Inorganica Chimica Acta, 8 (1974) 159–165

Kinetics of Water–Ammonia Exchange in the Series of Aquaamminecobalt(III) Complexes.

III. Activation Parameters, Outer Sphere Complex Formation, and Conjugate Base Mechanism for the Formation Reaction of the Hydroxopentaamminecobalt(III) Ion

S. BALT

Chemical Laboratory, Free University, De Lairessestraat 174, Amsterdam, The Netherlands

Received April 13, 1973

An extensive study of the influence of pH and ammonia concentration on the rate of the reaction between dihydroxotetraamminecobalt(III) and ammonia has further elucidated the role of outer sphere complex formation in this reaction. Evidence has been found for the operation of a conjugate base mechanism at high pH values. Activation parameters in the tetraamminecobalt(III) series, partly derived in the present study, are discussed.

Introduction

In the present series the mechanism of the reaction:

$$Co(NH_3)_4(OH)_2^+ + NH_3 \rightarrow Co(NH_3)_5OH^{2+} + OH^- \qquad (1)$$

has already been dealt with.[1] The principal reaction path appeared to be a dissociative interchange reaction of the outer sphere complex between the aquahydroxotetraamminecobalt(III) ion and ammonia.[1] No essential difference in rate between *cis*- and *trans*-aquahydroxo complexes has been found.[2] The mechanistic studies described have now been extended to the role of higher outer sphere complexes and the search for a conjugate base mechanism. Finally activation parameters have been obtained. These parameters are compared to the ones found earlier for isomerization[3] and tetramerization[4] reactions of the tetraammine.

Experimental Section

The general experimental procedure has been described previously.[1,3] The concentration of cobalt complex in all cases was 1.0×10^{-2} *M*. The pH was adjusted by varying the ammonia and the ammonium perchlorate concentration. The ionic strength was kept constant at 0.20±0.01 *M* by adding the calculated amount of sodium perchlorate. The temperature constancy was 0.01° C.

For pH measurements a glass electrode (EIL nr 33) and a $Hg/Hg_2SO_4/Na_2SO_4$ reference electrode were used. Calibrations were done with aqueous NBS buffers. The measured pH values could be reproduced within 0.01 pH. It was checked that during the reaction no pH change outside the 0.02 limit occurred.

The reactions were monitored at 19,800 and 20,750 cm^{-1}, as outlined before.[1] The measured absorbances as a function of time were found to obey a first order rate law;[1] the pseudo first order rate constants were obtained from applying the LSG computer program[5] on an IBM 1130 computer. The first order fit was better than 0.5%. In all cases treated the absorbance spectrum of the final product was identical to that of the hydroxopentaamminecobalt(III) ion. Consequently no reverse reaction needed to be taken into account. The reactions were followed up to 90% completion. For a few reactions under extreme conditions no 90% reaction could be obtained within a pH constancy of 0.02 pH. In these cases a lesser percentage of reaction was followed, keeping the 0.02 pH limit. For the conjugate base experiments for which the pH change during the reaction was the largest observed, only the first 25% of the reaction was considered. The pseudo first order rate constants obtained did not depend on the wavenumber, but the accuracy of the 20,750 cm^{-1} values was better, so only the rate constants obtained at this wavenumber were used.

Results and Discussion

Reaction Mechanism

The following sections will be based on the reaction mechanism deduced previously.[1,4] This mechanism uses the scheme of isomerization and acid dissociation reactions in the tetraamminecobalt(III) series, extended to the amido conjugate bases of the dihydroxotetraamminecobalt(III) complexes:

