53. *Kinetics of Formation of Ethylenediaminetetra-acetatocobalt*(III) *from the Corresponding Monoaquo- and Monohydroxo-complexes in Aqueous Solutions.*

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The kinetics of the formation of CoY^- from $CoYH_2O^-$, $HCoYH_2O$, and $CoYOH^{2-}$ in aqueous solutions have been followed spectrophotometrically (Y^{4-} = ethylenediaminetetra-acetate ion). The reactions of $HCoYH_2O$ and $CoYOH^{2-}$ are thought to be of the S_N1 type, but the unbound carboxylate ion in $CoYH_2O^-$ is believed to displace the ligand water molecule in an S_N2-type reaction.

IN addition to the sexidentate complex ion, CoY^-, the ethylenediaminetetra-acetate (enta) anion, Y^{4-}, forms a series of quinquedentate chelate compounds with cobalt(III) in which one of the four carboxylate groups is free.[1, 2] The sixth co-ordination position of the cobalt is occupied by a foreign ligand, L, which may be a molecule or a simple anion. Such complexes, represented by $CoYL^{(l-1)+}$, where l is the charge on the foreign ligand, are weak bases, for in solutions of sufficiently low pH the free carboxylate group takes up a proton. The acid dissociation constant of the acid form, $HCoYL^{l+}$, is about 10^{-3} mole $l.^{-1}$ and is little affected by the nature of L. Aqueous solutions of $CoYL^{(l-1)+}$ and $HCoYL^{l+}$ are unstable and eliminate L, forming CoY^-, which shows neither acidic nor basic properties. Aquoethylenediaminetetra-acetatocobalt(III), $CoYH_2O^-$, besides acting as a base, is also an acid of dissociation constant about 10^{-8} mole $l.^{-1}$, the conjugate base being $CoYOH^{2-}$. The pH-dependent relationships between these complexes can be summarised as

$$CoYOH^{2-} \underset{pH > 8}{\overset{pH < 8}{\rightleftarrows}} CoYH_2O^- \underset{pH > 3}{\overset{pH < 3}{\rightleftarrows}} HCoYH_2O$$

these equilibria being rapidly attained. It is apparent that $CoYOH^{2-}$ and $HCoYH_2O$ cannot coexist in solution in appreciable concentrations. Since in complexes of the type HCoYL the pK of the free carboxylic acid group is about 3, irrespective of the nature of L, it can be concluded that the ratio of the concentrations of the two isomers, $CoYH_2O^-$ and $HCoYOH^-$, is about $10^5 : 1$ at any pH.

The behaviour of certain cobalt(III)–enta complexes as oxidising agents led us to investigate their instability in aqueous solution. Here we present kinetic data on the elimination of the foreign ligand, with consequent formation of CoY^-, from the above three related complexes, obtained by using solutions in water of a solid salt of the anion $CoYOH^{2-}$. Since the species initially present in solution depend upon the pH, which varied in different experiments, we refer for convenience to an aqueous solution of $CoYOH^{2-}$ of any pH in the range studied as a solution of CoY(O), and define $[CoY(O)] = [CoYOH^{2-}] + [CoYH_2O^-] + [HCoYH_2O]$. The elimination reaction was followed spectrophotometrically. Molecular extinction curves of aqueous solutions of the ions CoY^-, $CoYH_2O^-$, and $CoYOH^{2-}$ are shown in Fig. 1; the corresponding curve for $HCoYH_2O$ is very similar to that of $CoYH_2O^-$ at wavelengths greater than 360 mμ and has been omitted for clarity. (These curves duplicate those published previously.[3]) Although in the absence of side-reactions it is possible to determine the individual concentrations of the three CoY(O) species and of CoY^- in solution from measurements of optical density at several different wavelengths, considerable errors are introduced on account of the similarity of the molecular extinction curves. Since the pH-dependent equilibria between the CoY(O) species are rapidly attained and the conversion into CoY^- is quantitative (see Experimental

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[1] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.
[2] Busch and Bailar, *J. Amer. Chem. Soc.*, 1953, **75**, 4574.
[3] Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

section), we only needed to estimate [CoY(O)]. Under our conditions, at constant pH, the positive difference $(D_t \sim D_\infty) \propto [\mathrm{CoY(O)}]_t$ at any given wavelength, where D_t represents the optical density of the reaction solution in a given cell at time t and D_∞ the optical density in the same cell when the reaction is complete. The precision with which $[\mathrm{CoY(O)}]_t$ can be found depends partly upon the magnitude of the change in $(D_t \sim D_\infty)$ for a given change in t, and hence upon the choice of wavelength. Plots of log $[\mathrm{CoY(O)}]_t$ against t were linear, so that in most kinetic experiments it was sufficient to plot log $(D_t \sim D_\infty)$ against t, obtaining from the gradient the corresponding first-order velocity constant, $k_{\mathrm{obs}} = -\mathrm{d}\ln[\mathrm{CoY(O)}]/\mathrm{d}t$.

