89. *The Isotopic Exchange Reaction of Carbonato-*cis*-diammine-(ethylenediamine)cobalt*(III) *Ion and Carbonate Ion in Aqueous Solution.*

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Carbonate ligand exchange has been studied for *cis*-$[CoCO_3(NH_3)_2en]^+$. Effects of changes in reactant concentration, pH, and temperature have been determined. The rates and mechanism of exchange are very similar to those of the tetra-ammine- and bisethylenediamine-carbonatocobalt(III) ions.

PREVIOUS publications have reported on the nature of the exchange reaction between $[^{14}C]$carbonate ion and the carbonate ligand in carbonatocobalt(III) ions. The complex ions studied include the tetra-ammine $[CoCO_3(NH_3)_4]^+$,[1] penta-ammine $[CoCO_3(NH_3)_5]^+$,[2] bisethylenediamine $[CoCO_3en_2]^+$,[3] and bistrimethylenediamine complexes $[CoCO_3tn_2]$.[4] The present paper extends the studies to the *cis*-isomer of the carbonatodiammine(ethylenediamine)cobalt(III) ion $[CoCO_3(NH_3)_2en]^+$.

The complex ions $[CoCO_3(NH_3)_4]^+$ and $[CoCO_3en_2]^+$ have been shown to undergo exchange by similar mechanisms and at similar rates; however, $[CoCO_3(NH_3)_5]^+$ and $[CoCO_3tn_2]^+$ do so at different rates because of the absence of co-ordinated water in the former complex when it dissolves in water and of steric hindrance by the trimethylenediamine ligands in the latter complex.

Evidence presented here shows that the rate of exchange of *cis*-$[CoCO_3(NH_3)_2en]^+$ is similar to that of $[CoCO_3(NH_3)_4]^+$ and $[CoCO_3en_2]^+$ ions, although the values of rate constants obtained are not in the order expected from a comparison of the structures of the three ions.

EXPERIMENTAL

Preparation, Purification, and Analysis of Materials.—Carbonatodiammine(ethylenediamine)cobalt(III) chloride was prepared by an extension of the work of Bailar and Peppard.[5] *cis*-$[CoCO_3(NH_3)en]_2CO_3$ was first obtained and converted into the chloride by either of the following methods:

(*a*) The carbonate, *cis*-$[CoCO_3(NH_3)en]_2CO_3$, was dissolved in a little cold water and a solution of the calculated amount of barium chloride added. The mixture was set aside overnight and the precipitated barium carbonate removed. The filtrate was evaporated to dryness in a vacuum desiccator over concentrated sulphuric acid. Additional barium carbonate that separated during the evaporation was filtered off and the drying continued. The solid thus obtained was recrystallised twice from hot water in which it is very soluble. The carmine-red

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[1] Harris and Stranks, *Trans. Faraday Soc.*, 1952, **48**, 137; Stranks, *ibid.*, p. 911.

[2] Stranks, *Trans. Faraday Soc.*, 1955, **51**, 505.

[3] Holden and Harris, *J. Amer. Chem. Soc.*, 1955, **77**, 1934.

[4] Boyle and Harris, *J. Amer. Chem. Soc.*, 1958, **80**, 782.

[5] Bailar and Peppard, *J. Amer. Chem. Soc.*, 1940, **62**, 105.

crystals obtained on cooling were collected, washed with a little ice-cold water, ethanol, and ether, and dried over concentrated sulphuric acid in a desiccator.

(*b*) The same *cis*-carbonate was shaken in water with an anion-exchange resin (Amberlite CG45, chloride form; 200 mesh). The suspension was filtered and the filtrate treated with a second batch of resin. The product was extracted as in (*a*).

Analysis was carried out by conventional micro-analytical methods {Found: C, 13·6; H, 6·1; N, 21·6; Cl, 13·8. Calc. for $[CoCO_3(NH_3)_2en]Cl,\frac{1}{2}H_2O$: C, 14·0; H, 5·9; N, 21·75; Cl, 13·8%}.

