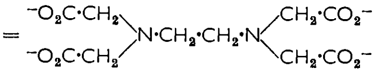
517. *Catalysis of the Elimination of Chloride Ion from Chloro(ethylenediaminetriacetatoacetate)cobaltate*(III) *and its Conjugate Acid by Metal Cations.*

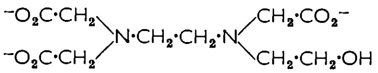
By R. Dyke and W. C. E. Higginson.

Activation energies and entropies have been found for the elimination of chloride ion from chloro(ethylenediaminetriacetatoacetate)cobaltate(III) catalysed by various metal cations in aqueous solution. A mechanism is proposed which involves the interaction of both the leaving chloride ion and the free carboxylate group with the catalyst. The elimination of chloride ion from the conjugate acid of this cobalt(III) complex is much less susceptible to cationic catalysis.

A KINETIC study of the Pb^{2+}-catalysed formation of ethylenediaminetetra-acetatocobaltate(III),* $Co(Y)^-$, from bromo(ethylenediaminetriacetatoacetate)cobaltate(III),* $Co(Y)Br^{2-}$, and its conjugate acid, $Co(HY)Br^-$, in aqueous solution was reported recently.[1] Here we describe the extension of the earlier work to other metal cations; for reasons discussed previously,[2] the chloro-complexes, $Co(Y)Cl^{2-}$ and $Co(HY)Cl^-$, have been used in place of the corresponding bromo-complexes. We have also briefly studied the effect

(Y) =


$$(Y) = \begin{matrix} ^-O_2C{\cdot}CH_2 \\ ^-O_2C{\cdot}CH_2 \end{matrix} > N{\cdot}CH_2{\cdot}CH_2{\cdot}N < \begin{matrix} CH_2{\cdot}CO_2^- \\ CH_2{\cdot}CO_2^- \end{matrix}$$

(YOH) =


$$(YOH) = \begin{matrix} ^-O_2C{\cdot}CH_2 \\ ^-O_2C{\cdot}CH_2 \end{matrix} > N{\cdot}CH_2{\cdot}CH_2{\cdot}N < \begin{matrix} CH_2{\cdot}CO_2^- \\ CH_2{\cdot}CH_2{\cdot}OH \end{matrix}$$

of these cations on the rate of loss of chloride from chloro(hydroxyethylethylenediaminetriacetato)cobaltate(III), $Co(YOH)Cl^-$. Most of the kinetic measurements were made at ionic strength 1·0M by conventional spectrophotometric methods, as described previously.[1,2]

For all catalysts other than Hg^{2+} we found that the kinetics of formation of $Co(Y)^-$ were described by the equation:

$$\begin{aligned} d\{[Co(Y)^-] + [Co(HY)H_2O]\}/dt &= -\,d[Co(Y)Cl]_T/dt \\ &= k_{obs}[M][Co(Y)Cl]_T + k_0[Co(Y)Cl]_T, \end{aligned} \qquad (1)$$

where M represents the catalyst cation, $[Co(Y)Cl]_T = [Co(Y)Cl^{2-}] + [Co(HY)Cl^-]$, k_0 is the pH-independent velocity constant for the uncatalysed elimination of chloride from both $Co(Y)Cl^{2-}$ and $Co(HY)Cl^-$, and k_{obs} is characteristic of M and varies with pH. The term in braces in eqn. (1) signifies that in solutions of low pH an equilibrium mixture of $Co(Y)^-$ and $Co(HY)H_2O$ is formed.[2] The rate of formation of this equilibrium mixture from $Co(Y)^-$ or $Co(HY)H_2O$ is such that near-equilibrium proportions of these products were maintained throughout the experiments at low pH. Although eqn. (1) holds up to [M] = 0·05M, experiments with Cd^{2+} and Pb^{2+} in 0·10M-H^+ showed that above this catalyst concentration k_{obs} decreased slightly, being about 10% lower at 0·10M-catalyst than in solutions of 0·05M-catalyst. Consequently, in experiments with other metal ions a concentration of 0·05M-catalyst was not exceeded. A similar change in k_{obs} with Cd^{2+} or Pb^{2+} concentration was found in experiments with these catalysts and $Co(YOH)Cl^-$ and it may be due to a salt effect, since association between the cobalt(III) complex and the catalyst, which could lead to similar behaviour, is less likely with $Co(YOH)Cl^-$. As discussed below, we believe such ion-pair formation occurs between $Co(Y)Cl^{2-}$ and certain cations at pH $\sim$ 5.

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* In names such as these, " tetra-acetato " denotes four carboxylate groups as ligands to the central metal, whereas " triacetatoacetate " denotes that, of four CO_2^- groups, only three function as ligands to the metal.

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

[2] Dyke and Higginson, *J.*, 1960, 1998.

The variation in k_{obs} with pH for the Pb^{2+}-catalysed loss of Br^- from $Co(Y)Br^{2-}$ and $Co(HY)Br^-$ has previously been interpreted[1] by postulating simultaneous second-order reactions between Pb^{2+} and each of these complexes, the pH-controlled equilibrium between the complexes being maintained throughout an experiment. The same interpretation holds for the chloro-complexes, and for their reactions with Cd^{2+}, Cu^{2+}, and Pb^{2+} we have obtained plots of k_{obs} against pH over the pH range 0·7—*ca.* 5 similar to that shown in the Figure in ref. 1. For these catalysts we found that $k_1 = -[M]^{-1} d \ln [Co(Y)Cl^{2-}]/dt$ is more than a hundred times greater than $k_2 = -[M]^{-1} d \ln [Co(HY)Cl^-]/dt$. Thus the contribution of reaction between the catalyst and $Co(Y)Cl^{2-}$ is considerable in solutions of low pH, even though the bulk of the chloro-complex is in the form of $Co(HY)Cl^-$. Consequently we were able to obtain values of k_1 for these and other cations from experiments in the pH range 0·7—2·3 as an alternative to the use of buffers at pH ~ 5. The rate equation can be written

$$-d[Co(Y)Cl]_T/dt = k_1[M][Co(Y)Cl^{2-}] + k_2[M][Co(HY)Cl^-] + k_o[Co(Y)Cl]_T. \qquad (2)$$

