and the iodine formed was effectively converted into $I_3^-$. The vapour

pressure of iodine was thus reduced and by keeping reaction vessels closed whenever possible iodine losses through sublimation were avoided.

The single-bridged complex shows a 1 : 1 stoichiometry confirming the overall reaction

$$2M_1^{5+} + 2I^- \xrightarrow{\text{H}^+} 4Co^{II} + 2O_2 + I_2 + 20NH_4^+.$$
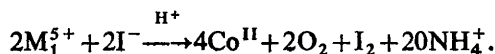
With the corresponding di- and tri-bridged complexes further quantities of iodide were consumed and 3 : 1 stoichiometries were observed. Solutions were 0·0003-0·0004 M in complex, 0·01 M in iodide, 1·8 N in acid, and reactions were in all cases complete within 1 h.

### KINETIC PROCEDURE

The low solubility of the $M_1^{5+}$ nitrate limited the concentration range of complex. Suitable rates with half-lives of about 5 min were obtained with iodide concentrations 20-200 times those of the complex, which was generally $\sim 0.00025$ M. Hydrolysis of $I_2$ is significant for reactions with smaller, near equivalent, amounts of iodide. Reactions were in $NaClO_4 + HClO_4$ solutions, $I = 2.0 \pm 0.01$ M, and were followed spectrophotometrically by measuring the concentration of $M_1^{5+}$ at 670 m$\mu$, absorption coefficients were as used previously.[3b] Fresh samples were taken for each O.D. measurement to avoid interference from oxygen bubbles which otherwise tend to collect on the sides of the optical cell as the reaction proceeds.

### RESULTS

Plots of $\log_{10}[M_1^{5+}]$ against time, fig. 1, were linear to at least 90 % reaction and gradients were a measure of the pseudo first-order rate constant $k_{obs}$. A five-fold variation in the initial concentration of $M_1^{5+}$ gave consistent $k_{obs}$ values to within $\pm 3$ % of each other.
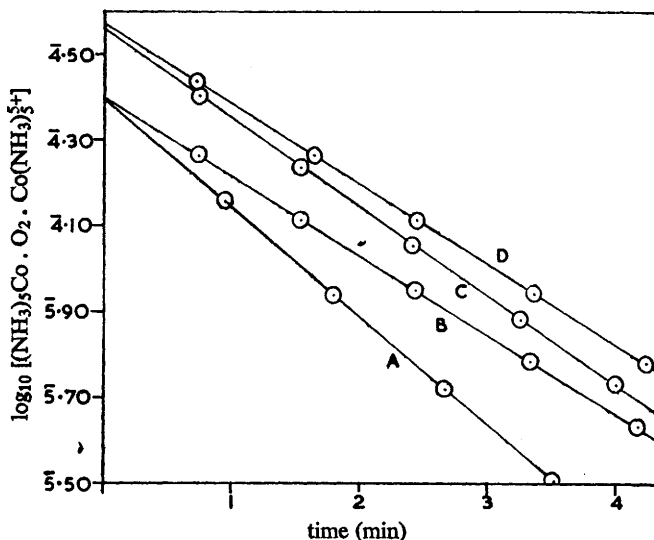


FIG. 1.—The effect of hydrogen ion concentration on first-order plots: in curve A [H$^+$] = 1·97 N, in B [H$^+$] = 0·075 N; in C [H$^+$] = 1·05 N. In curve D at [H$^+$] = 1·05 N the effect of 0·1 M chloride is shown. For A and B the initial concentrations of $M_1^{5+}$ were 0·00025 M, and for C and D 0·00036 M. Iodide concentrations were 0·0195 M; temp. 25°C.

Plots of $k_{obs}/[I^-]$ against $[I^-]$ are linear for fixed acid concentrations at temperatures 20, 25, and 30°C as shown in fig. 2, and $k_{obs}$ can be expressed as

$$k_{obs} = a[I^-]^2 + b[I^-],$$

where $a$ and $b$ are the gradient and intercept on the ordinate axis respectively. Of these $a$ shows an acid dependence of the form $a = a_1 + a_2[H^+]$ and a small hydrogen ion dependence, assumed to be of the same form, is also indicated for $b$. A more complete expression for $k_{obs}$ is therefore