$$\begin{tikzcd}
\textit{cis}\text{-T}(H_2O)_2 \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left] \arrow[d, leftarrow, shift right, "\text{⑤}"'] & \textit{trans}\text{-T}(H_2O)_2 \arrow[d, shift left, "\text{⑥}"] \arrow[d, leftarrow, shift right] & \\
\textit{cis}\text{-T}(OH)(H_2O) \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left, "\text{③}"] \arrow[d, leftarrow, shift right] & \textit{trans}\text{-T}(OH)(H_2O) \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left, "\text{④}"] \arrow[d, leftarrow, shift right] & Co(NH_3)_3(NH_2)(OH)(H_2O) \arrow[d, "\text{⑦}"] \\
\textit{cis}\text{-T}(OH)_2 \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left, "\text{①}"] \arrow[d, leftarrow, shift right] & \textit{trans}\text{-T}(OH)_2 \arrow[r] \arrow[d, shift left, "\text{②}"] \arrow[d, leftarrow, shift right] & \text{intermediate leading to tetramer} \\
\textit{cis}\text{-}Co(NH_3)_3(NH_2)(OH)_2 \ \text{⑨} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & \textit{trans}\text{-}Co(NH_3)_3(NH_2)(OH)_2 \ \text{⑩} & \text{⑧}
\end{tikzcd}$$

T = $Co(NH_3)_4$; the charges of the complex ions have been omitted. k_{pr} is defined as the rate constant for the isomerization reaction ⓟ → ⓡ. In this scheme the rapid acid–base reactions are governed by the acid dissociation constants K_{pq} describing the acid dissociation of complex ⓠ to form its conjugate base ⓟ. Gross constants $K_{pq,rs}$ are defined accordingly for acid dissociation of *cis–trans* equilibrium mixtures. The formation of the pentaammine ion can best be described as a dissociative interchange reaction of the outer sphere complexes between the complex cations and ammonia;[1] k_p^m is defined as the rate constant for the reaction route via the mth outer sphere complex of ion ⓟ, and β_p^m as the related outer sphere overall stability constant. When dealing with *cis–trans* equilibrium mixtures the products $k^m\,\beta^m$ are replaced by the gross products $k_{p,r}^m\,\beta_{p,r}^m$. When changing from individual to gross constants the expression for the rate constant keeps its original simple form, if we define:

$$k_{p,r}^m\,\beta_{p,r}^m = \frac{k_p^m\,\beta_p^m\,k_{rp} + k_r^m\,\beta_r^m\,k_{pr}}{k_{rp} + k_{pr}}$$

The observed pseudo first order rate constant is then given by (extension of equation (5) of reference 1)

$$k_{obsd} = \frac{1}{1+\beta_{1,2}^1\,(NH_3)}\{k(1,2) + k(3,4) + k(9,10)\} \qquad (2)$$

where k (p,r) is the rate contribution of the reaction route via the complexes ⓟ and ⓡ

$$k(1,2) = \sum_{l=1} k_{1,2}^l\,\beta_{1,2}^l\,(NH_3)^l$$

$$k(3,4) = \frac{[H^+]}{K_{13,24}} \sum_{m=1} k_{3,4}^m\,\beta_{3,4}^m\,(NH_3)^m$$

$$k(9,10) = \frac{K_{91,102}}{[H^+]} \sum_{n=1} k_{9,10}^n\,\beta_{9,10}^n\,(NH_3)^n$$

$[H^+]$ is the hydrogen ion activity, obtained from pH measurements, (NH_3) is the ammonia concentration. The important points that have not been completely solved as yet, will now be treated separately.

pH and Ammonia Dependence

The pH and ammonia dependence have been determined primarily under conditions where the term k(9, 10) of equation (2) could be neglected. This was accomplished by working in the region where the pseudo first order rate constant k_{obsd} is proportional to $[H^+]$, according to:[1]

$$k_{obsd} = a_0 + a_1[H^+] \qquad (3)$$

k_{obsd} has been obtained at four different temperatures. At each temperature the ammonia concentration was varied between 1 and 3 *M*. For each ammonia concentration four different pH values were chosen. Each group of four k_{obsd} values (at constant temperature and ammonia concentration) was fitted with equation (3), using a least squares method[1]; the fit achieved was better than 1%. Table I contains the resulting a_0 and a_1 values as a function of ammonia concentration and temperature. The average standard deviation of the a_0 values is 20%, of the a_1 values it is 3%.

As already suggested,[1] the a_0 values could be fitted with the relation:

$$a_0 = \frac{a_0^1\,(NH_3)}{1 + a_0^2\,(NH_3)} \qquad (4)$$

This is the relation for k(1,2) in equations (2), with l = 1: only the first complex has an appreciable contribution.