By combining (1) and (2) we obtain

$$k_{obs} = (k_1 - k_2)[Co(Y)Cl^{2-}]/[Co(Y)Cl]_T + k_2.$$

If the hydrogen-ion concentration remains constant throughout each experiment, then by introducing $K_H = [H^+][Co(Y)Cl^{2-}]/[Co(HY)Cl^-]$ we obtain

$$k_{obs} = (k_1 - k_2)K_H/(K_H + [H^+]) + k_2. \qquad (3)$$

Hence a plot of k_{obs} against $K_H/(K_H + [H^+])$ for a series of experiments in which $[H^+]$ is varied enables k_1 and k_2 to be obtained.

We obtained values of k_1 and k_2 in this way for Cd^{2+}, $Co(NH_3)_5H_2O^{3+}$, Cu^{2+}, Fe^{3+}, Pb^{2+}, and Tl^+. For Cu^{2+} and Fe^{3+} the ratio k_1/k_2 exceeds 10^3; in consequence the values obtained for k_2 are upper limits and we cannot quote acceptable values for $E^‡_2$ and $\Delta S^‡_2$, the corresponding activation parameters. Similar experiments with Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} gave values for k_1 with an uncertainty of ±5%, the error being rather large owing to the dominance of the uncatalysed route of reaction. For this reason we were unable to obtain values of k_2 for these cations. The catalytic effects of Ba^{2+}, Ca^{2+}, Mg^{2+}, and Sr^{2+} are so small that neither k_1 nor k_2 could be found from experiments with these ions at pH 2 or less.

In solutions of pH ~ 5 almost all the chloro-complex is in the form of $Co(Y)Cl^{2-}$ and, as eqn. (3) shows, under these conditions $k_{obs} = k_1$ within experimental error, since $K_H \sim 10^{-3}$ mole l.$^{-1}$ and k_1 exceeds k_2. We obtained values of k_1 subject to errors of *ca.* 2% for the cations Ba^{2+}, Ca^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, Sr^{2+}, Tl^+, and Zn^{2+} from experiments in acetate buffers. These experiments were done over a range of temperatures and at each temperature three otherwise identical experiments were performed in 0·0025M-, 0·0050M-, and 0·0075M-acetate. No significant change in k_1 with change in acetate concentration was observed and we conclude that complex formation with acetate is unimportant for these cations. Similar experiments with Mg^{2+} showed this ion to be a very weak catalyst and only an upper limit for $k_1 < 8 \times 10^{-4}$ l. mole^{-1} min.$^{-1}$ at 45° could be obtained.

Experiments with $Co(NH_3)_5H_2O^{3+}$ in acetate buffers at pH 4·6 showed evidence for ion-pair association between this cation and acetate, for the apparent value of k_1 decreased with increase in the acetate concentration. However, we were able to extrapolate the apparent values of k_1 obtained over the range 0·0050—0·020M-acetate to zero acetate concentration and so we found $k_1 = 0{\cdot}15 \pm 0{\cdot}025$ l. mole^{-1} min.$^{-1}$ at 49·9°, in moderate agreement with the value $k_1 = 0{\cdot}195 \pm 0{\cdot}025$ l. mole^{-1} min.$^{-1}$ obtained from experiments at pH 1·0—2·0. If the ion pair $\{Co(NH_3)_5H_2O^{3+},CH_3{\cdot}CO_2^-\}$ is assumed to be inactive as a catalyst, the variation in the apparent value of k_1 with acetate concentration is consistent with the value $\log K_A = 1\cdot1 \pm 0\cdot5$ where

$$K_A = [Co(NH_3)_5H_2O^{3+},CH_3{\cdot}CO_2^-]/[Co(NH_3)_5H_2O^{3+}][CH_3{\cdot}CO_2^-].$$

We used pyridine buffers for experiments with Cd^{2+}, Cu^{2+}, and Pb^{2+} in solutions of pH ~ 5. In the case of Pb^{2+} the values of k_1 varied little with changes in the buffer concentration and we conclude that complex formation between Pb^{2+} and pyridine is unimportant under our experimental conditions. With Cd^{2+} and Cu^{2+} the apparent value of k_1 decreased with increase in the buffer concentration. Association constants for the formation of complexes between these ions and pyridine are available,[3,4] and calculations made by using these constants showed that *ca.* 50% of the cation would be in the form of pyridine complexes at the highest buffer concentrations used. However, further calculations showed that the linear extrapolation to zero pyridine concentration of a plot of the reciprocal of the apparent value of k_1 against the corresponding value of the total pyridine concentration should give the true value of k_1, provided that not more than 20% of the cation is in the form of complex. Values of k_1 for Cd^{2+} and Cu^{2+} were obtained from such plots by using results from experiments in which the extent of complex formation was sufficiently low for the extrapolation to be satisfactory. We also found evidence that the monopyridine complexes of both cations are active catalysts. Relative values of k_1 for the monopyridine complex and the corresponding simple cation are $Cd\,py^{2+}/Cd^{2+} \sim 0\cdot4$, $Cu\,py^{2+}/Cu^{2+} \sim 0\cdot6$. Under our conditions less than 1% of these catalysts are in partially hydrolysed forms at pH ~ 5 and this is also true of the other catalysts investigated at this pH. Since we may expect partially hydrolysed forms to be less effective catalysts than their corresponding aquo-cations, we conclude that the influence of such hydrolysis on the rate of reaction is negligible.