The *cis*-configuration of this compound was confirmed by partial resolution on optically active quartz. Optical measurements were made on a Hilger standard polarimeter, Mark III, with the sodium-D line. The precision of measurements was no better than 0·010° and the average of seven readings indicated a rotation of 0·017°. Bailar and Peppard observed rotations of up to 0·04° with *cis*-$[CoCO_3(NH_3)_2en]_2CO_3$.

The *cis*-isomer was also characterised by determination of the infrared absorption spectrum.[6]

Sodium [^{14}C]carbonate was obtained from the Radiochemical Centre at Amersham.

Exchange Reactions.—The kinetic runs were made as described by other workers. The reaction vessel was a Pyrex-glass boiling-tube. Known amounts of complex were dissolved in suitable volumes of sodium carbonate and sodium hydrogen carbonate solutions to give a total volume of 14 ml. and the required total carbonate concentration and pH. Air was displaced from the vessel by a stream of carbon dioxide-free nitrogen and the solution left in a thermostat bath until aquation equilibrium had been reached. Then 1 ml. of active sodium carbonate solution was added and the whole mixed. After known reaction times, 1 ml. samples were withdrawn and the free carbonate was precipitated as barium carbonate. The specific activity was determined by end-window counting of uniformly spread barium carbonate samples on aluminium planchets. In some cases an accurately known volume of 0·045M-sodium hydrogen carbonate was added to the sample before precipitation in order to increase the weight of precipitate and to improve spreading.

Half-times of exchange were obtained from the conventional plots of log $(1 - f)$ against time, with least-squares analysis to achieve best fit.[7] The fraction of exchange is $f = (A_0 - A_t)/(A_0 - A_\infty)$, where A's are specific activities at times 0, t, and infinity, respectively. A_∞ was calculated from the equation $(a + b)A_\infty = bA_0$ where a and b are the total concentrations of complex and free carbonate (including hydrogen carbonate) ion, respectively, with all the activity initially in the free carbonate. In runs at higher pH values addition of the active carbonate solution disturbed the aquation equilibrium; the initial sample was then taken after 15 min. and the A_∞ value determined experimentally by allowing the exchange to proceed for at least seven half-times.

pH measurements were made on a Doran Universal pH meter using a Lock–Ingold single rod silver–silver chloride electrode.

RESULTS

Variation of Reactant Concentration.—A series of runs was made in which the concentrations of complex (a), total free carbonate (b), and hydrogen ion (h) were varied. In each run, pH control was achieved by adjustment of the ratio of carbonate and hydrogen carbonate ion concentrations. The half-times were obtained as described above and the rates of reaction calculated from the relation $R = \ln (2/t_{\frac{1}{2}})\, ab/(a + b)$. The results are summarised in Table 1 and the Figure.

Light and Surface Conditions.—Pairs of experiments were performed in which all concentrations remained the same, but one exchange was carried out in a blackened tube. No difference in rate was found. In other experiments glass beads were included. The increased surface area had no effect on the exchange rate.

Temperature-dependence.—In other experiments concentrations were constant but the temperature was varied. The apparent activation energy of the reaction, calculated from the plot of log R against $1/T$, is 22·7 kcal./mole. Pairs of runs in which concentrations were varied enabled calculation of rate constants to be made (see discussion). These results are summarised in Table 2.

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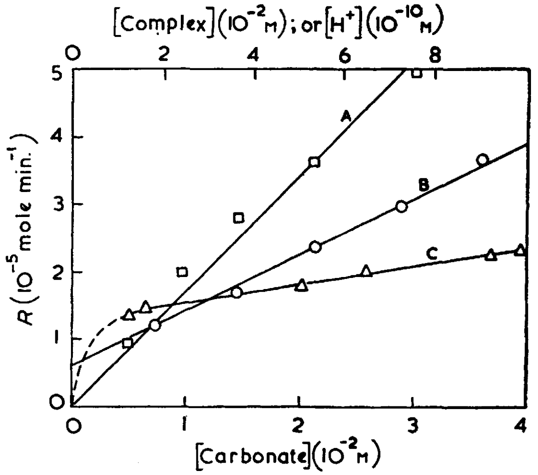
[6] Unpublished results.

[7] Friedlander and Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, 1955, p. 316.