The fitting was done by means of a steepest descend least squares computer program. The a_0^1 and a_0^2 values are in Table II. The values obtained for a_0 at 20° C could only be fitted by taking a_0^2 (20° C) = 0. This value has not been entered into the activation analysis (see later on). In view of the large error in the a_0 values the agreement between the a_0 values from equation (3) and the ones calculated from equation (4) (see Table I) is reasonable.

TABLE I. Parameters describing the pH dependence of the rate of pentaammine formation at constant ammonia concentration.[a]

(NH_3) M	10^5a_0 sec^{-1} (3)[b]	(4)[b]	$10^{-6}a_1$ M^{-1} sec^{-1} (3)[b]	(5)[b]
20.0° C				
3.00	0.19	0.18	0.63	0.62
2.00	0.16	0.12	0.31	0.33
1.50	0.06	0.09	0.23	0.22
1.00	0.01	0.06	0.15	0.13
0.73	0.04	0.04	0.09	0.09
25.2° C				
3.00	0.31	0.46	1.17	1.17
2.73	0.41	0.43	1.00	1.02
2.49	0.26	0.41	0.94	0.89
2.22	0.40	0.38	0.71	0.75
1.98	0.22	0.35	0.66	0.64
1.73	0.25	0.32	0.52	0.52
1.46	0.29	0.28	0.40	0.41
1.23	0.25	0.25	0.31	0.33
0.96	0.22	0.21	0.25	0.24
0.72	0.12	0.16	0.19	0.17
30.0° C				
2.99	0.75	0.81	1.62	1.59
1.99	0.74	0.59	0.86	0.95
1.49	0.47	0.46	0.67	0.67
0.98	0.21	0.32	0.49	0.42
0.73	0.24	0.25	0.32	0.30
35.0° C				
2.99	1.73	1.78	2.43	2.43
1.98	1.46	1.37	1.53	1.51
1.48	1.18	1.12	1.08	1.09
0.98	0.66	0.81	0.72	0.69
0.73	0.67	0.63	0.47	0.51

[a] The entries at each ammonia concentration have been obtained from four independent runs at different pH. [b] Calculated values obtained from fitting the equation indicated in parentheses (further see the text).

The values of the parameters a_1 as a function of the ammonia concentration were again found to obey the previously[1] introduced empirical relation (5):

$$a_1 = a_1^1\,(NH_3) + a_1^2\,(NH_3)^2 \qquad (5)$$

Results of a least squares analysis are in Table II, while Table I contains a comparison between initial and final a_1 values. Equation (5) however, does not have the exact form predicted by equation (2). Therefore, in accordance with equation (2), the a_1 values were also fitted with equation (6), using the a_0^2 values from the analysis of equation (4) (Table II).

$$a_1 = \frac{1}{1 + a_0^2\,(NH_3)}\{a_1^3\,(NH_3) + a_1^4\,(NH_3)^2 + a_1^5\,(NH_3)^3\} \qquad (6)$$

This procedure resulted in a much poorer fit for the experimental results than equation (5) could provide; for 25° C it even yielded negative parameter values. Therefore equation (6) has been abandoned. The consequence is that only the first term of equation (5) can be given a theoretical significance: a_1^1, having its significance at low ammonia concentrations, approximately equals a_1^3 (= $k_{3,4}^1\beta_{3,4}^1/K_{13,24}$). As a result the emphasis must be on low ammonia concentrations; therefore this concentration in the present work has not been raised as high as in the previous study (8M).[1]

Medium Effects

The presence of terms containing higher powers of the ammonia concentration in the expression for the rate constant (equation (5)) may stand for rate contributions from higher outer sphere complexes. However, it has been pointed out,[1] that these terms may also result from the change in medium at high ammonia concentrations. Principally, a considerable lowering of the dielectric constant compared to water can be expected at high ammonia concentrations, as the dielectric constants of water and ammonia differ considerably: water 78.5 (25° C) and liquid ammonia 21.6 (–35° C) and still lower at room temperature.[6]

TABLE II. Parameters describing the (NH_3) dependence of the rate of pentaammine formation.