The values of k_1 found for Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} at pH ~ 5 are in good agreement with those obtained from experiments in solutions of pH 0·7—2·3 but there are discrepancies between corresponding values of k_1 for Cd^{2+}, Cu^{2+}, and Pb^{2+}. At 25° these values are: Cd^{2+}, $2\cdot6_0$, $2\cdot9_6$; Cu^{2+}, $4\cdot7_5$, $5\cdot2_5$; Pb^{2+}, $8\cdot5_6$, $9\cdot2_1$ l. mole^{-1} min.$^{-1}$, the values at pH ~ 5 being given first. In obtaining values of k_1 at low pH by means of eqn. (3) we used $K_H = 1\cdot02 \times 10^{-3}$ mole l.$^{-1}$; this value was found by pH titration of $Co(HY)Cl^-$ with standard alkali at 1·0M-ionic strength and at 25°. The error in K_H is estimated as $\pm 3\%$ and in the kinetic measurements as $\pm 2\%$, so there is a real difference between the values of k_1 obtained by the two methods, at least for Cd^{2+} and Cu^{2+}. All three cations are known to associate strongly with carboxylate groups and the lower values of k_1 at pH ~ 5 may indicate that a small proportion of the substrate $Co(Y)Cl^{2-}$ is in the form of a complex with the catalyst, the latter being attached to the free carboxylate group. Such complex formation will reduce the value of the product $[Co(Y)Cl^{2-}] \times$ [Catalyst] below its apparent value and hence will reduce the rate of reaction below its expected value. In solutions of low pH, in which $Co(HY)Cl^-$ is the dominant form of the substrate, complex formation will still occur, but the relative change in $[Co(Y)Cl^{2-}] \times$ [Catalyst] will be much smaller since most of the $Co(Y)Cl^{2-}$ removed by complex formation will be replaced through the reaction $Co(HY)Cl^- \longrightarrow H^+ + Co(Y)Cl^{2-}$.

We have also investigated the effects of the ions Ba^{2+}, Ca^{2+}, Cd^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sr^{2+}, Tl^+, and Zn^{2+} on the rate of loss of chloride from $Co(YOH)Cl^-$. The kinetics of the spontaneous reaction, which yields the product $Co(YOH)H_2O$, have been studied previously.[5] Our experiments were carried out with *ca.* 0·05M-cation at 45·2° in solutions of pH 1—2. No significant changes were observed in the spontaneous rate of reaction owing to the presence of any of these cations except with Cd^{2+} and Pb^{2+}. For these two cations we obtained values of $k_3 = -[M]^{-1}\, d \ln [Co(YOH)Cl^-]/dt$.

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[3] Bjerrum, *Chem. Rev.*, 1950, **46**, 381.

[4] Leussing and Hansen, *J. Amer. Chem. Soc.*, 1957, **79**, 4270.

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

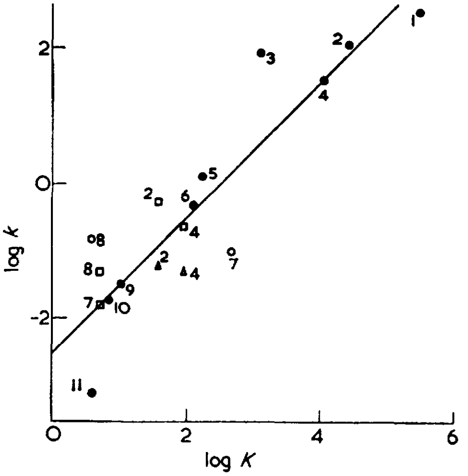
TABLE 1.

Catalyst	k_1 (25°) (l. mole^{-1} min.$^{-1}$)	$E‡_1$ (kcal. mole^{-1})	$\Delta S‡_1$ (cal. mole^{-1} deg.$^{-1}$)	Ref. for K K_A	K_{Cl}
Ca^{2+}	9×10^{-4}	27·8 ± 1·0	10·7 ± 3·3	*a*	*
Sr^{2+}	11×10^{-4}	27·6 ± 1·0	10·3 ± 3·3	*a*	*
Ba^{2+}..............	25×10^{-4}	24·0 ± 0·7	0·0 ± 2·4	*a*	*b*
Mn^{2+}	$0·024_3$	26·4 ± 0·5	12·4 ± 1·6		
Co^{2+}..............	$0·023_5$	26·4 ± 0·5	12·5 ± 1·6		*c*
Ni^{2+}	$0·026_4$	26·5 ± 0·5	12·9 ± 1·6	*d*	*c*
Cu^{2+}..............	$5·2_5$	26·7 ± 0·5	24·1 ± 1·6	*e*	*f*
Zn^{2+}	$0·074_4$	26·9 ± 0·5	16·3 ± 1·6	*g*	*h*
Cd^{2+}..............	$2·9_6$	23·2 ± 0·5	11·2 ± 1·6	*i*	*j*
Pb^{2+}..............	$9·2_1$	23·8 ± 0·5	15·8 ± 1·6	*k*	*j*
Fe^{3+}	$33·_0$	22·6 ± 1·0	14·2 ± 3·3	*	*l*
Tl^+	0·016	20·9 ± 0·7	−6·9 ± 2·4	*m*	*n*
	k_2 (25°) (l. mole^{-1} min.$^{-1}$)	$E‡_2$ (kcal. mole^{-1})	$\Delta S‡_2$ (cal. mole^{-1} deg.$^{-1}$)	k_2 (45°) (l. mole^{-1} min.$^{-1}$)	k_3 (45°)
Cu^{2+}..............	<0·003	—	—	—	—
Cd^{2+}..............	0·016	25·5 ± 1·5	8·9 ± 4·8	0·24	0·053
Pb^{2+}..............	0·038	25·1 ± 1·5	9·0 ± 4·8	0·54	0·062
Fe^{3+}	<0·004	—	—	—	—
Tl^+	0·002	22 ± 2	−7 ± 7	0·02	$<2 \times 10^{-3}$

* See text, p. 2792.

