406. *Equilibria and Kinetics in Solutions of Ethylenediaminetetra-acetatocobalt*(III) *and the Kinetics of the Formation of this Complex from Chloro*(*ethylenediaminetriacetatoacetate*)*cobalt*(III) *and its Conjugate Acid.*

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In aqueous solutions of pH <2, ethylenediaminetetra-acetatocobalt(III), CoY^-, is partly converted slowly into aquo(ethylenediaminetriacetatoacetic acid)cobalt(III), $HCoYH_2O$; $H^+ + H_2O + CoY^- \rightleftharpoons HCoYH_2O$. The equilibrium constant, $K_a = [HCoYH_2O]/[H^+][CoY^-]$, is 1·28 l. mole^{-1} at 25° and ionic strength 1·0. The rate constants for the forward (k_f) and backward (k_b) reaction have been found at various temperatures; $-d[CoY^-]/dt = k_f[H^+][CoY^-] - k_b[HCoYH_2O]$.

The kinetics of the elimination of chloride ion from chloro(ethylenediaminetriacetatoacetate)cobalt(III), $CoYCl^{2-}$, and its conjugate acid, $HCoYCl^-$, have been investigated. Both complexes react at the same rate, according to the equation $-d[(H)CoYCl]/dt = d[CoY^-]/dt = k_c[(H)CoYCl]$. There is no kinetic evidence for the co-existence in solution of geometric isomers of these chloro-complexes in comparable amounts, as has been found [1] for the corresponding bromo-complexes, $CoYBr^{2-}$ and $HCoYBr^-$.

PRELIMINARY results on the kinetics of the Pb^{2+}-catalysed formation of ethylenediaminetetra-acetatocobalt(III), CoY^-, from bromo(ethylenediaminetriacetatoacetate)cobalt(III), $CoYBr^{2-}$, and its conjugate acid, $HCoYBr^-$, were recently reported.[2] In extending this work to other metal cations as catalysts we changed to the corresponding chloro-complexes, $CoYCl^{2-}$ and $HCoYCl^-$, principally because relevant equilibrium data about complex formation between metal cations and halide ions are more plentiful for chloride ions.

As a preliminary we studied the kinetics of the uncatalysed reaction $(H)CoYCl \longrightarrow CoY^- + Cl^-(+H^+)$. A second important reason for preferring the use of the chloro-complexes has emerged as a result. In both the uncatalysed and the Pb^{2+}-catalysed formation of CoY^- from the bromo-complexes we found that the first-order rate plots were curved after an initial, linear portion, which was ascribed to simultaneous reaction of geometrical isomers of the bromo-complexes, present in comparable proportions.[1] This complication is absent in solutions of the chloro-complexes.

Equilibria and Kinetics in Strongly Acid Solutions of CoY^-.—Preliminary experiments in which the formation of CoY^- from (H)CoYCl was followed spectrophotometrically at 500 mμ gave apparently anomalous results in solutions of pH <2. Final values of the optical density of the reaction solutions were lower than those calculated by assuming

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[1] Morris and Busch, *J. Phys. Chem.*, 1959, **63**, 340.

[2] Higginson and Hill, *J.*, 1959, 1620.

complete conversion into CoY^-. Accordingly the spectra from 350 to 600 mμ were measured at various pH values in the range 0—7 for solutions of CoY^- made by dissolving the solid, $NaCoY,4H_2O$, in water and diluting the resulting solution with dilute perchloric acid or buffer solution to *ca.* 2×10^{-3}M-CoY^-. In the range of pH 2·5—7·0 the spectra were identical and in good agreement with a previous determination.[3] From pH 2·0 to pH 0 optical densities changed with time until constant values were obtained, the changes being greater in solutions of lower pH. The final spectra were intermediate in form between the spectra of CoY^- and $HCoYH_2O$. (The molecular extinction curves of CoY^- and $CoYH_2O^-$ are shown in Fig. 1 of ref. 3; at wavelengths greater than 400 mμ the curve for $HCoYH_2O$ is very similar to that of $CoYH_2O^-$.) When the pH of any of these solutions was made greater than 2·5 by the addition of a buffer solution, slow changes in optical density again occurred until constant values were obtained. The spectra observed when these changes were complete were identical with the spectrum of CoY^-.

