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A Kinetic Study of the Base Hydrolysis of (2-Aminoethanol)bis(ethylenediamine)halogenocobalt(III) Complexes

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The base hydrolysis of *cis*-$[CoX(etaH)(en)_2]^{2+}$(X=Cl or Br, etaH=2-aminoethanol, en=ethylenediamine) has been studied. The hydrolysis results in the formation of $[Co(eta)(en)_2]^{2+}$ (≈35%) and $[Co(OH)(etaH)(en)_2]^{2+}$ (≈65%) at I=1.0 (KNO_3), 25 °C, the product ratio being independent of the pH. The base hydrolysis has also been studied in the presence of sodium azide.

The base hydrolysis of *cis*-$[CoX(etaH)(en)_2]^{2+}$ has been studied by several workers. Chan and Leh,[1] Hay and Cropp[2] and Udovenko *et al.*[3] reported that the hydrolysis product of the chloro complex was the hydroxo complex $[Co(OH)(etaH)(en)_2]^{2+}$ in which the etaH is unidentate. On the other hand, the synthesis of $[Co(etaH)(en)_2]^{3+}$ complexes containing the chelated etaH *via* the base hydrolysis of *cis*-$[CoBr(etaH)(en)_2]^{2+}$ was reported by Buckingham *et al.*[4] Similarly, several complexes of the $[Co(amOH)(diamine)_2]^{3+}$ type (amOH=2-amino-1-alkanol) were synthesized through the base hydrolysis of $[CoX(amOH)(diamine)_2]^{2+}$.[5,6] The present investigation has been undertaken in order to clarify the products of the hydrolysis of *cis*-$[CoX(etaH)(en)_2]^{2+}$ and to elucidate the mechanism of the reaction.

Experimental

Materials. The *cis*-$[CoX(amine)(en)_2]X_2$(amine=$C_2H_5NH_2$ or etaH) and $[Co(etaH)(en)_2]Br_3$ were prepared according to the literature method.[4,7] All the other reagents were of a reagent grade.

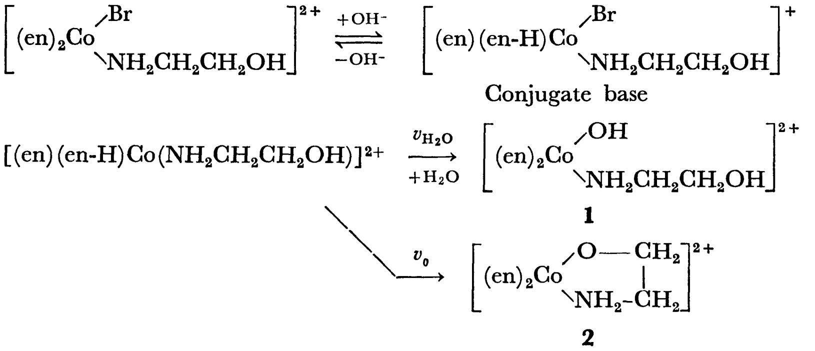
Kinetic Measurements. The base hydrolysis of *cis*-$[CoX(amine)(en)_2]^{2+}$ was followed by the pH stat method using a Metrohm Combi 6-1 titrator under a nitrogen atmosphere at 25 °C and I=1.0 (KNO_3). Product analyses were performed pH-metrically. The titrant was 0.05 M NaOH (1 M=1 mol dm^{-3}).

Results and Discussion

Equivalent amounts of the base are consumed during the course of base hydrolyses of $[CoX(amine)(en)_2]^{2+}$.[8] The rate of hydrolysis was measured by the pH stat method at pH 9—10. The data fit the rate law of $k_{obsd}=k[OH^-]$, the values of k being 51 and 31 M^{-1} s^{-1} for *cis*-$[CoBr(etaH)(en)_2]^{2+}$ and *cis*-$[CoBr(C_2H_5NH_2)(en)_2]^{2+}$ respectively at I=1.0(KNO_3) and 25 °C. The values for the former is somewhat smaller than that at I=0.1 reported by Buckingham *et al.*[4]