Refs.: (*a*) Nancollas, *J.*, 1956, 744. (*b*) Macdougall and Davies, *J.*, 1935, 1416. (*c*) Lister and Rosenblum, *Canad. J. Chem.*, 1960, **38**, 1827. (*d*) Fronaeus, *Acta Chem. Scand.*, 1952, **6**, 1200. (*e*) Bate, Davies, Morgans, and Monk, *Discuss. Faraday Soc.*, 1957, **24**, 94. (*f*) McConnell and Davidson, *J. Amer. Chem. Soc.*, 1950, **72**, 3164. (*g*) Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314. (*h*) Sillén and Liljeqvist, *Svensk kem. Tidskr.*, 1944, **56**, 85. (*i*) Leden, *Svensk kem. Tidskr.*, 1946, **58**, 129. (*j*) Austin, Matheson, and Parton, "The Structure of Electrolytic Solutions," ed. Hamer, Wiley, New York, 1959, Chap. 24. (*k*) Edmonds and Birnbaum, *J. Amer. Chem. Soc.*, 1940, **62**, 2367. (*l*) Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335. (*m*) Robinson and Davies, *J.*, 1937, 574. (*n*) Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

Most of our results are summarised in Table 1. The Figure shows values of log k_1 at 45° plotted against corresponding values of (log K_A + log K_{Cl}), and of log k_2 and log k_3, both at 45°, plotted against log K_{Cl}, where $K_A = [CH_3{\cdot}CO_2M]/[M][CH_3{\cdot}CO_2^-]$ and $K_{Cl} = [MCl]/[M][Cl^-]$. A plot obtained by using values of k_1 and k_2 at 25° was very similar, but at this temperature we have no results for Mg^{2+} and $Co(NH_3)_5H_2O^{3+}$. For the latter catalyst the values of log k_1 and log k_2 shown in the Figure were obtained by subtracting 0·3 from the corresponding values at 49·9°, the temperature of our experiments. The values of the association constants K_A and K_{Cl} used in constructing the



Relation between velocity constants and equilibrium constants.

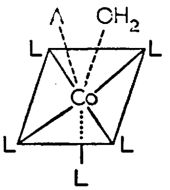
1, Fe^{3+}. 2, Pb^{2+}. 3, Cu^{2+}. 4, Cd^{2+}. 5, Zn^{2+}. 6, Ni^{2+}. 7, $Co(NH_3)_5H_2O^{3+}$. 8, Tl^+. 9, Ba^{2+}. 10, Ca^{2+}. 11, Mg^{2+}.

● log k_1 *vs.* (log K_A + log K_{Cl}) [for $Co(Y)Cl^{2-}$].
□ log k_2 *vs.* log K_{Cl} [for $Co(HY)Cl^-$].
△ log k_3 *vs.* log K_{Cl} [for $Co(YOH)Cl^-$].

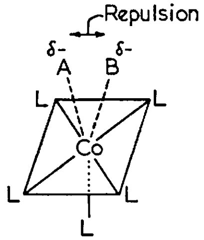
Temp. 45°; ionic strength 1·0M.

Figure were obtained from the references cited in Table 1; these constants hold at or near 25° and at zero ionic strength. Certain of these constants were found at ionic strength 0·2M and we have made an approximate correction to zero ionic strength by adding 0·6 to their logarithms. Other constants were found at ionic strength 1—3M and for these a correction of 0·8 has been added. We have assumed that the value of K_{Cl} for $Co(NH_3)_5H_2O^{3+}$ is similar to that for $Co(NH_3)_6{}^{3+}$ and have used $K_{Cl} = 5$ l. mole^{-1} at zero ionic strength (cf. ref. 6). The value $K_A \sim 100$ l. mole^{-1} at zero ionic strength has been estimated for $Co(NH_3)_5H_2O^{3+}$ from our approximate value at ionic strength 1·0M (see above). No value of K_A for Fe^{3+} appears to have been measured and we have estimated $K_A \sim 10^4$ l. mole^{-1} from the known association constants for Fe^{3+} with glycollate and oxalate.[7] Values of K_{Cl} have not been found for alkaline-earth cations, other than Ba^{2+}, for which $K_{Cl} = 0{\cdot}74$ l. mole^{-1} at zero ionic strength,[8] and we have assumed values of 0·4 and 0·2 l. mole^{-1} for Ca^{2+} and Mg^{2+} by comparing the activity coefficients recorded[9] for these and other bivalent cations. These values of K_{Cl} must be regarded as upper limits since it is difficult to distinguish between ionic association and the effects of long-range interactions in solutions of alkaline-earth halides.

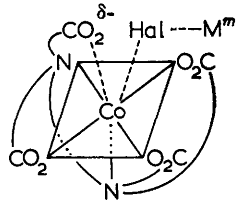
Discussion.—The formation of sexidentate $Co(Y)^-$ from quinquedentate $Co(Y)Br^{2-}$ or $Co(Y)Cl^{2-}$ in the absence of cationic catalysts has been interpreted[5,10] as a reaction of type S_N1 since each of the conjugate acids, $Co(HY)Br^-$ and $Co(HY)Cl^-$, reacts at the same rate as its parent base. It is possible that these are $S_N2_{(solv.)}$-type reactions, *i.e.*, of the type S_N2 with the solvent water as the entering ligand, for the rate of formation of $Co(Y)^-$ from $Co(Y)H_2O^-$ or $Co(HY)H_2O$ is very much faster than the rate of loss of halide from the halogeno-complexes and consequently it has not been shown whether or not these aquo-complexes are intermediates. On the other hand, the formation of $Co(Y)^-$ from $Co(Y)H_2O^-$ appears to be an internal S_N2-type reaction involving displacement of



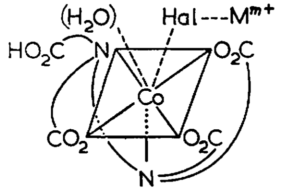
(I)



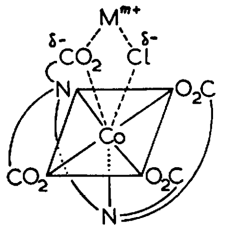
(II)



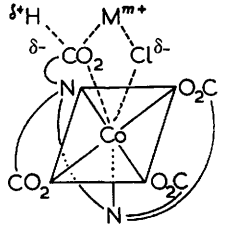
(III)



(IV)



(V)



(VI)

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[6] King, Espenson, and Visco, *J. Phys. Chem.*, 1959, **63**, 755.

