Articles

Contribution from the Institut de Chimie Physique,
Ecole Polytechnique Fédérale, CH-1015 Lausanne, Switzerland

Kinetics of Base Hydrolysis of (Nitrato)pentaamminecobalt(III): Stability and Reactivity of Its Ion Pairs with Perchlorate and Azide

François P. Rotzinger

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Base hydrolysis of the title complex has been studied in aqueous LiOH, NaOH, and KOH at 25 °C and variable ionic strength ($0.01 < I \leq 0.8$). The kinetics are independent of the nature of the alkali-metal ion and follow the rate law $-d[Co(NH_3)_5NO_3^{2+}]/dt = k[Co(NH_3)_5NO_3^{2+}]$ at $[OH^-]$ = constant with $k = k_{-NO_3}K_{OH}[OH^-]/(1 + K_{OH}[OH^-])$ and $K_{OH} = K_{OH,0}10^{-4AI^{1/2}/(1+BI^{1/2})}$. $K_{OH,0} = 5.63 \pm 0.47\ M^{-1}$ is the equilibrium constant for ion-pair formation of the reactant with OH^- at zero ionic strength, $k_{-NO_3} = 7.13 \pm 0.55\ s^{-1}$ is the first-order rate constant for nitrate substitution within the ion pair, $A = 0.509\ M^{-1/2}$ and $B = 1.56\ M^{-1/2}$ (25 °C) are physical constants, and I is the ionic strength. In the presence of $NaClO_4$ or NaN_3 ($0.3 < I \leq 1.02$) the reaction still follows first-order kinetics, which are described by $k = (k_{-NO_3}K_{OH}[OH^-] + k'_{-NO_3}K'_{OH}K_Y[OH^-][Y^-])/(1 + K_{OH}[OH^-] + K_Y[Y^-] + K'_{OH}K_Y[OH^-][Y^-])$ with Y = ClO_4 or N_3, $K_Y = K_{Y,0}10^{-4AI^{1/2}/(1+B'I^{1/2})}$ ($B' = 1.60$ and $1.82\ M^{-1/2}$ for Y = N_3 and ClO_4, respectively), and $K'_{OH} = K'_{OH,0}10^{-2AI^{1/2}/(1+B''I^{1/2})}$ ($B'' = 1.64$ and $1.72\ M^{-1/2}$ for Y = N_3 and ClO_4, respectively). $K_{Y,0}$ is the constant for ion-pair formation of the reactant with Y^- at zero ionic strength ($K_{ClO_4,0} = 5.6\ M^{-1}$ and $K_{N_3,0} = 5.5\ M^{-1}$), $K'_{OH,0}$ is the constant for aggregation of hydroxide to the ion pair with Y^- ($K'_{OH,0} = 1.4$ and $1.3\ M^{-1}$ for Y = ClO_4 and N_3, respectively), and k'_{-NO_3} (10.3 ± 2.5 and $12.8 \pm 3.6\ s^{-1}$ for ClO_4^- and N_3^-, respectively) is the first-order rate constant for nitrate substitution within the ion triplet formed by the reactant, hydroxide, and the anion present in solution (Y^-). The ion triplets with the poor nucleophile (ClO_4^-) and the good one (N_3^-) undergo nitrate substitution at equal rates, since k'_{-NO_3} is independent of the nature of Y^-. This behavior demonstrates the dissociative nature of the substitution.

Introduction

Base hydrolysis[1] of (acidato)pentaamminecobalt(III) complexes leads to hydroxopentaamminecobalt(III) as the product. In the presence of competing anions Y^- the corresponding $Co(NH_3)_5Y^{2+}$ complexes are also formed in addition to the hydroxo pentaammine complex. It is well-known[1,2] that the (acidato)pentaammine-cobalt(III) complexes with the leaving groups Cl^-, Br^-, FSO_3^-, $CF_3SO_3^-$, $CH_3SO_3^-$, SCN^-, I^-, ClO_4^-, and NO_3^- form 8.5–10.6% of azido complex in 1 M azide. At such high salt concentrations the cations certainly aggregate with the anions present in solution. The relation between the amount of azido complex formed and the amount of reaction proceeding via the ion-pair pathway is analyzed in this work.