Fig. 2 shows the variation in k_{obs} with pH at 15° and ionic strength 0·1. If we assume that $HCoYH_2O$, $CoYH_2O^-$, and $CoYOH^{2-}$ each decompose to CoY^-, the corresponding first-order velocity constants being k_1, k_2, and k_3, the dependence of k_{obs} upon the hydrogen-ion concentration is

FIG. 1.

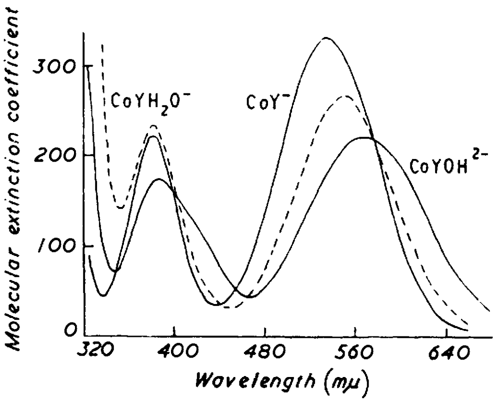
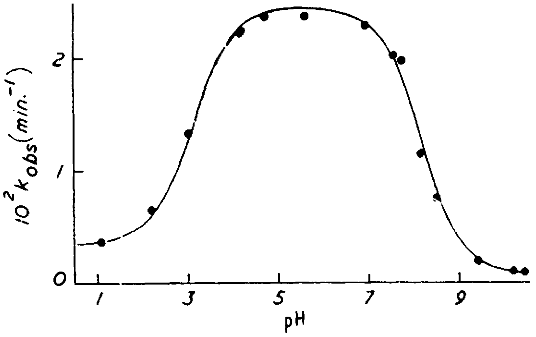


FIG. 2.



$$k_{\mathrm{obs}} = \{k_1[\mathrm{H}^+]^2 + k_2K_1[\mathrm{H}^+] + k_3K_1K_2\} \div \{[\mathrm{H}^+]^2 + K_1[\mathrm{H}^+] + K_1K_2\} \quad . \quad (1)$$

where K_1 and K_2 are acid dissociation constants, defined as

$$K_1 = [\mathrm{CoYH_2O^-}][\mathrm{H^+}]/[\mathrm{HCoYH_2O}]; \; K_2 = [\mathrm{CoYOH^{2-}}][\mathrm{H^+}]/[\mathrm{CoYH_2O^-}].$$

Values found for the velocity constants are given in the annexed Table, $pK_1 = 3{\cdot}1 \pm 0{\cdot}1$, $pK_2 = 8{\cdot}1 \pm 0{\cdot}1$ agreeing with values previously suggested.[1] The theoretical line constructed from these values is shown in Fig. 2. Other experiments at 15° were done at ionic strength 1·0 over the pH range 0·68—6·76, and the values of the constants deduced are $10^2k_1 = 0{\cdot}40 \pm 0{\cdot}05$ min.$^{-1}$, $10^2k_2 = 4{\cdot}6 \pm 0{\cdot}3$ min.$^{-1}$, $pK_1 = 3{\cdot}1 \pm 0{\cdot}2$. These experiments were not extended to alkaline solutions so that the corresponding values of k_3 and pK_2 cannot be given.

By substituting the values of these constants in eqn. (1) it can be seen that at pH = 1, $k_{\mathrm{obs}} = k_1$, at pH = 5—6, $k_{\mathrm{obs}} = k_2$, and at pH = 10—10·5, $k_{\mathrm{obs}} = k_3$. Hence by assuming that changes in the dissociation constants K_1 and K_2 with temperature are small, it was possible to obtain k_1, k_2, and k_3 at ionic strength 0·1 at temperatures other than 15° from kinetic experiments at pH 1·1, 5·6, and 10·5 respectively. From these values, which are summarised in the Table, the following activation energies (ΔE) and temperature-independent factors (A) were obtained: $HCoYH_2O$, $\Delta E_1 = 24{\cdot}9 \pm 1{\cdot}0$ kcal. mole^{-1}, $A = \exp_{10}(16{\cdot}4 \pm 0{\cdot}7)$ min.$^{-1}$; $CoYH_2O^-$, $\Delta E_2 = 25{\cdot}2 \pm 0{\cdot}7$ kcal. mole^{-1}, $A_2 = \exp_{10}(17{\cdot}5 \pm 0{\cdot}5)$ min.$^{-1}$.