After the base hydrolyses had been completed, the solutions were acidified with appropriate amounts of 0.1 M HCl and were then titrated with 0.05 M NaOH. The titration curve remained unchanged after the solution had been left standing at pH 10 at 25 °C for 1 h. The base hydrolysis of *cis*-$[CoBr(C_2H_5NH_2)(en)_2]^{2+}$ resulted in the formation of a product with a pK_a value of 6.25 at I=1.0(KNO_3) and 25 °C; this indicates that the product should be $[Co(H_2O)(C_2H_5NH_2)(en)_2]^{3+}$. The titration curve of the hydrolysis products of *cis*-$[CoBr(etaH)(en)_2]^{2+}$ shows two inflection points, as is shown in Fig. 1, indicating that two species, **1** and **2**, are produced during the base hydrolysis of $[CoBr(etaH)(en)_2]^{2+}$. The abundance ratio and pK_a values of these two species were determined by analyzing the titration curves in the manner described in the Appendix. The results are given in Table 1. Species **1** with a pK_a value of 6.2, is considered to be $[Co(H_2O)(etaH)(en)_2]^{3+}$ by a comparison of the pK_a value with those of several cobalt(III) complexes with a coordinated water.[9] Species **2** with a pK_a value of 4.0, is considered to be $[Co(etaH)(en)_2]^{3+}$, because the titration of the solution of $[Co(etaH)(en)_2]Br_3$ showed its pK_a to be 4.0 at I=1.0, 25 °C. These values are somewhat larger than those at lower ionic strengths reported in previous papers.[4,5]

The conjugate-base mechanism has been established for the base hydrolyses of cobalt(III) aniono amine complexes. According to the S_N1 CB mechanism, the base hydrolysis of $[CoX(etaH)(en)_2]^{2+}$ can be expressed by the following scheme.



$$\left[(en)_2Co\begin{smallmatrix}Br\\NH_2CH_2CH_2OH\end{smallmatrix}\right]^{2+} \underset{-OH^-}{\overset{+OH^-}{\rightleftharpoons}} \left[(en)(en\text{-}H)Co\begin{smallmatrix}Br\\NH_2CH_2CH_2OH\end{smallmatrix}\right]^{+} \xrightarrow{-Br^-}$$

$$[(en)(en\text{-}H)Co(NH_2CH_2CH_2OH)]^{2+} \underset{+H_2O}{\xrightarrow{v_{H_2O}}} \left[(en)_2Co\begin{smallmatrix}OH\\NH_2CH_2CH_2OH\end{smallmatrix}\right]^{2+} \quad (1a)$$

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$$\xrightarrow{v_0} \left[(en)_2Co\begin{smallmatrix}O-CH_2\\NH_2-CH_2\end{smallmatrix}\right]^{2+} \quad (1b)$$

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TABLE 1. PRODUCTS OF THE BASE HYDROLYSIS OF *cis*-$[CoX(etaH)(en)_2]^{2+}$ AS DETERMINED BY THE ANALYSIS OF THE TITRATION CURVES. $I=1.0(KNO_3)$, 25 °C

X	pH[a]	Complex-hydrolyzed mmol[b]	Species **1** mmol[c]	pK_1	[**1**]/[Complex-hydrolyzed]
Br	9.3	0.0229	0.0142	6.22	0.62
Br[d]	10.0	0.0304	0.0190	6.16	0.63
Br	10.6	0.0241	0.0151	6.27	0.62
Cl	10.0	0.0354	0.0232	6.22	0.65

a) The pH at which base hydrolysis was performed. b) The volume of the solution was 4 cm³. c) The deviation is ±0.005 mmol. d) In this run, the amount of Species **2** formed and the pK_2 were obtained as 0.0109 mmol and 3.98 respectively.

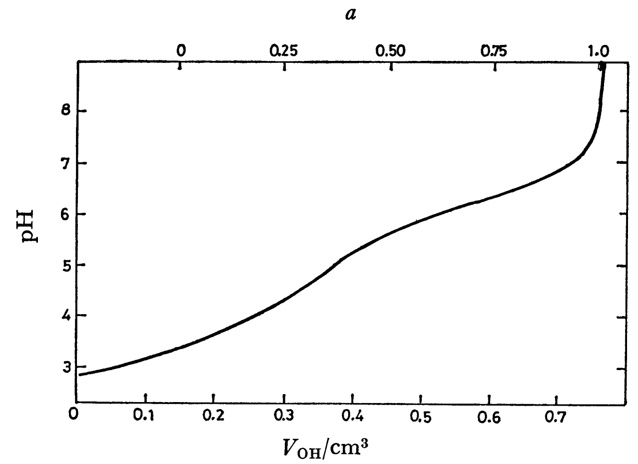
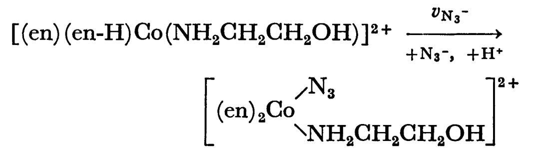


Fig. 1. Titration curve of products formed by the base hydrolysis of 0.0304 mmol *cis*-$[CoBr(etaH)(en)_2]Br_2$ at pH 10.0, followed by the addition of 0.038 mmol of HCl. $I=1.0$ (KNO_3), 25 °C. The abscissa V_{OH} is the volume of 0.05 M NaOH added during the titration and *a* is the ratio: [Moles of NaOH consumed for the dissociation of the complex]/[Moles of total complex].