[7] "Stability Constants," Chem. Soc. Special Publ., No. 6, 1957, pp. 2, 4.

[8] Macdougall and Davies, *J.*, 1935, 1416.

[9] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publns., London, 2nd edn., 1959, pp. 497—499.

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

the ligand H_2O by the initially unbound carboxylate group since this aquo-complex forms $Co(Y)^-$ more rapidly than does $Co(HY)H_2O$. The configuration of the transition state in this reaction of $Co(Y)H_2O^-$ is shown in (I), where A represents the initially unbound carboxylate group, now acting as an entering ligand. In this and subsequent diagrams a broken line represents a partly formed or a partly broken bond. If the halogeno-quinquedentate complexes reacted by a similar S_N2-type mechanism, the transition state would be represented by (II), where B is the leaving halide ion. The absence of S_N2-type behaviour may be ascribed to an abnormally high activation energy associated with species (II) owing to electrostatic repulsion between A and B, both of which would possess a fractional negative charge. We consider that repulsion of this type is an important factor in interpreting the observation, in the ligand-substitution of cobalt(III) complexes in general, that few examples are known in which direct S_N2-type substitution of one negatively charged ligand by another occurs.[11] The base-hydrolysis reactions of cobalt(III) complexes appear to provide the most numerous exceptions to this generalisation,[12] but in many cases their mechanisms are in dispute.

In an earlier interpretation of the Pb^{2+}-catalysed elimination of Br^- from $Co(Y)Br^{2-}$ and $Co(HY)Br^-$ it was suggested[1] that the greater reactivity of the former complex was due to the neutralisation by Pb^{2+} of the partial negative charge which would otherwise be present on the bromine atom in the transition state. Hence repulsion of the type shown in (II) would be reduced, thereby favouring an S_N2-type reaction. The Pb^{2+}-catalysed bromo-complex system was thus considered to be similar to the aquo-complex system, the basic forms of both aquo- and bromo-complexes reacting through internal S_N2-type mechanisms. No direct interaction between Pb^{2+} and the initially unbound carboxylate group was envisaged; the configuration of the corresponding transition state is depicted in (III) and that for the corresponding reaction with $Co(HY)Br^{2-}$ is shown in (IV). Here Hal represents Br, and M represents Pb^{2+}. We have placed the H_2O molecule in (IV) in parentheses since we could not distinguish experimentally between an S_N1 and an $S_N2_{(\text{solv.})}$-type mechanism. Our present experimental findings do not permit satisfactory interpretation in terms of these formulations and we now suggest that the transition states for the reactions of $Co(Y)Hal^{2-}$ and $Co(HY)Hal^-$ with a cationic catalyst M^{m+} are better represented by (V) and (VI), respectively. In both cases $Co(Y)^-$ is considered to be the immediate product, and M^{m+} and Hal^- remain in association as the transition complex breaks up, possibly with a water molecule intervening if M^{m+} is a Group IIA cation.

TABLE 2.

Cation	ΔH_A (kcal. mole^{-1})	$E\ddagger_1$ (kcal. mole^{-1})	ΔS_A (cal. mole^{-1} deg.$^{-1}$)	$\Delta S\ddagger_1$ (cal. mole^{-1} deg.$^{-1}$)
Ca^{2+}	0·91	27·8	8·7	10·7
Sr^{2+}	0·74	27·6	7·8	10·3
Ba^{2+}	−2·32	24·0	−2·5	0·0

The influence of the Group IIA cations on the rate of the reaction $Co(Y)Cl^{2-} \longrightarrow Co(Y)^-$ is quite small and may be regarded as a specific primary salt effect; in the presence of ~0·05M-catalyst the total rate of reaction is increased by *ca.* 2% for Mg^{2+}, 50% for Ca^{2+} and Sr^{2+}, and 100% for Ba^{2+}. Nevertheless a simple mechanistic interpretation of the role of these cations can be given and it provides part of our evidence in favour of formulation (V) rather than (III) for the transition state of this reaction. The affinity of these cations for halide ions is small and it is likely that a water molecule is interposed between cation and halide ion when they are associated.[13] Consequently, it seems

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[11] Basolo and Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 124; "Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press Inc., New York, 1961, Vol. III, p. 32.

[12] Tobe, *Sci. Progr.*, 1960, **48**, 483.