Temp. °C	$10^5a_0^1$ M^{-1} sec^{-1} (4)[a]	Act.[b]	a_0^2 M^{-1} (4)[a]	$10^5a_0^1/a_0^2$ sec^{-1} (4)[a]	Act.[b]	$10^{-5}a_1^1$ M^{-2} sec^{-1} (5)[a]	Act.[b]	$10^{-5}a_1^2$ M^{-3} sec^{-1} (5)[a]
20.0	0.06	–	–	–	–	0.92	0.91	0.38
25.2	0.27	0.24	0.25	1.07	1.19	1.78	1.87	0.72
30.0	0.37	0.46	0.13	2.93	2.38	3.73	3.52	0.52
35.0	1.01	0.91	0.23	4.35	4.82	6.50	6.67	0.56

[a] Calculated values obtained from fitting the equation indicated in parentheses (further see the text).

[b] Calculated values resulting from a least squares activation analysis of the figures in the preceding column.

The two possible causes for the relative rate enhancement at high ammonia concentrations were tentatively separated by following the influence of the dielectric constant of the medium on the rate constant at constant ammonia concentration. This was done by measuring the reaction rate at relatively low ammonia concentration (1*M*) in mixtures of water and dioxane. Addition of dioxane to water lowers the dielectric constant.[7] The results of kinetic runs, expressed in the a_0 and a_1 parameters (each set from four independent runs as before) are presented in Table III. The value of the parameter a_0 appears to be independent of the dielectric constant, while a_1 increases considerably on decreasing dielectric constant. This is a powerful indication that the extra pH dependent rate contribution at higher ammonia concentrations, as exemplified by the higher powers of (NH_3) in the equation (5), for a large part at least is a result of lowering the dielectric constant. The dielectric constant can exert two separable influences on the observed rate. In the first place, the values of the thermodynamic constants are a function of the dielectric constant. Secondly, a change in the dielectric constant can also change the liquid junction potential between the solution and the reference electrode in the pH measurements[8] and by that introduce an unpredictable factor into the measured pH. In this connection it is therefore important to note that the conclusion drawn about the influence of the dielectric constant of the solvent on the rate is unchanged when pH measurements are abandoned and the reaction is expressed as:

$$Co(NH_3)_4(OH)_2^+ + NH_4^+ \rightarrow Co(NH_3)_5OH^{2+} + H_2O \qquad (7)$$

and the acid dissociation constants accordingly. This is because in aqueous solutions the equilibrium constant $K = (NH_3)[H^+]/(NH_4^+)$ appears to be practically independent of the ammonia concentration; also the value of K varies little in the dioxane–water mixtures. This is illustrated by the following figures: from the pH measurements of this and a preceding study[1] the value of K varies from $2.7 \times 10^{-10}M$ ($(NH_3) = 1M$) to $2.5 \times 10^{-10}M$ (8*M*) at 25° C. At this temperature the values in dioxane–water range from $3.7 \times 10^{-10}M$ (25% dioxane) to $5.2 \times 10^{-10}M$ (50% dioxane). The conclusion of the foregoing must be that the possibility of describing the pH dependent part of the rate constant by equation (5) cannot be presented as evidence for the operation of outer sphere complexes $Co(NH_3)_4(OH)(H_2O)^{2+} \ldots nNH_3$ $(n > 1)$. Accepting that the main factor determining the rate enhancement at high ammonia concentration is the effect of lowering the dielectric constant on the rate parameter, there remains the question to be answered, what parameter must be held responsible for the observed behaviour of the rate constant. In this respect it must be remembered that the *cis–trans* isomerization reactions of the dihydroxotetraamminecobalt(III) complexes obey a rate equation similar to equation (3). The pH dependent part of the isomerization rate also increases at high ammonia concentrations,[2] while the pH independent part is not influenced by the ammonia concentration.[3] Now for both isomerization and pentaammine formation the rate determining steps are not expected to depend on the dielectric constant of the medium, as the postulated mechanisms are dissociative interchange (exchange between first and second coordination sphere) or intramolecular (see also the section discussion). For the dihydroxo ions (responsible for the pH independent part of isomerization and pentaammine formation) this postulate is born out by the experimental results. If this conclusion is also accepted for the aquahydroxo complexes (responsible for the pH dependent parts), a common factor must be sought in the expressions for the pH dependent part of isomerization[3] and pentaammine formation (k(3,4) of equation (2)). This factor is the acid dissociation constant of the aquahydroxo ion (K_{13} or $K_{13,24}$, see equation (2)). This constant then seems to accommodate the medium effects described.