$$k_{obs} = a_1[I^-]^2 + a_2[H^+][I^-]^2 + b_1[I^-] + b_2[H^+][I^-],$$

At 25°C, $a_1 = 875$ l.$^2$ mole$^{-2}$ min$^{-1}$, $a_2 = 162$ l.$^3$ mole$^{-3}$ min$^{-1}$, $b_1 = 4.5$ l. mole$^{-1}$ min$^{-1}$ and $b_2 \simeq 0.6$ l.$^2$ mole$^{-2}$ min$^{-1}$.
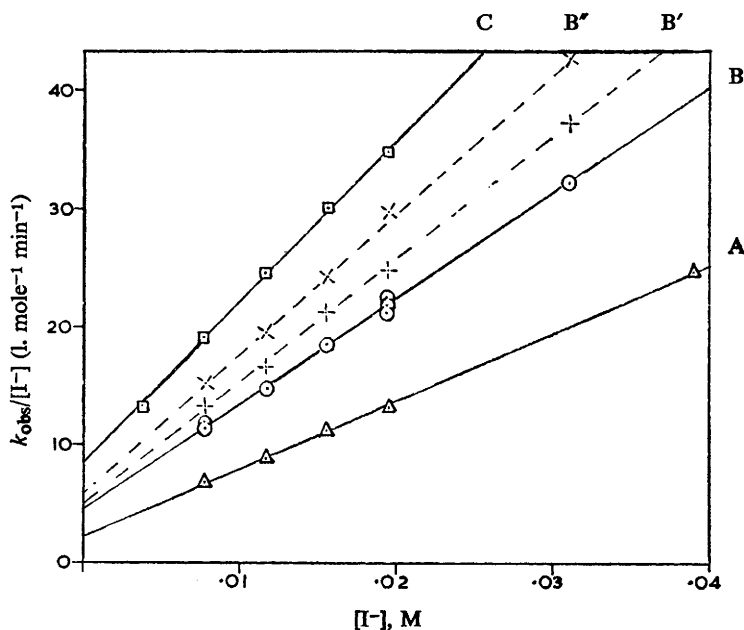


FIG. 2.—The iodide ion dependence of first-order rate constants, $k_{obs}$. Curves A, B and C were with the acid 0·075 N and temperatures 20, 25 and 30°C respectively. Curves B′ and B″ were with the acid 0·975 and 1·97 N respectively.

The reaction is inhibited by the addition of simple anions, and the effect of chloride ion concentrations up to 0·1 M were investigated at 25°C in 1·05 M acid solutions. Assuming ion pairs $M_1^{5+} + Cl^- \rightleftharpoons M_1Cl^{4+}$ to be formed, association constant $K$, and that these do not react appreciably with iodide, the expression $k_{obs}/k'_{obs} = 1 + K[Cl^-]$ can be derived, where $k'_{obs}$ is that rate constant obtained with chloride ions present. A plot of $k_{obs}/k'_{obs}$ against $[Cl^-]$ was linear with gradient $K = 1.26$ l. mole$^{-1}$.

## DISCUSSION

The iodide dependence $k_{obs} = c[I^-]^2/(1 + d[I^-])$ seemed to fit experimental results adequately, and a mechanism similar to that proposed for the $Fe^{III} + I^-$ reaction [5] seemed likely. On extending the range of iodide concentrations, however, the $1/[I^-]$ with $[I^-]/k_{obs}$ plots showed marked deviations from linearity and the expression

$$k_{obs} = a[I^-]^2 + b[I^-],$$

which is in agreement with experiments by Seufort, Liu, and Masterton in phosphate-buffered solutions [6] has, as indicated above, now been accepted.

The first term in the above expression can best be accounted for by a mechanism similar to that for the $Fe^{III} + I^-$ reaction,

$$M_1^{5+} + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_1 I^{4+} \tag{3}$$

$$M_1 I^{4+} + I^- \overset{k_2}{\to} M_1^{4+} + I_2^- \tag{4}$$

$$M_1^{5+} + I_2^- \to M_1^{4+} + I_2 \tag{5}$$

$$M_1^{4+} \overset{H^+}{\to} 2Co^{II} + O_2 + 10\,NH_4^+ \tag{6}$$

with reactions (5) and (6) fast and therefore not rate determining. Assuming the stationary-state approximation $d[M_1 I^{4+}]dt = 0$, the rate equation

$$-\frac{d[M_1^{5+}]}{dt} = \frac{2k_1 k_2 [M_1^{5+}][I^-]^2}{k_{-1} + k_2 [I^-]}$$

can be derived, and this is in agreement with experiment if $k_{-1} \gg k_2[I^-]$.