The reactivity of ion pairs of pentaamminecobalt(III) complexes with doubly and triply charged anions has been investigated[3] at constant ionic strength. The stability constants determined in the cited study,[3] however, do not describe the stability of the ion pair of the *free* complex with the anion, since the background electrolyte also forms ion aggregates with the cation. The stability and reactivity of the ion pairs with the background electrolyte as well as with singly charged anions are still unknown.

The present study reports the kinetics of base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ at variable ionic strength, in the absence and presence of perchlorate (a typical supporting electrolyte) and azide (a widely used nucleophile and competing anion). The stability and reactivity of these ion pairs are analyzed in detail. Additional evidence for the dissociative nature of the substitution process occurring in the base hydrolysis of mononuclear pentaammine complexes is obtained from the fact that the ion pairs of the reactant with perchlorate as well as azide (and thiocyanate[4]) exhibit equal rate constants for nitrate substitution. The nature of the intermediates and the mechanism of product formation is discussed in the following article.[5]

Experimental Section

Physical Measurements. The kinetics were measured on an Applied Photophysics stopped-flow spectrophotometer or a HI-TECH SFA-11 rapid mixing device thermostated to 25 °C. The UV-vis spectra were recorded on a HP 8450 A spectrophotometer.

Materials. $[Co(NH_3)_5NO_3](ClO_4)_2$ and $[Co(NH_3)_6](ClO_4)_3$ were prepared according to the literature.[6-8]

Kinetics. Solutions of the complex (2.5 mM) in 2 mM $HClO_4$ were reacted with solutions containing MOH/NH_3 (M = Li, Na, and K), $NaOH/NaClO_4/NH_3$, or $NaOH/NaN_3/NH_3$ (0.2 M NH_3). Ammonia was added in order to prevent the formation of amorphous cobalt(III) hydroxide, which perturbs the UV-vis spectrum. The product of the studied reaction, $Co(NH_3)_5OH^{2+}$, loses ammonia quite rapidly to form $Co(NH_3)_4(OH)_2^+$, but uniphasic kinetics were observed at the isosbestic point of the latter reaction ($\lambda = 325$ nm), because the added ammonia prevented ammonia loss from $Co(NH_3)_4(OH)_2^+$ on the time scale of the reaction of interest. The rate constants were calculated as the slopes of $\ln |D - D_\infty|$ vs $-t$ plots by weighted least-squares fits ($w = 1/(D - D_\infty)^2$).

In the presence of azide, also $Co(NH_3)_5N_3^{2+}$ was formed, which lost further ammonia as well. No isosbestic point for this reaction exists, and therefore, the experimental rate constants were obtained from weighted least-squares fits to Guggenheim[9] plots.

Results

Base Hydrolysis in Pure Alkali-Metal Hydroxide Solutions. In the absence of any supporting electrolyte or competing anions base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ proceeds as follows: In a rapid preequilibrium hydroxide forms an ion pair with the reactant. The ion pair itself is in equilibrium with the conjugate bases, which, however, are not present at detectable concentrations, since amine ligands coordinated to cobalt(III) are very weak acids.[10] The

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Scheme I

$$\mathrm{Co(NH_3)_5NO_3^{2+} + OH^-} \underset{\text{fast}}{\overset{K_{OH}}{\rightleftarrows}} \underset{\text{ion-pair}}{[\mathrm{Co(NH_3)_5NO_3,\ OH}]^+} \underset{\text{slow}}{\overset{k_{-NO_3}}{\rightarrow}} \mathrm{Co(NH_3)_5OH^{2+} + NO_3^-}$$