TABLE III. Rate parameters in dioxane–water mixtures.[a]

Wt.% of dioxane	Dielectric constant of solvent[b]	$10^6 a_0$ sec^{-1}	$10^{-6} a_1$ $M^{-1} sec^{-1}$
0	78.54	2.2	0.25
25	56.33	2.5	0.40
50	34.25	1.9	1.42

[a] Temp. = 25.2° C. For each solvent composition the parameter set has been obtained from four independent kinetic runs at different pH. [b] Values adopted from reference 7.

Conjugate Base Mechanism

At high pH values the observed rate constant no longer obeys equation (3). It has been suggested[1] that this could result from a rate contribution stemming from the amido conjugate base of the $Co(NH_3)_4(OH)_2^+$ ions. This reaction route would result in a rate contribution comprises a non-negligent part of the observed al to $[H^+]$. Reaction conditions, where this contribution comprises a nonnegligent part of the observed rate, could be realized by taking high ammonia concentrations without adding ammonium perchlorate. The buffer capacity of the ammonia buffers in this region is very small. As a result the pH was found to vary during the reactions. Therefore only the first 25% of the reaction was followed, in which the pH change in all cases was smaller than 0.02 pH units. Addition of sodium hydroxide at lower ammonia concentrations at first sight seems to be a better way of studying the conjugate base mechanism, but this procedure was found to complicate the analysis of the rate constant, as the reverse reaction could no longer be neglected.

The result of the kinetic measurements, again expressed in pseudo first order rate constants, are presented in Table IV. In order to make possible a separate treatment of the conjugate base part of the observed reaction rate, the earlier discussed rate contributions via the aquahydroxo (k(3,4)) and the dihydroxo (k(1,2)) complexes have been subtracted from the observed rate constants. The contributions mentioned were calculated for the conditions mentioned by using the equations (3), (4), and (5) and the parameter values of Table II, $k_{corr.} = k(1,2) + k(3,4)$. Equation (2) predicts $\Delta k = k_{obsd} - k_{corr.} = k(9,10)$ to be inversely proportional to $[H^+]$ and a function of the ammonia concentration. Trying possible combinations, it was found that the product $\Delta k[H^+]$ was not constant, but that within the (rather large) experimental error the relation (7)

$$\Delta k = \frac{a_2^0\,(NH_3)}{[H^+]} \tag{7}$$

yielded a constant value for a_2^0 (see Table IV). This definitely points to a conjugate base mechanism.

The simplicity of equation (7) is misleading and may be brought about by the high and of necessity limited range of ammonia concentrations. For this reason, as far as the (NH_3) dependence is concerned equation (7) is not complete. A comparison with equation (2) gives as the most likely interpretation of equation (7):

$$a_2^0 = k_{9,10}^1\,\beta_{9,10}^{1a}\,K_{91,102} \text{ with}$$
$$\beta_{9,10}^{1a} = \beta_{9,10}^1/(1+\beta_{1,2}^1\,(NH_3)_{average})$$

Direct substitution of $\beta_{1,2}^1$ from analysis of equation (4), because of the inaccuracy of especially this constant, did not improve the fit.