From these observations we concluded that in strongly acid solutions of CoY^- an equilibrium is slowly established, $CoY^- + H^+ + H_2O \rightleftharpoons HCoYH_2O$. A similar suggestion has been made previously to account for changes in the spectra of other EDTA complexes.[4] We therefore investigated the kinetics and equilibria in the CoY^- system quantitatively. The method was similar to that described above. The formation of the equilibrium mixture was found to obey the rate law

$$-d[CoY^-]/dt = k_{obs}\,([CoY^-] - [CoY^-]_{eq}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

plots of log $(D - D_{eq})$ against t being linear. (D is the optical density of the reaction solution at time t and D_{eq} the optical density when the reaction has ceased.) From values of D_{eq} at 500 mμ we calculated the equilibrium constant $K'_a = [HCoYH_2O]/[CoY^-]$ for various hydrogen-ion concentrations by using the molecular extinction coefficients for $HCoYH_2O$ and CoY^- at this wavelength. For equations of the form of (1) it can be shown that k_{obs} is the sum of a " forward " and a " backward " reaction velocity constant. In this case, $k_{obs} = k_f' + k_b$ where $k_f' = -d \ln [CoY^-]/dt$ and $k_b = -d \ln [HCoYH_2O]/dt$. The constants k_f' and k_b relate only to the *disappearance* of the species involved in these equations. Since K'_a $(= k_f'/k_b)$ has been found, we can obtain k_f' and k_b separately. Values of these constants are given in the annexed Table, together with $K_a = K'_a/[H^+] = [HCoYH_2O]/[H^+][CoY^-]$ and $k_f = k_f'/[H^+]$. The ionic strength was 1·0M in all the experiments summarised in this Table. It can be seen that k_f, k_b, and K_a are constant at a given temperature. The formation of $HCoYH_2O$ from CoY^- evidently follows the rate law $d[HCoYH_2O]/dt = k_f[H^+][CoY^-]$. In two of the experiments at 25° the equilibrium was approached from the $HCoYH_2O$-rich side by diluting a solution of $NaCoY,4H_2O$ in 4M-perchloric acid. The attainment of the new equilibrium was then followed spectrophotometrically, the appropriate kinetic equation being

$$-d[HCoYH_2O]/dt = k_{obs}([HCoYH_2O] - [HCoYH_2O]_{eq}) \quad . \quad . \quad . \quad (2)$$

where the velocity constant should be identical with that in equation (1) for experiments at the same hydrogen-ion concentration and temperature. It can be seen from the Table that this is so.

From Arrhenius plots obtained by using average values of the velocity constants at 15°, 25°, and 35°, we find:

$$k_f = \text{antilog}\,(15{\cdot}4 \pm 0{\cdot}3) \times \exp\{-(23{,}400 \pm 500)/\boldsymbol{R}T\}\ \text{l. mole}^{-1}\ \text{min.}^{-1},$$

$$k_b = \text{antilog}\,(16{\cdot}9 \pm 0{\cdot}3) \times \exp\{-(25{,}600 \pm 400)/\boldsymbol{R}T\}\ \text{min.}^{-1}$$

K_a, expressed in l. mole^{-1}, is given by:

$$\log K_a = -(-2220 \pm 200)/2{\cdot}303\boldsymbol{R}T + (-7{\cdot}1 \pm 0{\cdot}6)/2{\cdot}303\boldsymbol{R}$$

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[3] Shimi and Higginson, *J.*, 1958, 260.

[4] Margerum, *J. Phys. Chem.*, 1959, **63**, 336.