Table I. First-Order Rate Constants for Base Hydrolysis of $\mathrm{Co(NH_3)_5NO_3^{2+}}$ at Variable Ionic Strength and 25 °C

		k, s^{-1}	
[OH$^-$], M	I	obsd[a]	calcd[b]
0.00938[c]	0.0138	0.21 ± 0.01 (5)	0.23
0.0494[c]	0.054	0.79 ± 0.02 (3)	0.79
0.0594[d]	0.064	0.87 ± 0.03 (6)	0.89
0.0794[d]	0.084	1.03 ± 0.03 (5)	1.06
0.0994[c]	0.104	1.24 ± 0.02 (3)	1.21
0.149[d]	0.154	1.37 ± 0.03 (5)	1.51
0.199[c]	0.204	1.77 ± 0.01 (2)	1.74
0.299[c]	0.304	2.10 ± 0.03 (3)	2.11
0.399[e]	0.404	2.30 ± 0.02 (4)	2.39
0.499[c]	0.504	2.66 ± 0.05 (3)	2.61
0.599[e]	0.604	2.75 ± 0.03 (2)	2.81
0.799[c]	0.804	3.24 ± 0.04 (3)	3.12

[a] Errors are standard deviations. Numbers of determinations are given in parentheses. [b] Calculated according to rate law 2 with k_{-NO_3} = 7.13 ± 0.55 s^{-1} and $K_{OH,0}$ = 5.63 ± 0.47 M^{-1}. [c] Counterion Na$^+$. [d] Counterion K$^+$. [e] Counterion Li$^+$.

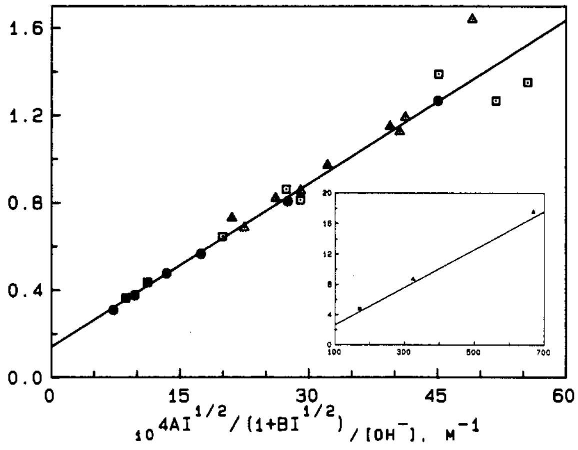

Figure 1. Plot of k^{-1} vs $10^{4AI^{1/2}/(1+BI^{1/2})}/[\mathrm{OH^-}]$ (rate constants determined in this work). Filled symbols: squares, LiOH; circles, NaOH; triangles, KOH. Open symbols: triangles, NaOH/NaClO$_4$; squares, NaOH/NaN$_3$. The solid line is a weighted least-squares fit according to rate law 2.

most reactive conjugate base subsequently undergoes nitrate substitution. Only the stability constant for ion-pair formation, K_{OH}, is ionic strength dependent.

The ionic strength dependence of K_{OH} was derived by using the Debye–Hückel expression $-\log f_i = z_i^2 AI^{1/2}/(1 + BI^{1/2})$ for the activity coefficients f_i, where $A = (2\pi N_A/1000)^{1/2}(e^2/\epsilon k_B T)^{3/2}$ = 0.509 M$^{-1/2}$ at 25 °C, $B = \beta r$ with $\beta = (8\pi N_A e^2/1000\epsilon k_B T)^{1/2}$ = 0.329 M$^{-1/2}$ Å^{-1} at 25 °C are physical constants, r = 4.74 Å[5] is the distance of closest approach, and I is the ionic strength (N_A, Avogadro's number; e, elementary charge; ϵ, dielectric constant of water; k_B, Boltzmann's constant). Thus, the ionic strength dependence of K_{OH} is given by eq 1, where $K_{OH,0}$ represents K_{OH}