In the preceding sections important medium effects have been found for the reaction route via the aquahydroxotetraamminecobalt(III) ions. These effects are presumably operative via the acid dissociation constants. This argument has been based on the expectation of an absence of medium dependence for the rate-determining dissociative step. If the same argument is applied to the rate-determining step of the conjugate base mechanism, the overall medium dependence of the rate of pentaammine formation from the $Co(NH_3)_4(OH)_2^+$ ions via their conjugate bases (as expressed in k(9,10) of equation (2)) will be governed by the acid dissociation constant $K_{91,102}$. In this respect it is instructive to compare this acid dissociation constant to the one defined above for the ammonium ion for which the medium dependence has been discussed above. It is clear that both acid dissociations show the same charge type. Compare:

$$Co(NH_3)_4(OH)_2^+ \rightleftarrows Co(NH_3)_3(NH_2)(OH)_2 + H^+ \ (K_{91,102})$$
$$NH_4^+ \rightleftarrows NH_3 + H^+ \ (K)$$

The acid dissociation constants $K_{91,102}$ and K have been defined above as mixed concentration–activity constants in exactly the same way.

TABLE IV. Results from experiments at high pH values (Conjugate Base Mechanism).

(NH_3) *M*	pH	10^5k_{obsd} sec^{-1}	$10^5k_{corr.}$[a] sec^{-1}	$10^5\Delta k$ sec^{-1}	$10^{19}a_2^0$ sec^{-1}	Average $10^{19}a_2^0$ sec^{-1} obsd.[b]	act.[c]
25.2° C							
6.47	12.07	1.05	1.01	0.04	0.48	0.67	0.76
6.97	12.11	1.08	1.05	0.03	0.30		
7.47	12.14	1.21	1.08	0.13	1.23		
30.0° C							
5.92	11.84	2.12	1.83	0.29	7.0	7.4	5.7
6.42	11.87	2.25	1.93	0.32	6.7		
6.91	11.91	2.38	1.98	0.40	7.2		
7.41	11.95	2.62	2.05	0.57	8.5		
35.0° C							
6.17	11.73	4.81	3.72	1.09	33	35	40
6.68	11.76	5.12	3.83	1.29	37		
7.20	11.80	5.43	3.92	1.51	36		
7.71	11.83	5.67	4.02	1.65	35		

[a] Calculated with the equations (3), (4), and (5) and the parameter values of Table II.

[b] Average value from the preceding column.

[c] Calculated value from the activation analysis on the averaged a_2^0 values at different temperatures.

For the constant K only a smal medium effect has been found. Consequently a similar near-constancy in the media employed may be expected for $K_{91,102}$. This means that the value of the parameter a_2^0 of equation (7) will not be a function of the ammonia concentration. This is in agreement with preliminary results obtained in our laboratory on the system $Co(NH_3)_4(OH)_2^+/Co(NH_3)_5OH^{2+}$ under equilibrium conditions.

Activation Parameters

In the preceding paragraphs the observed rate constant has been divided up into its constituent parts k(1,2), k(3,4) and k(9,10). For each part fitting procedures have given values for the rate parameters appearing in equation (2). This subsection will treat the temperature dependence of the rate constants, from which the activation parameters ΔS^* (pseudo entropy of activation) and ΔH^* (pseudo enthalpy of activation) have been obtained, using a computerized least squares analysis[9] on the basis of the Eyring formula in the usual way[10]. The results are presented in Table V, while Table IV compares the initial values of the parameters with the ones calculated in the activation analysis. Each of the three parts described will be commented on.

Contribution from $Co(NH_3)_4(OH)_2^+$ (k(1,2))

It is evident that $a_0^1 = k_{1,2}^1\ \beta_{1,2}^1$ and $a_0^2 = \beta_{1,2}^1$. $k_{1,2}^1$ is equal to a_0^1/a_0^2, if $\beta_1^1 = \beta_2^1$. This seems to be a reasonable assumption. In accordance with the general behaviour of outer sphere complexes[11] the stability constant $\beta_{1,2}^1$ (a_0^2) of the complex $Co(NH_3)_4(OH)_2^+ \ldots NH_3$ is nearly temperature independent. This can also be seen from the fact that the activation analysis for the quotient a_0^1/a_0^2 ($k_{1,2}^1$) gives nearly the same activation enthalpy as the one calculated for a_0^1 ($k_{1,2}^1\beta_{1,2}^1$).