The results in Table 1 show that the product ratio [Species **1**]/[Total amount of complex-hydrolyzed] is independent of the pH within the limit of experimental error. This means that both v_{H_2O} and v_0 are independent of the pH. Table 1 shows also that Species **2**, which contains an amino alcohol chelate ring, is the minor product of the base hydrolysis. The reaction paths by which Species **1** is converted into Species **2** will be described elsewhere.

Buckingham *et al.*[10–12] disclosed that the base hydrolyses of complexes of the *cis*-$[CoBr(\overset{\frown}{\underline{N}O})(en)_2]^{m+}$ type ($\overset{\frown}{NO}=NH_2CH_2COO^-$, $NH_2CH_2COOC_3H_7$, $NH_2CH_2CONH_2$, *etc.*; the underlining denotes the coordinating atom) result in the formation of two types of products, $[Co(OH)(\overset{\frown}{\underline{N}O})(en)_2]^{m+}$ and $[Co(\overset{\frown}{\underline{NO}})(en)_2]^{m+}$. The relative amounts of these two products were also reported; the formation ratio of the chelated species is 35—45% for various $\overset{\frown}{NO}$ ligands.[10–12] The similarity of the product ratios, including ours given in Table 1, indicates that the lifetime of the five-coordinate intermediate is not long enough to be able to distinguish various entering moieties, $-CH_2COO^-$, $-CONH_2$, $-CH_2OH$, *etc.*, with differing nucleophilicities.

The product ratio study was also performed in the presence of sodium azide. In this case, the procedure described in the Appendix could not be used because of the interference due to the HN_3–N_3^- equilibrium (pK_a ≈4.7). In the presence of azide, the base hydrolysis is assumed to proceed by Path 1c in addition to Paths 1a and 1b, by analogy with the base hydrolyses of various pentaaminehalogenocobalt(III) complexes.[12–15)]



$$[(en)(en\text{-}H)Co(NH_2CH_2CH_2OH)]^{2+} \xrightarrow[+N_3^-,\ +H^+]{v_{N_3^-}} \left[(en)_2Co\begin{matrix}N_3\\ NH_2CH_2CH_2OH\end{matrix}\right]^{2+} \qquad (1c)$$

3

The formation of the azido complex was confirmed spectrophotometrically by the appearence of an intense absorption at 516 nm. Since the azido complex is formed from the bromo complex without consuming the base, the amount of base consumed during the base hydrolysis should correspond to the amount of Species **1** and **2** formed:[8)]

$$\alpha \equiv \frac{\text{Moles of base consumed}}{\text{Moles of complex hydrolyzed}} = \frac{[\mathbf{1}]+[\mathbf{2}]}{[\mathbf{1}]+[\mathbf{2}]+[\mathbf{3}]}. \qquad (2)$$

According to the S_N1 CB mechanism, the product ratio should be related to the relative magnitudes of the rates of Paths 1a—1c:

$$\alpha = \frac{v_0+v_{H_2O}}{v_0+v_{H_2O}+v_{N_3^-}}. \qquad (3)$$

Equation 3 can be transformed to:

$$\frac{1-\alpha}{\alpha} = \frac{v_{N_3^-}}{v_0+v_{H_2O}}. \qquad (4)$$

The plots of the left-hand side of Eq. 4 against the azide concentration are given in Fig. 2 for $[CoBr(etaH)(en)_2]^{2+}$ and $[CoBr(NH_2C_2H_5)(en)_2]^{2+}$. They are almost straight lines, implying that $v_{N_3^-}$ is proportional to $[N_3^-]$ within the limits of experimental error. Such first-order dependence of product ratios has been reported and discussed for the base hydrolyses of several anionopentaaminecobalt(III) complexes.[13,14)] At the same azide concentration (1 M), the ratio of the amount of the azido complex in the products is 10% for $[CoBr(NH_3)_5]^{2+}$,[13,14)] 20% for $[CoBr(NH_2CH_2COO)(en)_2]^+$,[12)] 24% for $[CoBr(NH_3)(en)_2]^{2+}$,[13)] 30% for $[CoBr(etaH)(en)_2]^{2+}$, and 40% for $[CoBr(NH_2C_2H_5)$-

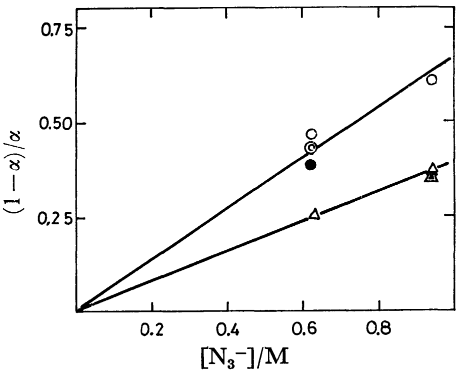


Fig. 2. The dependence of the product ratio of base hydrolysis on azide concentration, $I=1.0$ (KNO_3), 25 °C.
$[CoBr(NH_2C_2H_5)(en)_2]^{2+}$: pH 9.0 (○), pH 9.3 (◎), pH 9.6 (●) $[CoBr(etaH)(en)_2]^{2+}$: pH 9.3 (△), pH 9.6 (▲), pH 10.6 (◬).