Velocity constants (min.$^{-1}$).

Temp.	10^3k_1	10^3k_2	10^3k_3
0°	—	2.21 ± 0.1	—
7.5	0.96 ± 0.05	6.9 ± 0.3	—
15	3.4 ± 0.3	24.4 ± 1.0	0.84 ± 0.04
25	13.3 ± 0.5	—	2.6 ± 0.3

Discussion.—The conformation of enta in its quinquedentate complexes is relatively rigid and the unbound carboxylate group, which is adjacent to the foreign ligand, has little freedom of movement. Consequently a one-stage (S_N2) substitution of the foreign ligand, OH^- or H_2O, by this carboxylate group must be of the vicinal type; an edge-displacement mechanism [4] seems most improbable. The only other simple alternative is an S_N1 substitution in which elimination of the foreign ligand is followed by ring-closure. We suggest that the free carboxylate group in $CoYH_2O^-$ takes part in such an S_N2-type displacement of the ligand, H_2O. The lower rate of elimination of water from the complex $HCoYH_2O$ can be understood, since the carboxylic acid group is likely to be less effective than the corresponding ion. Indeed, it is probable that the carboxylic acid group takes no part in the rate-determining reaction which would thus be of the S_N1 type, leading to the formation of an intermediate in which cobalt has the co-ordination number five. The subsequent ionisation of the carboxylic acid group and co-ordination to cobalt would then follow as a relatively rapid reaction. Within experimental error the activation energies of the two reactions, $HCoYH_2O \longrightarrow CoY^- + H_2O + H^+$ and $CoYH_2O^- \longrightarrow CoY^- + H_2O$, are identical, the greater rapidity of the latter appearing as a higher temperature-independent factor. As might be expected for the S_N1-type elimination of a small molecule from a large substrate, the temperature-independent factor for the reaction of $HCoYH_2O$ is near to the "normal" value for a unimolecular reaction, 10^{15}—10^{16} min.$^{-1}$. For $CoYH_2O^-$ this factor is unusually high, corresponding to a small positive entropy of activation. This is in accord with an S_N2 mechanism, since the negative charge, initially present on the small free carboxylate ion, will be partly transferred to the complex as a whole in the transition state, with consequent liberation of solvated water molecules. We have assumed that $HCoYOH^-$, isomeric with $CoYH_2O^-$, is not of kinetic importance, although the fact that it can only be present in low concentration relative to $CoYH_2O^-$ is no guarantee that this assumption is correct.

The elimination of the hydroxyl ion from $CoYOH^{2-}$ cannot be compared directly with the reactions discussed above since in this complex the oxygen of the expelled ligand is in a different state of combination. However, we should not expect the free carboxylate group to take part in the rate-determining reaction on account of electrostatic repulsion in the transition state between this group and the incipiently-formed hydroxyl ion. Hence we favour the S_N1 mechanism in this case. Reinforcing this suggestion, preliminary experiments on the elimination of bromide ion from the complex ions $CoYBr^{2-}$ and $HCoYBr^-$ showed that the rate of formation of CoY^- is virtually unchanged over the pH range 1—7, the first-order velocity constant being approximately 4×10^{-3} min.$^{-1}$ at 25° and ionic strength 0·1. (These complexes correspond to $CoYH_2O^-$ and $HCoYH_2O$ with Br^- replacing H_2O; pK of the acid $HCoYBr^-$ is [1, 5] 3·0.) The obvious interpretation is that in neither bromo-complex does the free carboxylate or carboxylic acid group take part in the rate-determining reaction, and it therefore seems probable that this will be true of the similar complex $CoYOH^{2-}$. If this is so, a low temperature-independent factor is to be expected for the bromo-complexes and $CoYOH^{2-}$ since a unit negative charge, initially spread over the bulk of the complex, excluding the free carboxylate or carboxylic acid group, will be partly concentrated on the bromide or hydroxide ligand in the transition state. The latter is therefore likely to be more strongly solvated than the initial state, with a consequent negative entropy of activation. Although we have not quoted a

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[4] Brown, Ingold, and Nyholm, *J.*, 1953, 2674.

[5] Schwarzenbach and Heller, *Helv. Chim. Acta*, 1951, **34**, 576.

temperature-independent factor for the $CoYOH^{2-}$ reaction, a low value, 10^{11}—10^{12} min.$^{-1}$, can be estimated from the values of k_3 in the Table. For the two bromo-complexes the corresponding value is $10^{12\cdot7}$ min.$^{-1}$, again low for a unimolecular reaction.

