Inorganica Chimica Acta, *166* (1989) 263–271

Kinetics and Mechanism of the Decomposition and Anation of the *Trans*-Diaquatetrakis(pyridine)cobalt(III) Ion in Acidic Chloride Ion Solutions

DANA A. GOODEN, H. ALAN EWART and KENNETH E. HYDE*

Department of Chemistry, State University of New York, College at Oswego, Oswego, NY 13126 (U.S.A.)

(Received March 13, 1989; revised June 27, 1989)

Abstract

Kinetic and spectral studies were performed on solutions of *trans*-$Copy_4(H_2O)_2^{3+}$ ion in aqueous acidic chloride solutions at 30 and 40 °C. The simplest interpretation of the data at the experimental conditions is in terms of two consecutive first-order reactions. The fast reaction is dependent on chloride ion and exhibits a non-linear inverse dependence on hydrogen ion. Our analysis of the absorbance–time data suggests that the title complex undergoes an acid dissociation equilibrium and that the deprotonated form loses a bound pyridine. This is associated with substitution by water and chloride as parallel steps. A slower reaction follows and is found to be inversely dependent on hydrogen ion, but the chloride ion dependence is not simple. We associate this step with the decomposition and reduction of $Co(py)_3(H_2O)_3^{3+}$ and $Co(py)_3(H_2O)_2Cl^{2+}$ as well as their corresponding conjugate bases to ultimately form $Co^{2+}(aq)$. Mechanisms for the fast and slow steps are presented and mechanistic constants associated from these are estimated.

Introduction

The $Copy_n(H_2O)_{6-n}^{3+}$ family of complexes is analogous to the widely studied $Co(NH_3)_n(H_2O)_{6-n}^{3+}$ family. For the ammine family, all members with n = 1 to 6 have been reported and the rate of ammonia exchange [1, 2] is much slower than that of water exchange; hence, anation reactions [2–5] involve the replacement of coordinated water by appropriate anions.

Replacement of the ammonia ligand by pyridine appears to alter the properties of the cobalt(III) center. Only complexes with n = 4, 3 and 2 have been reported [6, 7] and for each, one geometrical isomer dominates [7]. Although the bidentate carbonato complex $Co(py)_4CO_3^+$ does exist as the *cis*-isomer, all other reported tetrakis(pyridine)cobalt(III) complexes occur as the *trans*-isomers [8]. For n = 3 the *mer*-isomer is formed [7] while the *cis*-isomer is important for the n = 2 complexes [6]. Loss of ligand pyridine has been reported [6] for the n = 4 and 3 aqua complexes at relatively mild conditions compared with those necessary for the loss of ligand ammonia [9, 10]. The spontaneous reduction occurs at n = 3 for the ammine complexes [10] but at n = 2 and milder conditions for the pyridine complexes [6].

Our intention in the present work is to investigate the reactions of *trans*-$Co(py)_4(H_2O)_2^{3+}$ in chloride solutions of moderate acidity ($[H^+]$ = 0.01 to 1.0 M) and ionic strength (I = 1.0 M). Mallen [11] attempted such a study in highly acidic chloride solutions, ($[H^+]$ = 5.0 M) using an aliquot sampling method and found that at chloride concentrations greater than 0.3 M *trans*-$[Co(py)_4Cl_2]Cl$ precipitated while at other conditions reduction to $Co^{2+}(aq)$ occurred.

It has been reported [12–15] that $Co(py)_4Cl_2^+$ undergoes substitution at approximately the same rate under both acidic and basic conditions. It is unclear as to whether hydrolysis or spontaneous reduction is the kinetic process observed. The identity of the product was not determined in any of the above references, and the rates reported are similar to those found [11] for the decomposition of $Co(py)_4Cl_2^+$ to $Co^{2+}(aq)$. If aquation is indeed the rate determining step [12–15] for the decomposition then the rate of spontaneous reduction of the intermediate $Co(py)_4(H_2O)Cl^{2+}$ formed by either aquation of $Co(py)_4Cl_2^+$ or anation of $Co(py)_4(H_2O)_2^{3+}$ must be faster than that observed for the decomposition of *trans*-$Co(py)_4Cl_2^+$. We explore the chloride anation of the diaqua complex in the present study and find that the $Co(py)_4(H_2O)Cl^{2+}$ intermediate is not produced.