TABLE V. Parameters obtained from least squares activation analysis.[a]

Symbol of rate constant	(Pseudo) Enthalpy of activation kcal mol^{-1}	(Pseudo) Entropy of activation cal degree^{-1}	Ref.
A[b]			
$k_{1,2}^1\beta_{1,2}^1$	24.3 ± 1.0	–2.7 ± 4	
$k_{1,2}^1$	25.5 ± 1.3	4.5 ± 4	
$k_{3,4}^1\beta_{3,4}^1/K_{13}$	23.2 ± 0.8	43.3 ± 3	
$k_{9,10}^1\beta_{9,10}^{1a}K_{91,102}$	71.7 ± 5	94.3 ± 5	
B[c]			
$k_{12} + k_{21}$	26 ± 2	13 ± 6	3
$(k_{34} + k_{43})/K_{13}$	10 ± 1	5 ± 3	3
$k_{43}\ K_{46}$	30 ± 2	15 ± 5	3
$(k_{34} + k_{43})^*$	32 ± 2	41 ± 7	4
k_{43}^*	33 ± 2	46 ± 4	4
k_{28}^*	57 ± 1	126 ± 2	4
$k_{78}\ K_{47}^*$	49 ± 1	60 ± 3	4

[a] I = 0.20*M*, unless the rate constant is marked with an asterisk. In that case I = 1.00*M*. [b] From the present work. [c] Calculated or copied from the references indicated, as discussed in the text.

Contribution from $Co(NH_3)_4(OH)(H_2O)^{2+}$ (k(3,4))

It has been argued above that a_1^1 may be set equal to $a_1^3 = k_{3,4}^1\ \beta_{3,4}^1/K_{13,24}$. The parameter a_1^2 in equation (5) shows an irregular temperature dependence, undoubtedly due to the complicated nature of this expression discussed above.

Contribution from the amido conjugate base $Co(NH_3)_3(NH_2)(OH)_2$(k(9, 10))

For the activation analysis the values of the parameter a_2^0 obtained at 20° C have been left out, as no reasonable fit for the equation (7) could be found at this temperature, due to the inaccuracy of the very small values of Δk. The suggested incompleteness of equation (7) especially concerning the (NH_3) dependence, will bear on the constant $\beta_{9,10}^{1a}$ and consequently mainly on the entropy value, as the enthalpy changes related to outer sphere complex formation are small.[11]

Conclusion

The complexity of the problem set by the present series of reactions has prevented a full analysis of the reaction kinetics of the pentaammine formation according to equation (2), to the extent that for part of the analysis approximate expressions had to be used. In spite of that, the present study has provided a reliable overall picture of the pentaammine formation.

With the results obtained it is now possible to relate the parameters found in the tetraammine series. To this end activation parameters from previous studies have been brought together in Table VB. The entries in Table VB need some comment. The expressions

$(k_{34} + k_{43})/K_{13}$ and $k_{43}\ K_{46}$ are simplifications of $(k_{34}/K_{13} + k_{43}/K_{24})$

and $(k_{34}\ K_{35} + k_{43}\ K_{46})$ respectively, of reference 3. This simplification has been made possible by finding that[4] K_{13} nearly equals K_{24} and that $K_{46} \gg K_{35}$, while $k_{43} > k_{34}$. A recalculation of the parameter values reported in reference 3 was necessary because the present work uses a different definition of the acidity constants. The parameter values for $(k_{34} + k_{43})$ at I = ionic strength = 1.00*M* have been obtained from an activation analysis of the experimental values of reference 4.

A number of conclusions arise from a survey of Table V:

(1) The dihydroxotetraamminecobalt(III) ion has comparable activation enthalpy values for isomerization and pentaammine formation. This conclusion is not straigthforward, as the constants in Table V are gross constants of which the relations are not immediately clear. The cited equality for the dihydroxo ion is deduced from the values for $k_{1,2}{}^1$ and the sum ($k_{12} + k_{21}$) in Table V, combined with the fact that[3] the quotient k_{21}/k_{12} is nearly temperature independent. The equality of the enthalpy values for the dissociative interchange and the isomerization reaction strongly suggest that both processes are determined by the same factor, e.g. breaking of the Co–OH bond. There may also be another factor at stake. It is well known[3, 13] that at high pH values (the dihydroxo region) no study of the isomerization is possible because of the rapid decomposition of the tetraammine complex under the loss of ammonia. This decomposition can be stopped by adding ammonia[3]. This means that the rate of loss of ammonia for the dihydroxo ion is larger than the rate of isomerization. Consequently, the isomerization in the presence of ammonia may also take the route via ammonia (besides OH^-) exchange. If either one of these conclusions is accepted, the isomerization of the dihydroxo compound has an intermolecular mechanism.