$(en)_2]^{2+}$. The rather large variation in these competition ratios is in contrast with the similarity of the $[Co(\overset{\frown}{\underline{NO}})(en)_2]$/[Total amount of complex hydrolyzed] ratio. It may at least partly be attributed to the ion-pair effect between the cobalt(III) complex and azide ions; the $[CoBr(NH_2CH_2COO)(en)_2]^+$ ions show a smaller value than the $NH_2C_2H_5$ or the etaH complex with a +2 charge. The importance of the ion-pair effect in the product ratio has been pointed out by Buckingham *et al.*[12,16] The smaller value for the etaH complex than that for the $NH_2C_2H_5$ complex may be partly due to the presence of Path 1b in the hydrolysis of the former.

Appendix

The titration curves of mixtures of $[Co(H_2O)(etaH)(en)_2]^{3+}$ (abbreviated as AH) and $[Co(etaH)(en)_2]^{3+}$ (BH) are analyzed in the following manner in order to determine the ratio of the amounts of these species as well as their pK_a values. The abbreviations given by Eqs. 5—8 are used:

$$[A]_T = [AH] + [A^-] = [AH](1+K_1/[H^+]), \tag{5}$$

$$[B]_T = [BH] + [B^-] = [BH](1+K_2/[H^+]), \tag{6}$$

where K_1 and K_2 are the acid-dissociation constants of AH and BH respectively;

$$[Co]_T = [A]_T + [B]_T, \tag{7}$$

$$[Cl^-] = (\text{Moles of HCl added after base hydrolysis})/V, \tag{8}$$ [8]

where V is the volume of the solution under titration. When the balance of the positive and negative charges is taken into account, the following equation is obtained:

$$[AH] + [BH] + [H^+] = [Cl^-] - \frac{N_{OH}V_{OH}}{V}, \tag{9}$$

where N_{OH} is the concentration of sodium hydroxide used for the titration and V_{OH} is the volume of the hydroxide solution added during the titration. The substitution of Eqs. 5—8 into Eq. 9 gives:

$$\frac{[B]_T(K_2-K_1)}{[H^+]+K_2} = [H^+] + [Co]_T - [Cl^-] + \frac{N_{OH}V_{OH}}{V} - \frac{K_1}{[H^+]}\left([Cl^-] - \frac{N_{OH}V_{OH}}{V} - [H^+]\right), \tag{10}$$

$$\frac{[A]_T(K_2-K_1)}{[H^+]+K_1} = [Cl^-] - [H^+] - [Co]_T - \frac{N_{OH}V_{OH}}{V} + \frac{K_2}{[H^+]}\left([Cl^-] - \frac{N_{OH}V_{OH}}{V} - [H^+]\right). \tag{11}$$

When $K_2 \gg K_1$ and $[H^+] \ll K_2$, Eq. 11 can be simplified as:

$$\left([Cl^-] - \frac{N_{OH}V_{OH}}{V}\right)^{-1} = \left(1 + \frac{K_1}{[H^+]}\right)\frac{1}{[A]_T}. \tag{12}$$

Plotting the left-hand side of Eq. 12 against $[H^+]^{-1}$, one should obtain a straight line; from its slope and intercept, the values of K_1 and $[A]_T$ can be calculated. The $[B]_T$ value can be obtained by the use of Eq. 7 if $[A]_T$ is known.

The right-hand side of Eq. 10 can be calculated provided the K_1 value is known. The condition $K_2 \gg K_1$ being assumed, the following equation is obtained:

$$(\text{The right-hand side of Eq. 10})^{-1} = \left(1 + \frac{[H^+]}{K_2}\right)\frac{1}{[B]_T}. \tag{13}$$

The plot of the left-hand side of Eq. 13 against $[H^+]$ gives a straight line; from its slope and intercept, the values of K_2 and $[B]_T$ can be calculated.

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8) Strictly speaking, the amount of base required is in a slight excess (≈0.001 mmol) over the amount of complex hydrolyzed. The excess base is required to bring the pH of the solution to the pH at which the base hydrolysis is performed. This amount was evaluated by titrating the solution containing an appropriate amount of KNO_3 (and/or NaN_3), but no complex. The amount of base in Eq. 2 and those of hydrochloric acid in Eq. 8 and Fig. 1 are the values corrected for the excess base.
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