[13] Diamond, *J. Amer. Chem. Soc.*, 1958, **80**, 4808.

improbable that the polarisation by these cations of the leaving chloride ion would sufficiently reduce the repulsion between it and the carboxylate group to permit the close approach of the latter in the configuration shown in (III). Yet this close approach is necessary for the partial bonding between carboxylate group and cobalt atom which we believe must occur since k_1 greatly exceeds k_2 (which is too small to be measured) for each of the ions Ba^{2+}, Ca^{2+}, and Sr^{2+}. We suggest that if the catalyst interacts with both the leaving chloride ion and the entering carboxylate group, then the repulsion between these ligands could be reduced sufficiently for the transition state depicted in (V) to be energetically feasible. Since the affinity of these catalysts for carboxylate groups greatly exceeds their affinity for halide ions we might expect that differences in their activation parameters would reflect primarily the differences in the corresponding equilibrium quantities for their complex formation with carboxylate groups. Table 2, in which the equilibrium quantities ΔH_A and ΔS_A refer to complex formation with acetate ions,[14] shows that there is an effect of this kind for Ba^{2+}, Ca^{2+}, and Sr^{2+}. A similar correspondence is found if values of ΔH and ΔS for association with formate ions are used. We consider that this provides further evidence of a direct interaction between the catalyst and the unbound carboxylate group present in $Co(Y)Cl^{2-}$. It is possible that the transition state is attained by the intermediate formation of a complex between the catalyst and this carboxylate group. Although we have no evidence of this for these Group IIA cations, we have mentioned above that association appears to occur between $Co(Y)Cl^{2-}$ and Cd^{2+}, Cu^{2+}, and Pb^{2+}; these are cations of relatively high affinity for carboxylate groups.

In accordance with our postulate of a two-fold interaction between catalyst and $Co(Y)Cl^{2-}$ the Figure shows that there is a rough correlation between log k_1 and (log K_A + log K_{Cl}) for several of the catalysts. Similar correlations can be shown by plotting log k_1 against either log K_A or log K_{Cl}. However, the gradients of these two plots exceed 2·0 and it is abnormal for the proportionality factor in a linear relationship between activation and equilibrium free energies to be so much in excess of unity. The gradient in the Figure is 1·0; in an earlier investigation of catalysis by metal cations a gradient of 1·3 was found in the corresponding plot.[15] As the Figure shows, Mg^{2+} is a relatively poor catalyst; in order to fit on the line, K_{Cl} for Mg^{2+} would have to be one-tenth of the value we have assumed and we consider this unlikely. Although the values of K_A for Ba^{2+}, Ca^{2+}, Mg^{2+}, and Sr^{2+} are similar, it has been suggested[14] that in the association between Mg^{2+} and acetate a water molecule is interposed between the ions, whereas there is direct contact between each of the other three cations and acetate. If this is so in the corresponding transition complexes, we can interpret the weak activity of Mg^{2+} by suggesting that the bridge formed by this cation between the free carboxylate group and chlorine atom of $Co(Y)Cl^{2-}$ does not bring the carboxylate group as near to the cobalt atom as do the shorter bridges formed by the other cations. Consequently, the extent of bonding between this carboxylate group and the cobalt atom in the transition state will be relatively low for catalysis by Mg^{2+}. A similar effect was shown by the catalyst $Co(NH_3)_5H_2O^{3+}$. Reference to the Figure shows that, by chance, values of log k_2 plotted against log K_{Cl} for various catalysts lie fairly close to the line relating log k_1 with (log K_A + log K_{Cl}); the value of k_2 for $Co(NH_3)_5H_2O^{3+}$ is not abnormal in this respect. However, log k_1 shows a marked negative deviation from the line in the Figure. Even if the values of K_A and K_{Cl} which we have used are questioned, the ratio $k_1/k_2 \approx 6$ also implies a relatively small degree of bonding between the substrate cobalt atom and the carboxylate group in the transition complex involving $Co(NH_3)_5H_2O^{3+}$ and $Co(Y)Cl^{2-}$. Corresponding values of this ratio are *ca.* 10^4 for Fe^{3+} and *ca.* 10^2 for bivalent cations. Such a weak contribution from cobalt–carboxylate bonding is to be expected if our mechanism is correct since the bridge formed by $Co(NH_3)_5H_2O^{3+}$ between carboxylate group and chlorine atom is likely to be longer than that formed by a monoatomic cation.

[14] Nancollas, *J.*, 1956, 744.

[15] Prue, *J.*, 1952, 2331.

The activity of $Co(NH_3)_5H_2O^{3+}$ shows that relatively long-range interactions can be effective in this catalysis and the similarity of the activation parameters for Co^{2+}, Mn^{2+}, and Ni^{2+} shows an absence of highly specific effects for these three catalysts. In the cases of Zn^{2+} and Cu^{2+} there does appear to be evidence of highly specific behaviour in that the activation entropies obtained for these two catalysts are considerably higher than those for the other three transition ions, although all five are of similar radius. We are unable to provide a plausible interpretation of this effect. For all these transition ions and the Group IIA cations it seems probable that the catalytic effect is largely due to the action of the cation in bringing the carboxylate group into a configuration in which an internal S_N2-type displacement can take place. The high activation entropies compared with that of the unimolecular spontaneous reaction ($\Delta S^\ddagger = -7{\cdot}3$ cal. mole^{-1} deg.$^{-1}$; cf. ref. 2) presumably reflect the partial desolvation of the carboxylate group on entering into the transition complex and also a less negative entropy of the partial formation of the chloride ion in the presence of a positive ion.

Apart from Ba^{2+}, for which the negative value of ΔH_A is considered to influence $E^\ddagger_1$, the only cations for which $E^\ddagger_1$ is lower than 26 kcal. mole^{-1} are Cd^{2+}, Fe^{3+}, Pb^{2+}, and Tl^+. Of these, Cd^{2+}, Pb^{2+}, and Tl^+ show much higher values of the ratio k_2/k_1 than do the other cations, and Hg^{2+} also shows a relatively high reactivity with $Co(HY)Cl^-$. We ascribe these effects to a strong polarisation of the chlorine atom in the transition complex by these four ions, in contrast to the other catalysts, with a consequent weakening of the cobalt–chlorine bond. It is significant that these four cations differ from the others in belonging to a group in which the affinity for chloride ions exceeds that for fluoride.[16] Apart from their specific effect upon $E^\ddagger_1$, Cd^{2+} and Pb^{2+} also show the favourable effect upon $\Delta S^\ddagger_1$ characteristic of bivalent cations in general. The negative value of $\Delta S^\ddagger_1$ found for Tl^+ appears to be a consequence of the low charge of this catalyst; compare, for example, the entropies of association of chloride with Cd^{2+}, Pb^{2+}, and Tl^+ which are[17] 12·2, 11·6, and −1·7 cal. deg.$^{-1}$ mole^{-1}, respectively. The activation entropy for the reaction of Fe^{3+} with $Co(Y)Cl^{2-}$ is less positive than we might expect for a triply charged cation. This may be due to a relatively weak interaction between Fe^{3+} and the chlorine atom in the transition complex; it is significant that in the reaction with $Co(HY)Cl^-$ the value of k_2 for Fe^{3+} is much smaller than that for Pb^{2+} although the values of K_{Cl} for these two catalysts are similar.