[H⁺] (M)	$10^2k_f'$ (min.⁻¹)	10^2k_f (l. mole⁻¹) min.⁻¹)	10^2k_b (min.⁻¹)	K'_a	K_a (l. mole⁻¹)
		At 15°			
1·00	0·478	0·478	0·332	1·44	1·44
0·807	0·376	0·466	0·324	1·16	1·44
0·605	0·284	0·470	0·326	0·872	1·44
0·403	0·188	0·467	0·322	0·584	1·45
		At 20°			
1·00	0·865	0·865	0·655	1·32	1·32
		At 25°			
1·00	1·74	1·74	1·36	1·29	1·29
1·00 *	1·81	1·81	1·41	1·28	1·28
0·808	1·42	1·76	1·38	1·03	1·28
0·606	1·06	1·75	1·38	0·768	1·27
0·505 *	0·92	1·82	1·44	0·639	1·26
0·404	0·73	1·81	1·42	0·514	1·27
		At 30°			
1·00	3·38	3·38	2·78	1·22	1·22
		At 35°			
1·00	6·58	6·58	5·92	1·11	1·11
0·807	5·00	6·20	5·60	0·893	1·11
0·605	3·90	6·45	5·80	0·673	1·11
0·403	2·57	6·37	5·73	0·448	1·11

* In these experiments, equilibrium was approached from the $HCoYH_2O$-rich side.

It is possible to calculate the equilibrium constant, $K_b = [CoYH_2O^-]/[CoY^-]$, by combining K_a and the first acid dissociation constant of $HCoYH_2O$, $K_1 = [H^+][CoYH_2O^-]/[HCoYH_2O]$, since $K_b = K_aK_1$. At 15°, $K_a = 1{\cdot}44$ l. mole⁻¹ and $K_1 \simeq 8 \times 10^{-4}$ mole l.⁻¹ (ref. 3), whence $K_b \simeq 1{\cdot}2 \times 10^{-3}$. Thus, at any pH, at equilibrium, a solution always contains *ca.* 0·1% of CoY^- in the form of $CoYH_2O^-$. In sufficiently alkaline solutions $CoYH_2O^-$ loses a proton, forming $CoYOH^{2-}$:

$$K_2 = [H^+][CoYOH^{2-}]/[CoYH_2O^-] \simeq 8 \times 10^{-9} \text{ mole l.}^{-1} \text{ (refs. 3, 5).}$$

By combining K_b and K_2 we find $K_c = [H^+][CoYOH^{2-}]/[CoY^-] = K_bK_2 \simeq 9 \times 10^{-12}$ mole l.⁻¹. Attempts to verify this prediction by measuring K_c were unsuccessful owing to the decomposition of CoY^- at the high pH values necessary.

A possible route for the reaction $CoY^- + H^+ + H_2O \rightleftharpoons HCoYH_2O$ is the sequence $CoY^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoYH_2O^- \underset{(K_1)}{\overset{\text{fast}}{\rightleftharpoons}} HCoYH_2O$. The second stage involves only a proton-transfer and can be assumed to be rapid. For strongly acidic solutions we therefore deduce $-d[CoY^-]/dt = k_1[CoY^-] - k_{-1}K_1[HCoYH_2O]/[H^+]$. This equation is not of the form found from our kinetic experiments, $-d[CoY^-]/dt = k_f[H^+][CoY^-] - k_b[HCoYH_2O]$; nevertheless the route *via* $CoYH_2O^-$ must contribute to the establishment of the equilibrium between CoY^- and $HCoYH_2O$. However, k_{-1} has been found[3] to be *ca.* $4{\cdot}6 \times 10^{-2}$ min.⁻¹ at 15° and therefore $k_1 = k_{-1}K_b \simeq 6 \times 10^{-5}$ min.⁻¹. Comparing values of k_1 with $k_f[H^+]$ and values of $k_{-1}K_1/[H^+]$ with k_b we find that the route *via* $CoYH_2O^-$ contributes only 3% to the total rate at 0·4M-hydrogen ion and 1% at 1·0M. These proportions are similar to the experimental error in the determination of k_f and k_b, and so the contribution of this route cannot be demonstrated under the conditions of our experiments.