Experimental

Syntheses of Complexes

Diaquachlorotris(pyridine)cobalt(III) perchlorate, $[Co(py)_3(H_2O)_2Cl](ClO_4)_2 \cdot 2H_2O$

The complex was prepared [6] from $[Co(py)_3CO_3Cl]$ and recrystallized in perchloric acid. Purity

---

*Author to whom correspondence should be addressed.

0020-1693/89/$3.50

was verified by comparison of the observed spectral parameters (λ (nm), ε): max. (602, 30.9); (539, 32.8); and min. (579, 31.2); (470, 16.6) with those previously reported [16] in cold perchloric acid solution (2 M): max. (602, 32.3); (535, 33.5); and min. (579, 32.1); (472, 18.0). The complex was stored in a desiccator.

trans-Diaquatetrakis(pyridine)cobalt(III) perchlorate, trans-[Co(py)$_4$(H$_2$O)$_2$](ClO$_4$)$_3$·4H$_2$O

The complex was prepared from [Co(py)$_4$CO$_3$]-ClO$_4$ and recrystallized in perchloric acid as reported [8]. Purity was checked by comparison of the observed spectral parameters: max. (555, 42.9); (490, 50.7); and min. (540, 42.1); (435, 25.7) with those reported in nitric acid [8] max. (560, 43.9); (490, 51.0); and min. (540, 43.3); (435, 25.8). The crystals remained stable for several months when stored under nitrogen in a desiccator at 2 °C.

trans-Dichlorotetrakis(pyridine)cobalt(III) chloride trans-[Co(py)$_4$Cl$_2$]Cl·6H$_2$O

The complex was prepared from CoCl$_2$ by the method of Elgy and Wells [14], and recrystallized in 50% vol./vol. aqueous ethanol [17]. Since this compound is hygroscopic, it was not possible to obtain the reported spectral parameters. As a check for purity the ratios (A_{634}:A) of the observed absorbance at 634 nm to the observed absorbance at the other maximum and minima were calculated. These ratios (λ (nm), ratio): max. (507, 1.44); and min. (562, 2.57); (473, 1.79) were compared to those calculated from the reported spectral parameters [17]: max. (505, 1.45); and min. (559, 2.61); (470, 1.79).

Instrumentation

Absorption measurements were taken on a CARY 14 or a Bausch and Lomb Spectronic 2000. The Spectronic 2000 permitted absorbance–time data to be displayed on a X-Y recorder or to be transferred to a PDP 11/10 minicomputer using the Kinetic Interface System software and hardware by Yogis [18].

Kinetic Measurements

Kinetic measurements were in the form of absorbance–time data taken at a single wavelength (295 nm) or repetitive scans of absorbance versus wavelength (660–360 or 350–295 nm). Experiments were performed in which the concentrations of the complex, chloride, and hydrogen ion were varied at temperatures of 30 and 40 °C. In most kinetic runs the absorbance at 295 nm was collected over time. The absorbance–time data was plotted on semilog graph paper with ($D_t - D_\infty$) being the logarithmic variable.

Results

Preliminary Observations

Our preliminary kinetic experiments were with the Co(py)$_4$(H$_2$O)$_2$$^{3+}$ complex in 1 M HCl at 40 °C. The absorbance–time data for these experiments showed an increase in absorbance followed by a decrease (see Fig. 1). The simplest interpretation of this data suggests consecutive reactions with a single intermediate whose molar absorbtivity is greater than that of the reactant.

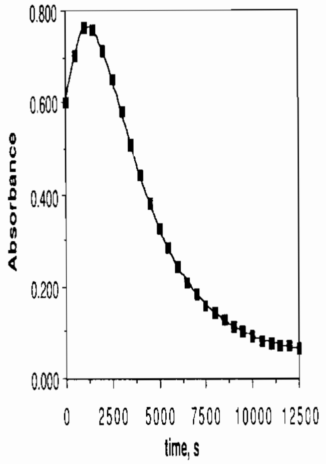

Fig. 1. Plot of absorbance vs. time data for the decomposition of *trans*-Co(py)$_4$(H$_2$O)$_2$$^{3+}$ in 1 M HCl at 40 °C.