The reaction $Co(HY)Cl^- \longrightarrow Co(Y)^-$ is relatively insensitive to catalysis and we were only able to obtain satisfactory values of the corresponding velocity constant k_2 for the cations which we believe polarise strongly the chlorine atom of the cobalt complex. Of the remaining cations investigated we obtained evidence of weak catalysis by Cu^{2+} and Fe^{3+}; these two are highly effective catalysts for the reaction of $Co(Y)Cl^{2-}$. Our original suggestion of an S_N1(or $S_N2_{(solv.)}$)-type replacement of the halogen corresponding to the transition state shown in (IV) seems to fit these observations, but further evidence has led us to prefer formulation (VI). We include in Table 1 values of k_2 and k_3 [the latter velocity constant applies to the catalysed loss of chloride from $Co(YOH)Cl^-$] for catalysis by Cd^{2+}, Pb^{2+}, and Tl^+. Now, the unimolecular rate constants for the spontaneous loss of chloride from $Co(HY)Cl^-$ and $Co(YOH)Cl^-$ are fairly similar, the constant for the latter complex being $\sim 1{\cdot}5$ times that for the former.[5] Yet in the catalysed reactions this order is reversed, k_2/k_3 being ~ 4 for Cd^{2+}, ~ 8 for Pb^{2+}, and >10 for Tl^+. We suggest that this is due to weak bonding in the transition complex between the carboxylic acid group present in $Co(HY)Cl^-$ and cobalt atom and, more tentatively, that interaction occurs between the catalyst and this carboxylic acid group, bringing it into the appropriate configuration. If this is so, and the reaction of $Co(HY)Cl^-$, like that of $Co(Y)Cl^{2-}$, involves an internal S_N2-type displacement on the cobalt atom, then $Co(Y)^-$ rather than

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[16] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[17] Nancollas, *Quart. Rev.*, 1960, **14**, 412.

$Co(HY)H_2O$ should be the immediate product. Owing to the relative rapidity of the reaction $Co(HY)H_2O \longrightarrow Co(Y)^-$ we were unable to confirm this by experiment, whereas the much faster rates attainable with Pb^{2+} and $Co(Y)Cl^{2-}$ at pH ~ 5 allowed us to show that this complex does give $Co(Y)^-$ directly. However, it is significant that $Co(Y)^-$ is the immediate product of the reaction of Hg^{2+} with $Co(HY)Cl^-$. As described below, the catalysis by Hg^{2+} differs in some respects from that by other cations, but we believe that these differences should not affect the nature of the product.

Catalysis by Hg^{2+}.—A few experiments were performed, in collaboration with Dr. R. Westbury, with a " stopped-flow " apparatus for following the kinetics of rapid reactions, to investigate the behaviour of Hg^{2+} as a catalyst of the reaction $Co(HY)Cl^- \longrightarrow Co(Y)^-$. These experiments were done at *ca.* 22° in sodium perchlorate–perchloric acid media of ionic strength $1{\cdot}2 \pm 0{\cdot}2$M. Initial concentrations were $3{\cdot}0 \times 10^{-3}$M-$Co(HY)Cl^-$, 0·10M-, 0·30M-, or 1·00M-H^+, and 0·0055—0·125M-Hg^{2+}. For Hg^{2+} concentrations of *ca.* 0·03M or greater, good linear plots of log $[Co(HY)Cl^-]_t$ against time, t, were obtained. The first-order rate constants derived from these plots were not proportional to $[Hg^{2+}]$, but tended to limiting values with increase in $[Hg^{2+}]$. Within an experimental error of $\pm 3\%$ no change in the rate constants was observed with increase in $[Hg^{2+}]$ from 0·08M to 0·125M; the limiting values were found to be 15·3, 13·2, and 12·3 sec.$^{-1}$ in 0·10M, 0·30M, and 1·00M-H^+, respectively. These observations suggest that a rapid association equilibrium occurs between Hg^{2+} and the cobalt complex, followed by a relatively slow unimolecular breakdown of this association product leading to the formation of $HgCl^+$. In solutions of both 0·10M- and 1·00M-H^+ the rate constants obtained at concentrations of Hg^{2+} below 0·08M were consistent with a value of 120 ± 30 l. mole^{-1} for the equilibrium constant of the association reaction $Co(HY)Cl^- + Hg^{2+} \rightleftharpoons Co(HY)ClHg^+$. Since the value of this constant was hardly affected by the hydrogen-ion concentration we conclude that the equilibrium is as stated and is not $Co(HY)Cl^- + Hg^{2+} \rightleftharpoons Co(HgY)Cl + H^+$. This implies that Hg^{2+} is primarily associated with the chlorine atom of the cobalt complex rather than with the carboxylate group unattached to cobalt. Reinforcing this suggestion, we were unable to detect significant association between Hg^{2+} (0·05M) and $Co(HY)H_2O$ in solutions of 1·0M-H^+, although pK_{acid} is ~3 for both this complex and $Co(HY)Cl^-$. The small increase in the limiting unimolecular rate constant with decrease in the hydrogen-ion concentration from 1·00M to 0·10M suggests that the association complex is in equilibrium with its conjugate base, $Co(HY)ClHg^+ \rightleftharpoons H^+ + Co(Y)ClHg$, and that the latter breaks down more rapidly, presumably owing to greater bonding in the transition state between cobalt and the carboxylate group than in that between cobalt and the carboxylic acid group. If we assume that the acid dissociation constant of $Co(HY)ClHg^+$ is similar to that for $Co(HY)Cl^-$ and $Co(HY)H_2O$, *i.e.*, *ca.* 10^{-3} mole l.$^{-1}$, and that replacement of sodium ions by hydrogen ions at constant ionic strength has little salt effect upon the values of the velocity constants, then the change in the observed first-order constant due to change in hydrogen-ion concentration is consistent with a value of *ca.* 360 sec.$^{-1}$ for the reaction of $Co(Y)ClHg$ and 11·9 sec.$^{-1}$ for $Co(HY)ClHg^+$. Under our conditions, the bulk of the reaction proceeds through the decomposition of $Co(HY)ClHg^+$, but final readings of optical density showed that $Co(Y)^-$ is the only cobalt complex produced. Were $Co(HY)H_2O$ an immediate product it would be detected at the conclusion of the chloride-abstraction since the rate of formation of $Co(Y)^-$ from $Co(HY)H_2O$ is relatively slow.[2] This supports our suggestion that a carboxylic acid group can participate in an internal S_N2-type reaction in these catalysed systems. In other respects the behaviour of Hg^{2+} does not resemble that of the other catalysts; although there is some evidence of weak association in solutions of pH ~ 5 between $Co(Y)Cl^{2-}$ and Cd^{2+}, Cu^{2+}, and Pb^{2+}, this is probably due to interaction between these catalysts and the free carboxylate group. The chlorine atom of the substrate is likely to bear a fractional negative charge and the strong association between this atom and Hg^{2+} is presumably related to its extremely high affinity for chloride ions.