EXPERIMENTAL

Reagents were "AnalaR" or were purified by appropriate methods. Sodium ethylenediaminetetra-acetatocobalt(III) tetrahydrate was prepared *via* sodium hydrogen bromoethylenediaminetetra-acetatocobalt(III) trihydrate as previously described.[1] Dihydrogen aquoethylenediaminetetra-acetatocobalt(II) dihydrate was prepared by mixing equal volumes of 0·5M-cobalt sulphate and 0·5M-disodium dihydrogen ethylenediaminotetra-acetate dihydrate and concentrating the solution to half its original volume. After 1 day, crystals of the *complex* were obtained [Found: Co, 14·3%; *M*, 408 (pH titration). $H_2Co(C_{10}H_{12}O_8N_2),3H_2O$ requires Co, 14·6%; *M*, 403·2]. 20 g. of this complex were dissolved in about 60 ml. of *ca.* M-sodium carbonate solution, the final pH being about 9. The solution was cooled to 0°, and maintained at 0° for the remainder of the preparation. 25 ml. of cold hydrogen peroxide (100-vol.) were added gradually with stirring. At the end of the addition the pH was adjusted, if necessary, to 9. When evolution of oxygen ceased, 200 ml. of ethanol, cooled to 0°, were added with stirring. A dark-blue oily liquid separated and the supernatant aqueous ethanol was then decanted. A small quantity of cold absolute ethanol was added with vigorous stirring, decanted, and the process repeated until the oil solidified. After further washing and decantation the blue solid was filtered off and dried under vacuum at room temperature over anhydrous magnesium perchlorate. The solid, a hydrate of disodium hydroxoethylenediaminetetra-acetatocobalt(III), is hygroscopic, and unstable when moist [Found: C, 26·0; H, 3·80; Co, 12·1%; *M*, 476 (pH titration). Calc. for a trihydrate: $Na_2Co(C_{10}H_{12}O_8N_2)OH,3H_2O$: C, 25·9; H, 4·12; Co, 12·7%; *M*, 464]. Samples of the complex gave quantitative decomposition in acetate buffers to CoY^- within 3% as shown spectrophotometrically.

The molecular extinction curves for CoY^- and the three CoY(O) species were determined in buffered solutions by using a Unicam S.P. 500 spectrophotometer. The pH values of the solutions were 1·1 for $HCoYH_2O$, 5·6 for $CoYH_2O^-$ and CoY^-, and 10·5 for $CoYOH^{2-}$. On account of their instability, solutions of the CoY(O) complexes were frequently renewed. Solutions of the four complexes, and appropriate mixtures, obeyed Beer's law at the wavelengths used in the kinetic experiments.

Solutions for kinetic experiments were made by dissolving a known weight of the solid hydroxo-complex in various aqueous buffer solutions; the ionic strength was made 0·1 or 1·0 by the addition of potassium chloride solution. In most experiments the concentration of the cobalt complex was 2—4 × 10^{-3}M. The buffers and corresponding pH ranges were phosphoric acid–dihydrogen phosphate (2—3), acetic acid–acetate (4—5·6), dihydrogen phosphate–monohydrogen phosphate (6—7·5), boric acid–borate (8—9·4) and bicarbonate–carbonate (10—10·5). Hydrochloric acid was used for experiments at pH = 0·7—1·6. The pH of the solution was measured (by meter) at the beginning and end of each kinetic experiment. Reactions were carried out in stoppered flasks in a thermostat, and samples were removed at intervals for measurement of the optical density at various wavelengths. Measurements were made at 500 and 576 mμ. Readings at 500 mμ were used to construct the logarithmic plots against time. At 576 mμ the molecular extinction coefficients of the three CoY(O) species and CoY^- are almost identical and the constancy of these measurements showed the absence of side-reactions from pH 0·7 to 7·0. From pH 7·0 to 10·5 measurements were also taken at 349 and 620 mμ and it was possible to calculate the separate concentrations of CoY^-, $CoYOH^{2-}$, and $CoYH_2O^-$. Although these were subject to considerable error and were unsatisfactory for kinetic plots, it was evident that the ratio $[CoYOH^{2-}]/[CoYH_2O^-]$ remained approximately constant throughout the reaction. In these experiments in alkaline solutions, the optical density at 576 mμ decreased slightly with time, showing the presence of a side-reaction which we believe results in the formation of CoY^{2-}, the enta complex of cobalt(II). The extent of this side-reaction was never more than 5% of the total. At pH values in excess of 10·5 the extent of the side-reaction was increased.

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