Previous work [11] described the formation of a precipitate of *trans*-[Co(py)$_4$Cl$_2$]Cl at conditions of higher ionic strength (I = 5.0 M) and concentrations of complex, chloride ion and hydrogen ion, than those used in the present study; hence, our first interpretations of the rise and fall of absorbance were associated with the formation of the dichloro complex and its subsequent decomposition. To verify the contention of a dichloro intermediate, absorbance–time behaviors of solutions of *trans*-Co(py)$_4$Cl$_2$$^+$ were studied at conditions identical to those described above. The data showed only a loss of absorbance and its dependance on time could be described by a simple first-order process, but the observed rate constants were approximately one order of magnitude smaller than those found for the slow step observed during the decomposition of *trans*-Co(py)$_4$-(H$_2$O)$_2$$^{3+}$ in acidic chloride solutions (see Table 1). We are forced to conclude that under our conditions the dichloro complex did not form in kinetically significant amounts. A similar argument may be used to eliminate as our intermediate the partially anated complex Co(py)$_4$(H$_2$O)Cl^{2+} since a report has appeared on its decomposition kinetics [19]. It should be noted that Table 1 does indicate that the decomposition of Co(py)$_4$(H$_2$O)Cl^{2+} occurs faster than the

TABLE 1. Observed rate constants for the reduction of some tetra(pyridine)cobalt(III) complexes at various chloride concentrations in 1 M acid at 40 ℃

$[Cl^-]$	$10^4 \times k_{obs}$ (s^{-1})		
	$Copy_4Cl_2^+$	$Copy_4(H_2O)_2^+$	$Copy_4Cl(H_2O)^+$
1.00	0.497	3.79	
0.50	0.400	2.20	
0.10	0.331[a]	1.05	0.48[b]

[a]The value reported [14] in pure water or $[Cl^-] = 0.005$ M is 4.1×10^{-5}. [b]Estimated from Fig. 5 of ref. 19.

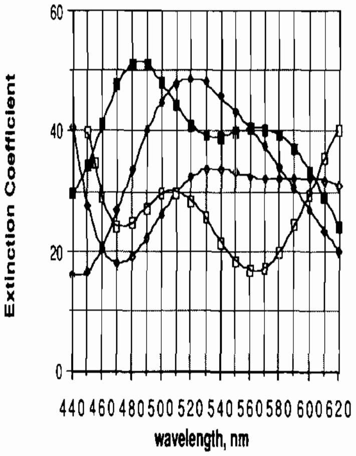

Fig. 2. Plot of extinction coefficient vs. wavelength for several aquapyridine cobalt(III) complexes: ■ = *trans*-$Co(py)_4(H_2O)_2^{3+}$ (ref. 16), □ = *trans*-$Co(py)_4Cl_2^+$ (this work), ◆ = *mer*-$Co(py)_3(H_2O)_3^{3+}$ (ref. 16), ◇ = *mer*-$Co(py)_3Cl(H_2O)_2^{2+}$ (ref. 16).

decomposition of $Co(py)_4Cl_2^+$ and hydrolysis rather than spontaneous reduction may be the rate determining step for the decomposition of the latter complex. The remainder of this report focuses on the identification of our intermediate and on an investigation of its decomposition kinetics.

Repetitive Scan Experiments

A number of wavelength–scan experiments were initiated in the visible region to aid in the identification of the intermediates that form during the kinetic run conditions. In one such experiment $Co(py)_4(H_2O)_2^{3+}$ was dissolved in 1 M perchloric acid at 40 ℃. The first scan gave spectral parameters (λ (nm), ϵ): (490, 50.2) and (555, 41.9) that were similar to those reported [8, 16] for the diaqua complex: (490, 51.0) and (560, 43.9). The second (10 min later) crossed over the first at points [(510, 46.5) and (570, 40.1)] that are close to the isosbestics estimated from Fig. 2 [7, 16] for $Co(py)_4(H_2O)_2^{3+}$ and $Co(py)_3(H_2O)_3^{3+}$: (505, 46.5) and (560, 41.0). After 1 h, the spectrum appeared to be that of *cis*-$Copy_2(H_2O)_4^{3+}$ with the observed spectral parameters: (547, 42.8) and (448, 13.6) close to those reported [16]: (547, 45) and (448, 10). At longer time periods, the reduction of cobalt(III) to Co^{2+}(aq) dominates since the peak positions no longer shift but a consistent decrease in absorbance is observed, which ultimately produced the spectrum expected for Co^{2+}: (510, 4.8) [20]. These results are consistent with earlier work [6, 21] that noted the stepwise loss of pyridine from the *trans*-$Co(py)_4(H_2O)_2^{3+}$ complex in perchloric acid solutions.