Table 1.

Effect of variation of reactant concentrations on the rate of exchange between complex and free carbonate ion at 25·80°.

pH	$[\mathrm{CoCO_3(NH_3)_2en}]^+$ (mole/l.)	$[\mathrm{CO_3}^{2-} + \mathrm{HCO_3}^-]$ (mole/l.)	$t_{\frac{1}{2}}$ (min.)	10^5R (mole $\mathrm{l.^{-1}}$ $\mathrm{min.^{-1}}$)
9·33	0·0296	0·0072	440	1·18
9·33	0·0296	0·0144	410	1·65
9·33	0·0296	0·0216	370	2·34
9·33	0·0296	0·0290	335	2·95
9·33	0·0296	0·0360	320	3·63
9·05	0·0121	0·0150	510	0·91
9·05	0·0244	0·0150	330	1·96
9·05	0·0362	0·0150	260	2·83
9·05	0·0530	0·0150	225	3·60
9·05	0·0756	0·0150	175	4·99
9·01	0·0296	0·0144	295	2·27
9·03	0·0296	0·0144	305	2·20
9·19	0·0296	0·0144	333	1·95
9·30	0·0296	0·0144	415	1·76
9·79	0·0296	0·0144	472	1·42
9·91	0·0296	0·0144	503	1·33



Variation of exchange rate with reactant concentration:

A, [Complex] variable; [Carbonate] = 0·0150M; $[\mathrm{H}^+] = 8{\cdot}91 \times 10^{-10}$M.

B, [Carbonate] variable; [Complex] = 0·0296M; $[\mathrm{H}^+] = 4{\cdot}68 \times 10^{-10}$M.

C, $[\mathrm{H}^+]$ variable; [Complex] = 0·0296M; [Carbonate] = 0·0144M.

Table 2.

Effect of temperature on the rate of exchange between complex and free carbonate ion.

pH	$[\mathrm{CoCO_3(NH_3)_2en}]^+$ (mole/l.)	$[\mathrm{CO_3}^{2-} + \mathrm{HCO_3}^-]$ (mole/l.)	Temp.	$t_{\frac{1}{2}}$ (min.)	10^5R (mole $\mathrm{l.^{-1}}$ $\mathrm{min.^{-1}}$)
9·19	0·0296	0·0144	25·8°	333	1·95
9·19	0·0296	0·0144	29·9	190	3·53
9·19	0·0296	0·0144	35·3	105	6·38
9·24	0·0351	0·0245	29·9	181	5·53
9·24	0·0351	0·0245	35·3	109	9·15

DISCUSSION

Since the compound being studied, *cis*-$[\mathrm{CoCO_3(NH_3)_2en}]^+$, is intermediate in structure between $[\mathrm{CoCO_3(NH_3)_4}]^+$ and $[\mathrm{CoCO_3en_2}]^+$ it is to be expected that the carbonate exchange mechanism operating in this case will be similar to that in the above-mentioned examples. Boyle and Harris[4] have proposed a comprehensive detailed mechanism applicable to both these ions based on the following steps:

$$\mathrm{CoLCO_3^+ + H_2O \rightleftharpoons CoLCO_3H_2O^+} \qquad (1)$$

$$\mathrm{CoLCO_3H_2O^+ + H^*CO_3^- \rightleftharpoons CoL^*CO_3H_2O^+ + HCO_3^-} \qquad (2)$$

$$\mathrm{CoL^*CO_3H_2O^+ \rightleftharpoons CoL^*CO_3^+ + H_2O} \qquad (1')$$

$$\mathrm{CoLCO_3H_2O^+ + H^+ \rightleftharpoons CoLHCO_3H_2O^{2+}} \qquad (5)$$

$$\mathrm{CoLHCO_3H_2O^{2+} + H_2O \rightleftharpoons CoL(H_2O)_2^{3+} + HCO_3^-} \qquad (6)$$

$$\mathrm{CoL(H_2O)_2^{3+} + H^*CO_3^- \rightleftharpoons CoL^*CO_3H_2O^{2+} + H_2O} \qquad (6')$$

$$\mathrm{CoLH^*CO_3H_2O^{2+} \rightleftharpoons CoL^*CO_3H_2O^+ + H^+} \qquad (5')$$