The second term indicates an alternative path for reaction

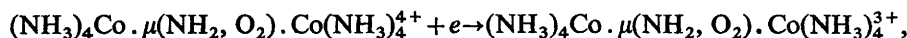$$M_1 I^{4+} \overset{k_3}{\to} M_1^{4+} + I^\circ \tag{7}$$

$$I^\circ + I^\circ \to I_2 \tag{8}$$

and/or $\qquad\qquad I^\circ + I^- \to I_2^- \tag{9}$

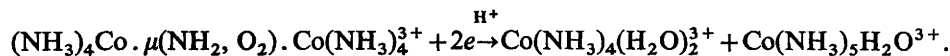Making the same stationary-state assumption $-d[M_1 I^{4+}]/dt = 0$ for eqn. (3)-(9) the full iodide ion dependence is

$$k_{obs} = \frac{2k_1 k_2 [I^-]^2}{k_{-1} + k_3 + k_2 [I^-]} + \frac{(2)k_3 k_1 [I^-]}{k_{-1} + k_3 + k_2 [I^-]},$$

where the bracketed two before the second term depends on whether iodine atoms react according to (8) or (9). With $k_{-1} + k_3 \gg k_2[I^-]$, this reduces to an equation of the required iodide dependence and constants $a$ and $b$ from experiment can be identified as $2k_1 k_2/(k_{-1} + k_3)$ and $(2)k_1 k_3/(k_{-1} + k_3)$ respectively. The ratio $a/b$ is therefore a measure of $(2)k_2/k_3$ and values 250, 198, and 157 l. mole$^{-1}$ can be evaluated from fig. 2, for 0·075 N acid solutions at 20, 25, and 30°C respectively. From the Arrhenius plot of these quantitites the difference in activation energies, $E_3^\ddagger > E_2^\ddagger$, is 9·0 kcal mole$^{-1}$.

The 3 : 1 stoichiometries found for the reactions of the di- and tri-bridged complexes $(NH_3)_4Co . \mu(NH_2, O_2) . Co(NH_3)_4^{4+}$ and $(NH_3)_3Co . \mu(NH_2, OH, O_2) . Co(NH_3)_3^{3+}$ are consistent with recent observations on the $(NH_3)_4Co . \mu(NH_2, O_2) . Co(NH_3)_4^{4+} + Fe^{II}$ reaction at $[H^+] < 0·3$ N,[3b] and more recent observations on the $(NH_3)_3Co . \mu(NH_2, OH, O_2) . Co(NH_3)_3^{3+} + Fe^{II}$ reaction.[3c] The reduced forms of these ions, the 3 + and 2 + ions respectively, are much more stable than $M_1^{4+}$ ions, and are probably formed as intermediates thus :

$$(NH_3)_4Co . \mu(NH_2, O_2) . Co(NH_3)_4^{4+} + e \to (NH_3)_4Co . \mu(NH_2, O_2) . Co(NH_3)_4^{3+},$$

further quantities of iodide reacting :

$$(NH_3)_4Co . \mu(NH_2, O_2) . Co(NH_3)_4^{3+} + 2e \overset{H^+}{\to} Co(NH_3)_4(H_2O)_2^{3+} + Co(NH_3)_5 H_2 O^{3+}.$$

In a similar reaction with $(CN)_5Co . O_2 . Co(CN)_5^{5-} + I^-$, Haim and Wilmarth found the stoichiometry to be 2·84 : 1.[7] Since they also found that the reduced form of the complex, $(CN)_5Co . O_2 . Co(CN)_5^{6-}$, interacts with $H^+$ to give hydrogen peroxide, intermediate formation of the latter is possible.

[1] Ashurst and Higginson, *J. Chem. Soc.*, 1953, 3044.
[2] Higginson and Sykes (A. G.), *J. Chem. Soc.*, 1962, 2841.
[3] Sykes (A. G.), (*a*) *Trans. Faraday Soc.*, 1962, **58**, 543 ; (*b*) 1963, **59,** 1325 ; (*c*) unpublished work.
[4] Werner, *Ann.*, 1910, **375,** 105.
[5] Sykes (K. W.) and Fudge, *J. Chem. Soc.*, 1952, 124.
[6] Seufort, Liu and Masterton, *Abst. Paper*, 136*th Meeting Amer. Chem. Soc.*, 1959, p. 37 N.
[7] Haim and Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83,** 509.