In another repetitive scan experiment, $Co(py)_4(H_2O)_2^{3+}$ was dissolved in 1 M HCl (30 ℃). Isosbestic points were observed for approximately 1 h with the following spectral parameters: (451, 33.8) and (598, 33.1). These values are close to those estimated from Fig. 2 for the *trans*-$Co(py)_4(H_2O)_2^{3+}$ and *mer*-$Co(py)_3Cl(H_2O)_2^{2+}$ system: (442, 31.5) and (605, 31.0). A new set of isosbestic points appeared later: (612, 29.5) and (446, 34.5) but held for a much shorter time before reduction to Co^{2+}(aq) occurred. The species responsible for the latter pair of isosbestic points has not been identified.

In a third set of repetitive scan experiments *trans*-$Co(py)_4(H_2O)_2^{3+}$ was dissolved in 0.05 M acid and 1.0 M chloride ion (30 ℃). At this lower acidity, the first scan was not that of the reactant but was somewhat similar to that expected for $Co(py)_3(H_2O)_3^{3+}$ [observed: max. (513, 51.2) and min. (457, 43.3); reported: max. (523, 51) and min. (443, 15)]. The spectra changed quite rapidly; no isosbestic points were observed; and at long times (~30 min), the scans are reminiscent of those expected for $Co(py)_3Cl(H_2O)_2^{2+}$. The observed spectral parameters (602, 33.0) and (481, 18.7) compare favorably with those reported by Loan [16] (602, 32.3) and (481, 18.7). This repetitive scan experiment suggests that under the conditions of low acidity and high chloride ion concentration, the rate of the loss of pyridine from $Co(py)_4(H_2O)_2^{3+}$ is faster than the rate of chloride anation of the same complex. Later scans suggest that the reduction process becomes prominent with the formation of Co^{2+}(aq).

In a final repetitive scan experiment, *mer*-$Co(py)_3Cl(H_2O)_2^{2+}$ was dissolved in 1 M HCl (30 ℃). The first scan suggested that little decomposition had occurred. Isosbestic points (586, 31.2) and (476, 17.2) held for approximately 30 min. The loss of the isosbestic points is attributed to the formation of Co^{2+}(aq). The temporary isosbestic points may be those corresponding to the $Co(py)_3Cl(H_2O)_2^{2+}$ and $Co(py)_3Cl_2(H_2O)^+$ system which would imply that the monochloro complex undergoes further anation at these conditions. The isosbestic point parameters for $Co(py)_3Cl(H_2O)_2^{2+}$ and $Co(py)_3Cl_2(H_2O)^+$, as estimated from a figure by Laier *et al.* [7], are (600, 35) and (480, 21). In view of complications associated with additional anation and pyridine loss, these are in reasonable agreement with the observed values.

Determination of D_∞

For a first-order reaction a plot of $\ln(D_t - D_\infty)$ versus time will be linear. Since the total decomposition of $Co(py)_4(H_2O)_2{}^{3+}$ results in the reduction of a Co(III) complex to $Co^{2+}(aq)$ with the liberation of coordinated pyridine it was expected that D_∞ would be a constant equal to the product of the molar absorptivity of $Co^{2+}(aq)$ and the total cobalt concentration. The measured value of D_∞ was always greater than that calculated for a solution of $Co^{2+}(aq)$ and pyridine and the apparent D_∞ usually decreased slowly over time. Since the odor of chlorine gas was noted during some of the high chloride kinetic runs, we associate a higher than calculated and slowly decreasing D_∞ with the slow escape of this product.

Since D_∞ could not be measured accurately nor calculated with sufficient confidence, it was fit graphically so that a plot of $\ln(D_t - D_\infty)$ versus time was linear. The graphical procedure was verified by a computer fit of the absorbance–time data to the integrated form of the first-order rate law.