$$K_{OH} = K_{OH,0}10^{-4AI^{1/2}/(1+BI^{1/2})} \qquad (1)$$

at I = 0. In the absence of supporting electrolyte, at variable ionic strength but constant [OH$^-$], first-order kinetics with respect to the reactant were observed. The first-order rate constant k given in rate law 2 was deduced from Scheme I by assuming that the ion-pair formation is much faster than nitrate substitution. Of course, the ion pair with hydroxide is in equilibrium with the conjugate bases, which are the reactive species.[1] Since the constants for these unfavorable equilibria[10] are not precisely known, the conjugate bases were omitted in Scheme I, which contains exclusively experimentally available parameters. The conversion of the ion pair to the product is described by the overall first-order rate constant k_{-NO_3}. The experimental rate constants are presented in Table I and Figure 1 (filled symbols). As predicted by rate law 2, plots of k^{-1} vs $10^{4AI^{1/2}/(1+BI^{1/2})}/[\mathrm{OH^-}]$ are linear (Figure 1, filled symbols). The nature of the alkali-metal ions (Li$^+$, Na$^+$, and K$^+$) does not affect the kinetics in this case, but dramatic effects due to the cations have been observed in the base hydrolysis of bis(ethylenediamine)cobalt(III) complexes containing chelated thioether or selenoether ligands.[11] A weighted least-squares fit to rate law 2 provided the parameters k_{-NO_3} = 7.1 ± 0.6 s^{-1} and $K_{OH,0}$ = 5.6 ± 0.5 M^{-1} at 25 °C. (The function $\sum_i w_i(k_{obsd}{}^{-1} - k_{calcd}{}^{-1})^2$ with $w_i = k_{obsd}{}^4/s_k{}^2$ was minimized.)

$$k = \frac{k_{-NO_3}K_{OH,0}[\mathrm{OH^-}]10^{-4AI^{1/2}/(1+BI^{1/2})}}{1 + K_{OH,0}[\mathrm{OH^-}]10^{-4AI^{1/2}/(1+BI^{1/2})}} \qquad (2)$$

A = 0.509 and B = 1.56 M$^{-1/2}$ at 25 °C

Table II. First-Order Rate Constants for Base Hydrolysis of $\mathrm{Co(NH_3)_5NO_3^{2+}}$ in the Presence of NaClO$_4$ and NaN$_3$ at Variable Ionic Strength and 25 °C

			k, s^{-1}		
[OH$^-$], M	[Y$^-$], M	I	obsd[a]	calcd[b]	k'_{-NO_3}, s^{-1} [c]
0.00938	1.00[d]	1.01	0.057 ± 0.002 (4)	0.059	9.8
0.0194	1.00[d]	1.02	0.115 ± 0.004 (4)	0.120	9.5
0.099	0.40[d]	0.504	0.61 ± 0.01 (4)	0.70	5.8
0.149	0.80[d]	0.954	0.84 ± 0.02 (6)	0.85	9.9
0.099	0.20[d]	0.304	0.89 ± 0.03 (6)	0.83	14.2
0.199	0.60[d]	0.804	1.17 ± 0.01 (5)	1.15	10.8
0.199	0.40[d]	0.604	1.22 ± 0.02 (6)	1.24	9.8
0.199	0.20[d]	0.404	1.46 ± 0.03 (5)	1.39	12.9
					10.3 ± 2.5 (av)
0.099	0.30[e]	0.404	0.72 ± 0.03 (6)	0.78	8.8
0.099	0.48[e]	0.584	0.79 ± 0.03 (4)	0.70	17.6
0.099	0.60[e]	0.704	0.74 ± 0.03 (4)	0.67	16.4
0.199	0.48[e]	0.684	1.16 ± 0.04 (3)	1.25	10.0
0.199	0.60[e]	0.804	1.23 ± 0.01 (3)	1.20	13.6
0.303	0.60[e]	0.908	1.55 ± 0.03 (4)	1.66	10.6
					12.8 ± 3.6 (av)

[a] Errors are standard deviations. Numbers of determinations are given in parentheses. [b] Calculated according to rate law 3 by using the parameters from Table III. The B, B', and B'' values were calculated as described in the text. [c] Calculated as described in the text. [d] Y$^-$ = ClO$_4^-$. [e] Y$^-$ = N$_3^-$.