The kinetics of the formation of CoY^- from $HCoYH_2O$ have been investigated previously by direct measurements, with solutions of $HCoYH_2O$ obtained by acidifying solutions of $CoYOH^{2-}$.[3] The values of the activation energy, (24·9 ± 1·0) kcal. mole⁻¹, and the temperature-independent factor, antilog (16·4 ± 0·7) min.⁻¹, were then obtained at ionic strength 0·1, but are in reasonable agreement with the more precise values found in this work. In the earlier work it was suggested that this reaction is of the type S_N1 and occurs in three steps, the initial loss of the co-ordinated water molecule with the formation of an intermediate in which cobalt has the co-ordination number five, followed by ionisation of the carboxylic acid group and co-ordination of the resulting carboxylate group to the cobalt atom. We now emphasise that there is no compelling reason for

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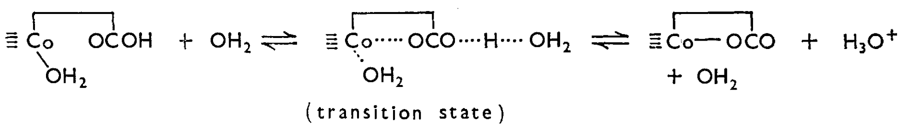
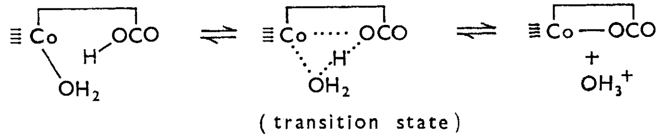
[5] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.

accepting this suggestion. The three stages originally envisaged may be merged into one, *viz.*,



Alternatively, it is possible that H_2O and H^+ are eliminated together, as H_3O^+:



The use of models suggests that these two schemes also are feasible and consequently the detailed mechanism of this reaction is uncertain.

Kinetics of the Formation of CoY^- *from* (H)CoYCl.—Owing to the formation of $HCoYH_2O$ from CoY^- in solutions of pH 0—2, within this range we followed the loss of chloride ion from $HCoYCl^-$ at 597 mμ. At this wavelength the molecular extinction coefficients of CoY^- and $HCoYH_2O$ are equal, so that it is immaterial if the equilibrium between these two species is not maintained during the experiment. Since the relative change in optical density is greater at 500 mμ, we used this wavelength in experiments at pH >2. Over the range of pH 2·0—6·1, linear plots of log (ΔD) against t were obtained up to 95% reaction, ΔD being the positive difference between the optical density at time t and the optical density when the reaction has ceased. The linearity of these plots showed that the reaction is of first order in (H)CoYCl and that isomers of differing reactivity are not present in these solutions in comparable concentrations, in contrast to the behaviour of solutions of (H)CoYBr.[1] Evidently the method of preparation[6] of the solid salt, $NaHCoYCl,2H_2O$, from which our solutions were made leads to an isomerically pure product, presumably an isomer in which the chlorine atom is *trans* to nitrogen.[7]

At 45° and ionic strength 1·0, values of the velocity constant $k_c = -\mathrm{d}\ln[(\mathrm{H})\mathrm{CoYCl}]/\mathrm{d}t$ were constant and equal to $(1{\cdot}92 \pm 0{\cdot}04) \times 10^{-3}$ min.$^{-1}$ in the pH range 2·0—6·1. Since the pK of the acid $HCoYCl^-$ is *ca.* 3, this constancy shows that $HCoYCl^-$ and $CoYCl^{2-}$ lose chloride ion at the same rate. A similar observation for the conjugate acid–base pair $HCoYBr^-$ and $CoYBr^{2-}$ has been interpreted[1,3] as showing that the elimination of halide is an S_N1 process involving the formation of an intermediate in which cobalt has the co-ordination number five. The value of k_c decreased slightly in strongly acidic solutions; at pH $= 0{\cdot}2$ $k_c = 1{\cdot}78 \times 10^{-3}$ min.$^{-1}$ and the logarithmic plots were slightly curved. We do not consider that this variation implies a change in mechanism, but ascribe it to a side-reaction of minor importance. Values of $10^3 k_c$ (min.$^{-1}$) obtained in experiments at pH $=$ 4·34 were 0·580, 1·115, 3·57, 6·01 at 35°, 40°, 50°, 55°, respectively. An Arrhenius plot was constructed from these values and the average value at 45°. We find:

$$k_c = \text{antilog}\,(13{\cdot}4 \pm 0{\cdot}3) \times \exp\{-(23{,}450 \pm 400)/\boldsymbol{R}T\}\ \text{min.}^{-1}$$

These values are similar to those previously obtained from experiments in 0·1M-sodium nitrate.[1]

In solutions of sufficiently low pH, the ultimate product of the loss of chloride ion from $HCoYCl^-$ is an equilibrium mixture of CoY^- and $HCoYH_2O$. It would be of interest to decide whether $HCoYH_2O$ is a primary product of this reaction or whether it is formed

[6] Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1958, **80**, 4480.

[7] Weakliem and Hoard, *J. Amer. Chem. Soc.*, 1959, **81**, 549; Smith and Hoard, *ibid.*, p. 556.

subsequently from the primary product, CoY^-. It is possible to calculate the concentrations of CoY^- and $HCoYH_2O$ at any time during a reaction by using the constants k_f, k_b, and k_c. Whether we assume $HCoYCl^- \xrightarrow{k_c} CoY^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} HCoYH_2O$ or $HCoYCl^- \xrightarrow{k_c} HCoYH_2O \underset{k_f}{\overset{k_b}{\rightleftharpoons}} CoY^-$, the concentrations of CoY^- and $HCoYH_2O$ in solutions in the pH range 0—1 are calculated to be so near to their equilibrium values that no distinction can be made experimentally between these two extreme cases. The reason is that k_c is much smaller than k_f and k_b. Thus, the rate of loss of chloride from $HCoYCl^-$ in strongly acidic solutions can be followed at any wavelength at which the change in optical density is adequate, k_c being obtainable as above from plots of log (ΔD) against t. However, it would then be necessary to take measurements at the temperature of the experiment, otherwise erroneous values would be obtained owing to the relatively rapid change in the CoY^-–$HCoYH_2O$ equilibrium with change in temperature. Since we adopted a sampling technique for the experiments with HCoYCl, the use of 597 mμ was necessary. In the catalysis of this reaction by metal cations, much greater rates of loss of chloride can be obtained, so that during the early part of a kinetic experiment CoY^- and $HCoYH_2O$ cannot be present in near-equilibrium concentrations. Under these conditions it is advantageous to take measurements at 597 mμ even if temperature-controlled optical cells are used. In this connection, the loss of chloride catalysed by Hg^{2+} is apparently instantaneous and we have shown that in M-perchloric acid less than 2% of the total $HCoYCl^-$ is initially converted into $HCoYH_2O$, CoY^- being within experimental error the sole primary product. We cannot, however, conclude from this observation that CoY^- is the only primary product in the uncatalysed reaction.

EXPERIMENTAL

Reagents were of " AnalaR " grade or were purified by appropriate methods. Sodium ethylenediaminetetra-acetatocobalt(III) tetrahydrate was prepared by a method described previously;[5] sodium chloro(ethylenediaminetriacetatoacetic acid)cobalt(III) dihydrate was prepared from this compound by Dwyer and Garvan's method.[6] These products were shown to be pure by appropriate analyses.

Reaction solutions were prepared by adding a freshly made solution of the complex, $NaCoY,4H_2O$ or $NaHCoYCl,2H_2O$, in water to a solution (in a thermostat-bath) containing a buffer or perchloric acid, the ionic strength being made 1·0M by addition of sodium perchlorate solution. The concentration of the complex was usually *ca.* 0·002M. In the experiments with $NaCoY,4H_2O$, a portion of the solution was placed in a 1 cm. optical cell in the temperature-controlled cell-compartment of a Unicam S.P. 500 spectrophotometer. Measurements of optical density were made on this sample at intervals of time, and the final reading was found identical with that obtained from a second sample. The reaction was allowed to proceed to completion so that the equilibrium concentrations of the species CoY^- and $HCoYH_2O$ could be evaluated. In the experiments with $NaHCoYCl,2H_2O$, separate samples were withdrawn from the thermostat bath for each measurement of optical density (1 cm. optical cell).