[where L = $(NH_3)_4$ or en_2].†

An analysis of the reaction steps leads to an overall rate law for the carbonate exchange:

$$R = \frac{k_2K_1[H_2O]}{k_1[H_2O]+1}\,ab\,\frac{h}{h+K_4} + \frac{k_6K_5K_1[H_2O]^2}{K_1[H_2O]+1}\,ah$$

In this small k's are forward rate constants and large K's are equilibrium constants where K_4 refers to the reaction

$$\mathrm{HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}}. \qquad (4)$$

In the pH range studied $h/(h + K_4)$ is nearly constant since K_4 is $4{\cdot}69 \times 10^{-11}$ at 25°.[8] The rate law may thus be written as

$$R = k'ab + k''ah.$$

This predicts that the overall exchange reaction should be of the first order in complex concentration and partly of zero order and partly of first order in carbonate and hydrogen ion concentrations. A good fit can be obtained between theoretical predictions and experiment if k' is assigned the value $2{\cdot}9 \times 10^{-2}$ l. mole^{-1} min.$^{-1}$ and k'' the value $3{\cdot}76 \times 10^5$ l. mole^{-1} min.$^{-1}$ from the data at 25·8°.

We may now compare the carbonate exchange behaviour of the three carbonato-cobalt(III) complexes. The relevant values, calculated for 25·0°, are summarised in Table 3.

TABLE 3.

Rate data calculated for 25·0°.

	Direct exchange		Exchange *via* aquation	
Complex	$10^4k'$ (l. mole^{-1} sec.$^{-1}$)	E' (kcal. deg.$^{-1}$)	$10^{-4}k''$ (l. mole^{-1} sec.$^{-1}$)	E'' (kcal. deg.$^{-1}$)
$[CoCO_3(NH_3)_4]^+$	3·5	16·7	2·8	20·6
$[CoCO_3en_2]^+$	2·7	~15	1·0	—
$[CoCO_3(NH_3)_2en]^+$	4·3	18·7	0·53	26·1

In the pH range studied $h/(h + K_4)$ is approximately 0·8 and, if K_1 is assumed to be large, $K_1[H_2O]/\{K_1[H_2O] + 1\} = 1$ so that $k' \simeq k_2$. The activation energy (E') calculated from the Arrhenius plot of log k' against $1/T$ will therefore be almost identical with E_2, the activation energy of the direct exchange reaction. The entropy of activation can then be calculated from the conventional transition-state theory equation

$$k = \kappa(\boldsymbol{k}T/\boldsymbol{h})\exp\exp(\Delta S^{\ddagger}/\boldsymbol{R})\exp(-E/\boldsymbol{R}T).$$

The value for *cis*-$[CoCO_3(NH_3)_2en]^+$ is -18 kcal. mole^{-1} degree^{-1} (e.u.) compared with -25 for $[CoCO_3(NH_3)_4]^+$ and -32 for $[CoCO_3en_2]^+$, calculated from data in refs. 4 and 9.

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† Reactions have been numbered in accordance with Boyle and Harris's scheme.

[8] Harned and Scholes, *J. Amer. Chem. Soc.*, 1941, **63**, 1706.

[9] Stranks, " Modern Coordination Chemistry," editors Lewis and Wilkins, Interscience Publ. Inc., New York, 1960, p. 141.

These values, whilst not in close agreement, confirm the view that the three complexes named undergo direct exchange by a similar mechanism. The entropy of activation for $[CoCO_3tn_2]^+$ at 25° is —4 e.u., and Boyle and Harris postulated a different mechanism because of steric hindrance by the trimethylenediamine ligands.

The aquation mechanism is a composite process consisting of reactions (1), (5), and (6) and $k'' = k_6K_5[H_2O]$. Since no value of K_5 is available, k_6 cannot be calculated; also $E'' = E_6 + \Delta H_5$ and no value for ΔH_5 is available and hence E_6 cannot be calculated. It is not possible, therefore, to calculate an entropy of activation for the aquation.

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