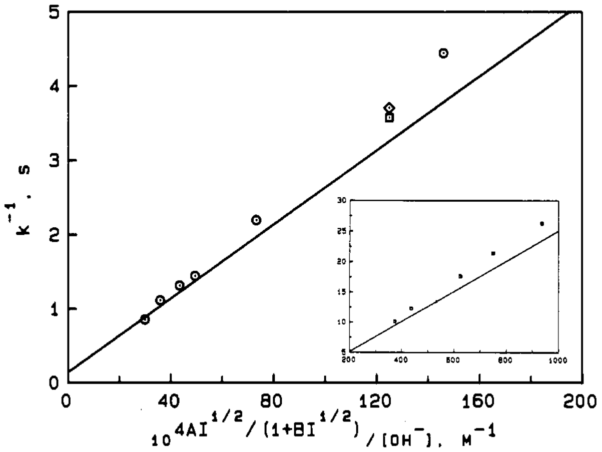

Figure 2. Plot of k^{-1} vs $10^{4AI^{1/2}/(1+BI^{1/2})}/[\mathrm{OH^-}]$ (rate constants from the literature[4,12]): circles, I = 0.119 (LiClO$_4$); squares, I = 1.0 (NaClO$_4$); diamond, I = 1.0 (NaNCS).

Base Hydrolysis in the Presence of NaClO$_4$ or NaN$_3$. Most of the base hydrolysis kinetics reported[1] in the literature were studied at 25 °C and constant ionic strength maintained with NaClO$_4$. The role of perchlorate in such reactions, however, is unknown.

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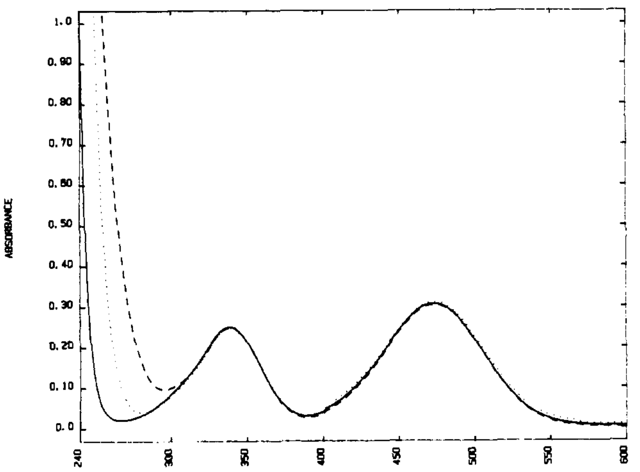


Figure 3. Absorption spectrum of $Co(NH_3)_6^{3+}$ (5 mM, 1 cm path length) in H_2O (solid line), 0.5 M NaCl (dotted line), and 0.5 M NaOH (dashed line).

A typical and widely used competing anion is azide. Thus, the chosen salts represent typical conditions for kinetic or competition experiments.

The experimental rate constants obtained in the presence of ClO_4^- or N_3^- at variable ionic strength and 25 °C are given in Table II and Figure 1 (open symbols). For comparison, the literature values[4,12] are presented in Figure 2; the solid line is the same as in Figure 1 (it was calculated according to rate law 2 on the basis of the data given in Table I). Surprisingly, no effect due to the added anions appears in the kinetics, which still follow rate law 2, although in the presence of azide and thiocyanate[4] $Co(NH_3)_5N_3^{2+}$, $Co(NH_3)_5NCS^{2+}$, and $Co(NH_3)_5SCN^{2+}$ are formed along with $Co(NH_3)_5OH^{2+}$ as the primary products.

UV–Vis Spectrum of $Co(NH_3)_6^{3+}$. In order to study the effect of hydroxide on coordinated ammonia ligands, the UV–vis spectrum of the similar, but substitution-inert, $Co(NH_3)_6^{3+}$ complex was measured. Figure 3 shows that addition of 0.5 M NaCl (dotted line) and 0.5 M NaOH (dashed line) has no effect on the ligand field bands but that the charge-transfer band is sensitive to the composition of the solution. Deprotonation of an ammonia ligand would red-shift at least one ligand field band. Clearly, in 0.5 M NaOH no detectable deprotonation of coordinated ammonia occurs.