Measurements were made at 500 and 597 mμ for the CoY^-–$HCoYH_2O$ system, the molecular extinction coefficients being: for CoY^-, $\varepsilon_{500} = 235$, $\varepsilon_{597} = 120$; for $HCoYH_2O$, $\varepsilon_{500} = 134$, $\varepsilon_{597} = 120$. The plots of log ($D - D_{eq}$) against time were obtained from the readings at 500 mμ, k_{obs} being found from the gradients of these plots. The readings at 597 mμ showed the absence of side-reactions. Readings were taken at the same wavelengths in the two experiments in which equilibrium was reached from solutions containing a high proportion of $HCoYH_2O$. Here, log ($D_{eq} - D$) was plotted against time. In these experiments, 4 cm. optical cells were used and the final concentrations of the mixture of cobalt(III)–ENTA complexes were 0·001M (1·0M-$HClO_4$) and 0·0005M (0·5M-$HClO_4$ plus 0·5M-$NaClO_4$). Before dilution to these concentrations, the solution was of 0·004M-$NaCoY,4H_2O$ in 4·0M-perchloric acid. The proportion of cobalt in the form of $HCoYH_2O$ in this solution at equilibrium was *ca.* 84%.

In the (H)CoYCl decomposition at pH >2, measurements were made at 500 and 574 mμ, the molecular extinction coefficients being: for CoY^-, $\varepsilon_{574} = 228$; for (H)CoYCl, $\varepsilon_{500} = 34·0$

$\varepsilon_{574} = 228$. At pH <2, measurements were made at 597 mμ, ε_{597} for HCoYCl being 225. The rate constant k_c was obtained from the gradients of plots of log (ΔD) against t, ΔD being the positive difference between the optical density at time t and that at the conclusion of the reaction. The measurements at 574 mμ (pH >2) showed the absence of side-reactions. In experiments at pH <2, final values of the optical density showed that products other than CoY^- and $HCoYH_2O$ were formed; the extent of this side-reaction was *ca.* 5% at pH 0. Experiments at pH >2 were conducted with different total concentrations of buffer for a given buffer ratio, these duplicate experiments showed that the rate of reaction was unaffected by the buffer. Buffers were chloroacetic acid–chloroacetate (pH 3·28), acetic acid–acetate (4·34—4·92), dihydrogen phosphate–monohydrogen phosphate (5·17—6·09). The contribution of the buffer to the total ionic strength was usually less than 5%. Solutions of pH <2 were obtained by using appropriate concentrations of perchloric acid (0·01—1·00M). All pH measurements were made by meter at 25° with reference to a solution of 0·01M-perchloric acid plus 0·99M-sodium perchlorate. The pH of this solution was arbitrarily assumed to be 2·00.

The initial product of the reaction of Hg^{2+} with $HCoYCl^-$ was found as follows. A solution of mercuric perchlorate in dilute perchloric acid was mixed with a solution of $HCoYCl^-$ at room temperature (*ca.* 15°). The concentrations immediately after mixing were 0·05M-Hg^{2+}, 0·00200M-$HCoYCl^-$, 1·0M-H^+. The optical density at 500 mμ of a sample of the solution was taken at various intervals after mixing, and the plot of log (ΔD) against time was extrapolated to zero time. Thus, the value of the optical density of the solution immediately after mixing was calculated and was found to be 0·470 (1 cm. optical cell), exactly equal to that of a solution of CoY^- of the same concentration. This showed that not less than 98% of the $HCoYCl^-$ was converted by Hg^{2+} into CoY^-.

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