EXPERIMENTAL

Sodium ethylenediamine-*NNN'N'*-tetra-acetatocobaltate(III) tetrahydrate,[18] sodium chloro-(ethylenediamine-*NNN'*-triacetato-*N'*-acetic acid)cobaltate(III) dihydrate,[19] and sodium-chloro-(*N*-hydroxyethylethylenediamine-*NN'N'*-triacetato)cobaltate(III) sesquihydrate [20] were prepared and purified by methods described previously. Other reagents were of " AnalaR " grade or were prepared in solution from " AnalaR " reagents by simple methods, *e.g.*, by dissolving the corresponding carbonate in perchloric acid for barium, calcium, magnesium, and strontium perchlorate, by dissolving the oxide in perchloric acid for copper(II) perchlorate, by precipitating the hydroxide or oxide and then dissolving it in perchloric acid for cadmium, iron(III), mercury(II), lead, and thallium(III) perchlorate, by double decomposition between the sulphate and barium perchlorate for cobalt(II), manganese, nickel, and zinc perchlorate. Thallium(I) perchlorate was obtained by evaporating a mixture of thallium(I) nitrate and 60% perchloric acid almost to dryness and recrystallising the product three times from water. Aquopentamminecobalt(III) perchlorate was prepared as previously described.[21] Solutions of metal perchlorates were standardised by methods described by Schwarzenbach,[22] or, in a few cases, by other standard methods. Several of these solutions contained free perchloric acid which was found as the difference between the total equivalent concentration of cations (determined by cation-exchange on Amberlite IR-120 resin) and the equivalent concentration of the metal cation.

Kinetic experiments, except those with Hg^{2+}, were made spectrophotometrically by using a Unicam S.P. 600 spectrophotometer equipped with a temperature-controlled cell compartment. Details of the procedures employed and of the method of establishing the pH values of reaction solutions have been given previously.[1,2] The operation and construction of the stopped-flow apparatus used for experiments with Hg^{2+} will be described elsewhere; a brief account has already been given.[23] In connection with the kinetic experiments we showed that the molecular extinction coefficients of the cobalt complexes, both reactants and products, were substantially unaffected by the presence of the catalysts. We also investigated the influence of the catalysts upon the equilibrium $Co(Y)^- + H^+ + H_2O \rightleftharpoons Co(HY)H_2O$ in solutions of pH < 2, since under these conditions both these complexes appear as products of the reaction of $Co(HY)Cl^-$, and their molecular extinction coefficients differ at 500 mμ, the most convenient wavelength at which to follow this reaction. None of the catalysts, which were present in concentrations similar to those employed in the kinetic experiments, significantly affected the position of this equilibrium in strongly acid solutions and so the final optical density in the kinetic experiments depended only on pH and the initial concentration of $Co(HY)Cl^-$. The rate of attainment of the equilibrium mixture from $Co(Y)^-$ was also unaffected except by Hg^{2+}, which at a concentration of 0·05M caused an increase of *ca.* 4% in this rate. We also investigated the effect of Tl^{3+} upon this equilibrium and found a large shift in the final optical density and a considerable increase in the rate of equilibration. Our measurements suggest that under these conditions an additional reaction, $Co(Y)^- + Tl^{3+} + H_2O \rightleftharpoons Co(TlY)H_2O^{2+}$, must be taken into account. With the exception of catalysis by Hg^{2+}, the rate of loss of chloride ion from the chloro-complexes in strongly acid solution was always considerably less than the rate of equilibration between $Co(Y)^-$ and $Co(HY)H_2O$, and so the pH-controlled equilibrium between these products was maintained throughout the catalysis experiments. In the case of Hg^{2+} the rate of loss of chloride was very much greater than the equilibration rate and it was evident that $Co(Y)^-$ was the sole immediate product.

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