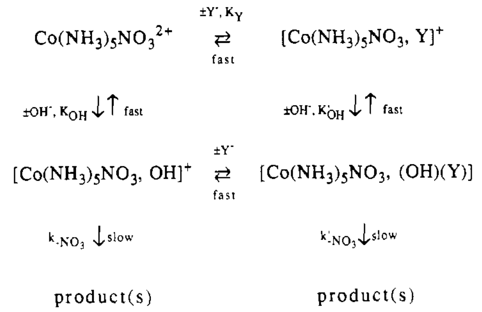
Discussion

Kinetics in Pure Alkali-Metal Hydroxide Solutions. Base hydrolysis of $Co(NH_3)_5NO_3^{2+}$, measured in the absence of supporting electrolyte or competing anions at variable ionic strength, follows rate law 2. Two parameters, namely k_{-NO_3} and $K_{OH,0}$, were observed. $K_{OH,0}$ is the constant for ion-pair formation of the reactant with hydroxide, and k_{-NO_3} is the first-order rate constant for nitrate substitution within the ion pair (Scheme I). From work at constant ionic strength only one parameter, usually denoted as k_{OH}, was available from the kinetics.

The constant $K_{OH,0}$ is not the constant for deprotonation of $Co(NH_3)_5NO_3^{2+}$ by hydroxide: from the experimental $K_{OH,0}$ value a pK_a of 13.24 could be calculated for the deprotonation of the most acidic N–H proton of $Co(NH_3)_5NO_3^{2+}$ (25 °C and $I \rightarrow 0$). This value is far too low for pentaammine complex in comparison to the known[10] pK_a values of $Co(en)_3^{3+}$ (14.9) and $Co(NH_3)_5NO_2^{2+}$ (16.8), which have been determined[10] spectrophotometrically in $DMSO/H_2O$ mixtures.

In order to obtain further evidence for the assignment of $K_{OH,0}$, the UV–vis spectrum of the similar, but substitution inert $Co(NH_3)_6^{3+}$ complex has been measured. (The pK_a of $Co(NH_3)_6^{3+}$ is expected to be similar or possibly even lower than those of $Co(NH_3)_5NO_3^{2+}$.) Addition of 0.5 M NaOH or 0.5 M NaCl affected the charge-transfer band in a similar fashion, but no shift of the ligand field bands was observed (Figure 3) and therefore, no detectable amounts of $Co(NH_3)_5NH_2^{2+}$ were formed. The N–H protons are much less acidic than water, and a $pK_a = 13.24$ does not exist. Furthermore, calculation of the stability constant for ion-pair formation of $Co(NH_3)_5NO_3^{2+}$ with OH^- according to the equation of Fuoss[13] ($r = 4.74$ Å[5]) leads to $K_{OH,0} = 5.46$ M^{-1}, a value that is in excellent agreement with the experimental value of 5.6 ± 0.5 M^{-1} and the stability constant of the ion pair $[Co(NH_3)_5NO_2,Cl]^+$ reported[14] as 4.8–9.1 M^{-1}.

Scheme II



Kinetics in the Presence of $NaClO_4$ and NaN_3. Surprisingly, the presence of $NaClO_4$ or NaN_3 as well as NaNCS[4] does not alter the kinetics. Rate law 2 still appears to fit the data (Figure 1, open symbols, and Figure 2). Moreover, it is striking that the poor nucleophile ClO_4^-, widely used as an "innocent" anion to maintain the ionic strength, as well as the excellent nucleophiles and competing anions N_3^- and NCS^{-4} produce the same kinetics. The rate constant from the literature[4] determined in 1 M NCS^- (the best competing anion) is perfectly in line with the points measured in pure alkali-metal hydroxide solutions (Figure 2, diamond). All these observations may lead to the wrong conclusion that the anions do not interfere in the kinetics at all.