(2) The aquahydroxo ion presents a different picture. The pseudo activation enthalpy found for the combination $(k_{34} + k_{43})/K_{13}$ is much smaller than the value found for $k_{3,4}{}^1\ \beta_{3,4}{}^1/K_{13}$. As the enthalpy of the outer sphere reaction exemplified by $\beta_{3,4}{}^1$ is close to zero, this certainly means that the isomerization of the aquahydroxo complex goes via an intramolecular mechanism (for instance a "twist") not needing the activation enthalpy for breaking a Co–OH_2 bond. At present it is difficult to understand why the intramolecular mechanism for the isomerization is easier for the aquahydroxo ion that it is for the dihydroxo ion (that has an intermolecular mechanism at a lower rate – see point 1), or, put differently, why the dihydroxo ion is more "rigid" than the aquahydroxo ion.

(3) It is also necessary to consider the parameters found for the higher ionic strength of $1M$. It is not difficult to see from a straigthforward combination of the entries in Table V, that the value found for the activation enthalpy of isomerization of the aquahydroxo ion at $I = 1.00M$ is too high compared to the entries belonging to $I = 0.20M$. This shows that it is dangerous to compare activation parameters at widely different ionic strengths. In the present connection it is also instructive to compare the analogous $Co(en)_2(OH)_2{}^+$ complexes for which the equilibrium and rate constants have been reported[14] to deviate strongly at high concentrations. In the present case an additional and possibly more disturbing factor in the comparison of rate constants obtained at high and low ionic strengths, is the pH measurement and the assumptions involved as discussed above and previously[1].

(4) Finally the finding of rather high values for the activation enthalpy of the conjugate base mechanism to some extent is paralleled by the report of equally high values for the activation parameters of tetramerization, for which the reaction route exemplified by $k_{78}\ K_{47}$ (Table VB) also involves an amido conjugate base mechanism.

Acknowledgement

The author acknowledges the valuable help of Mrs. E.G.A.M. Bohte.

References

1 S. Balt, *Inorg. Chem. Acta, 7,* 453 (1973).
2 E.G.A.M. Bohte and S. Balt, *Rec. Trav. Chim., 92,* 826 (1973).
3 S. Balt, *Rec. Trav. Chem., 91,* 1026 (1972).
4 S. Balt and P.M. Kwantes, *J. Inorg. Nucl. Chem., 35,* 240 (1973).
5 D.F. Detar, Ed., Computer Programs for Chemistry vol. 1, Benjamin, New York–Amsterdam, 1968, program LSG.
6 J. Baldwin and J.B. Gill, *Phys. Chem. Liquids, 2,* 25 (1970).
7 G. Akerlöf and O.A. Short, *J. Am. Chem. Soc., 58,* 1241 (1936).
8 R.G. Bates, Determination of pH, New York, 1964.
9 D.F. Detar, Ed., Computer Programs for Chemistry, vol. III, Benjamin, New York–Amsterdam, 1969, program ACTENG.
10 A.A. Frost and R.G. Pearson, Kinetics and Mechanism, 2nd ed., Wiley, New York–London, 1961.
11 V.E. Mironov, *Russian Chem. Rev., 39,* 319 (1970). (English translation.)
12 S. Balt and W. de Kieviet, *Inorg. Chem., 9,* 2251 (1972).
13 G. Schwarzenbach, J. Boesch, and H. Egli, *J. Inorg. Nucl. Chem., 33,* 2141 (1971).
14 F. Yajima, Y. Koike, T. Sakai, and S. Fujiwara, *Inorg. Chem., 11,* 2054 (1972).