On the basis of the Fuoss equation[13] the constants for the formation of tight ion pairs of $Co(NH_3)_5NO_3^{2+}$ with ClO_4^- or N_3^-, $K_{ClO_4,0}$ and $K_{N_3,0}$, were calculated as 5.6 and 5.5 M^{-1}, respectively ($r = 5.53$ and 4.86 Å were used[5]). From the magnitude of these constants it is clear that ion pairs with ClO_4^- and N_3^- were formed under the conditions of the experiments (Table II). If the ion pairs were unreactive, retardation of the reaction upon addition of $NaClO_4$ or NaN_3 would have been observed (in addition to the effect caused by the increase of the ionic strength). Since this was not the case, it is concluded that the ion pairs must be reactive in order to compensate for the expected retardation and, furthermore, the ion pair with the poor nucleophile ClO_4^- and the ones with the excellent competing anions N_3^- and NCS^{-4} exhibit the same reactivity (Figure 1, open symbols, and Figure 2). The fact that the overall rate of base hydrolysis does not depend on the nature of the associated anion supplies strong evidence for the dissociative character of the substitution process. (The good nucleophiles N_3^- and NCS^- would accelerate the reaction, if the substitution was associative.) In the base hydrolysis of pentaamminecobalt(III) complexes (measured at constant ionic strength) ion pairs with doubly and triply charged anions have been reported to be reactive as well.[3] It is interesting that in the spontaneous and acid-catalyzed cleavage of the monool $(NH_3)_5CoOHCo(NH_3)_5^{5+}$ the reactive ion pairs with Cl^- and $CH_3SO_3^-$ also escaped detection in the kinetics but that the product analysis revealed their existence.[15-17]

Ion triplets are also expected to be present at high ionic strengths. Since the ion pairs are not spherical, stability constants for the aggregation of an anion to an ion pair probably are not predicted accurately by the Fuoss equation.[13] In pure alkali-metal

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Table III. Kinetic and Thermodynamic Parameters for Base Hydrolysis of $Co(NH_3)_5NO_3^{2+}$ at 25 °C

param	value at $I \rightarrow 0$	value at $I = 1$
k_{-NO_3}	7.13 ± 0.55 s^{-1}	7.13 ± 0.55 s^{-1}
k'_{-NO_3}	10.3 ± 2.5,[a] 12.8 ± 3.6[b] s^{-1}	10.3 ± 2.5,[a] 12.8 ± 3.6[b] s^{-1}
K_{OH}	5.63 ± 0.47, 5.46[c] M^{-1}	0.902 M^{-1}
K'_{OH}[c]	1.42,[a] 1.31[b] M^{-1}	0.60,[a] 0.54[b] M^{-1}
K_{ClO_4}[c]	5.63 M^{-1}	1.07 M^{-1}
K_{N_3}[c]	5.46 M^{-1}	0.90 M^{-1}

[a] In the presence of ClO_4^-. [b] In the presence of N_3^-. [c] Calculated by using the Fuoss equation.[13]

hydroxide solutions the ion triplets $[Co(NH_3)_5NO_3,(OH)_2]$ certainly exist, but they escaped detection in the kinetics. In solutions containing ClO_4^- or N_3^- they are assumed to escape in the same way; however, they are implicitly included in the previously determined k_{-NO_3} and $K_{OH,0}$ values. The ion triplets $[Co(NH_3)_5NO_3,Y_2]$ were also neglected.

Since reactive ion pairs must exist, base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ in the presence of azide or perchlorate is expected to involve at least the ion aggregates shown in Scheme II (the conjugate bases again are omitted for the sake of clarity). The ion triplet $[Co(NH_3)_5NO_3,(OH)(Y)]$ must be included, because it is the source for the conjugate base containing an associated anion Y^-. Rate law 3 was deduced by treating all the ion-aggregation equilibria as fast compared to nitrate substitution. The

$$k = \frac{k_{-NO_3}K_{OH}[OH^-] + k'_{-NO_3}K'_{OH}K_Y[OH^-][Y^-]}{1 + K_{OH}[OH^-] + K_Y[Y^-] + K'_{OH}K_Y[OH^-][Y^-]} \qquad (3)$$

$$Y = ClO_4 \text{ or } N_3$$

ion-pair formation constants K_{OH}, K_Y, and K'_{OH} depend on the ionic strength according to eq 1, 4, and 5. The corresponding

$$K_Y = K_{Y,0}10^{-4AI^{1/2}/(1+B'I^{1/2})} \qquad (4)$$

$$K'_{OH} = K'_{OH,0}10^{-2AI^{1/2}/(1+B''I^{1/2})} \qquad (5)$$

B' and B'' values were calculated by using $r = 5.53$ and 4.86 Å as distances of closest approach[5] of the reactant with ClO_4^- and N_3^-, and $r = 5.24$ and 4.98 Å were estimated as center to center contact distances of hydroxide to the ion pairs $[Co(NH_3)_5NO_3,ClO_4]^+$ and $[Co(NH_3)_5NO_3,N_3]^+$, respectively.

The studies in pure alkali-metal hydroxide solutions (Table I) showed that the experimental constant for ion pairing of $Co(NH_3)_5NO_3^{2+}$ with hydroxide ($K_{OH,0}$) is in excellent agreement with the value calculated by using the Fuoss equation.[13] Hence, it is justified to calculate $K_{Y,0}$ and to estimate $K'_{OH,0}$ in this manner. A summary of calculated and measured parameters is presented in Table III. Rate law 3 now contains only k'_{-NO_3} as an unknown parameter, which is available by solving eq 3 for k'_{-NO_3}. Table II shows that for a given anion the calculated k'_{-NO_3} values are constant as expected. In both perchlorate and azide media equal k'_{-NO_3} values were obtained (Table II), although perchlorate is a poor nucleophile whereas azide is an excellent one. Since the good nucleophile does not accelerate nitrate substitution, this reaction must exhibit dissociative character.

The rate constants k'_{-NO_3} were determined on the basis of calculated values for $K_{Y,0}$ and $K'_{OH,0}$, which may exhibit systematic errors. Inspection of eq 3 shows that k'_{-NO_3} is much more susceptible to the errors of $K_{Y,0}$ and especially $K'_{OH,0}$ than is the product $k'_{-NO_3}K'_{OH,0}K_{Y,0}$. Comparison of the accurately known k_{-NO_3} value with k'_{-NO_3} is inappropriate. The overall rate constant (k) for base hydrolysis of $Co(NH_3)_5NO_3^{2+}$, however, is independent of the nature of the anions present in solution.

Relation between the Amount of Ion Pairs Converted into Products and the Amount of Azido Pentaammine Complex Formed. It is well-known[7,18] that in the presence of 1 M NaN_3 10.4–10.6% of $Co(NH_3)_5N_3^{2+}$ are produced along with $Co(NH_3)_5OH^{2+}$. The present kinetic and thermodynamic data (Table III) allow us to check the hypothesis whether for every ion pair of the reactant with azide converted a $Co(NH_3)_5N_3^{2+}$ ion has been formed. In this case, the fraction (F) of $Co(NH_3)_5N_3^{2+}$ formed in azide would be expressed by eq 6. According to this equation, 49.2% of

$$F = \frac{k'_{-NO_3}K'_{OH,0}K_{N_3,0}[N_3^-]}{k_{-NO_3}K_{OH} + k'_{-NO_3}K'_{OH,0}K_{N_3,0}[N_3^-]} \qquad (6)$$

$Co(NH_3)_5N_3^{2+}$ is predicted to be formed in 1 M azide at $I = 1.0$, which by no means compares to the experiment.[7,18] Equation 6 does not predict the amount of $Co(NH_3)_5N_3^{2+}$ formed, because the hexacoordinated intermediate,[5] $[Co(NH_3)_4(NH_2)\cdots ONO_2]^+$, formed in the rate-determining steps, equilibrates rapidly with azide to form an ion pair during its lifetime. The amount of $Co(NH_3)_5N_3^{2+}$ formed does not depend on the parameters determined in the kinetics but on the stability of the ion-paired intermediate and on the individual rate constants for the substitution of nitrate by water and azide (see following article[5]).

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Registry No. $Co(NH_3)_5NO_3^{2+}$, 15077-47-1; ClO_4^-, 14797-73-0; N_3^-, 14343-69-2.

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