A judgment was made with respect to the appropriateness of treating the absorbance–time data as that expected for consecutive first-order reactions

$$\Delta = \ln(D_t - D_\infty) - \beta \exp(-k_s t) = \ln(\alpha) - k_f t \qquad (1)$$

If it was determined that there was meaningful data at times prior to the linear portion of the $\ln(D_t - D_\infty)$ versus time plot, then an estimate of k_{fast} could be made from a plot of Δ versus time (see eqn. (1)).

The last stage in the data treatment involves the refinement of the value of k_{fast}. The data is fit by a non-linear least-squares (NLLS) method to the equation that describes the absorbance–time behavior of a system exhibiting consecutive first-order kinetics [22]:

$$D_t = D_\infty + \alpha \exp(-k_f t) + \beta \exp(-k_s t) \qquad (2)$$

where $\alpha = [(\epsilon_B - \epsilon_A)k_f + (\epsilon_A - \epsilon_C)k_s][A]_0/(k_s - k_f)$ and $\beta = (\epsilon_C - \epsilon_B)k_f[A]_0/(k_s - k_f)$. In the above equations, ϵ_A, ϵ_B and ϵ_C are the molar absorptivities of species A, B and C respectively. At conditions of low $[H^+]$ and low $[Cl^-]$, the loss of pyridine is accelerated while the rate of anation is retarded and no appreciable buildup of a chloride containing intermediate occurs. Under these conditions the fit of the absorbance–time data is inadequate and it is not possible to obtain k_{fast}. Values of k_{fast} and k_{slow} obtained at 30 and 40 ℃ are collected in Table 2.

Experiments were performed to verify the contention that the observed reactions were first-order with respect to the complex concentration. Table 3 indicates that when the concentration of the complex ion was increased by a factor of 36, both k_{fast} and k_{slow} were altered by a factor of about 1.2, which we believe is within our experimental error. This same Table illustrates the results of experiments that were performed to determine if the observed rates varied with the concentration of added $Co^{2+}(aq)$. Since a large excess of Co^{2+} had little effect on the observed rates, no attempt has been made to include a Co^{2+} concentration term in the experimental rate law.

Discussion

The Fast Step

At both temperatures k_{fast} shows a non-linear reciprocal hydrogen ion dependency with negligible intercepts and a leveling off at low $[H^+]$ (Fig. 3). This behavior is consistent with an acid-base equilibrium with the deprotonated form being the reactive species

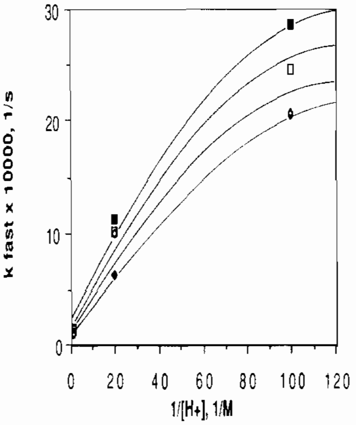

Fig. 3. Plot of k_{fast} vs. $1/[H^+]$ at 30 ℃ for the fast step in the decomposition of *trans*-$Co(py)_4(H_2O)_2{}^{3+}$ in acidic solutions (■ = 0.75 M $[Cl^-]$; □ = 0.50 M $[Cl^-]$; ◆ = 0.10 M $[Cl^-]$; ◇ = 0.05 M $[Cl^-]$).

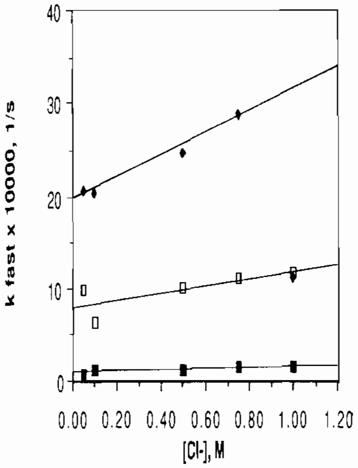

Fig. 4. Plot of k_{fast} vs. $[Cl^-]$ at 30 ℃ for the fast step in the decomposition of *trans*-$Co(py)_4(H_2O)_2{}^{3+}$ in acidic chloride solutions (■ = 1.00 M $[H^+]$; □ = 0.05 M $[H^+]$; ◆ = 0.01 M $[H^+]$).

TABLE 2. Extracted rate constants[a] ($10^3 \times k_{obs}$ (s^{-1})) for the two-step decomposition of the *trans*-diaquatetrakis(pyridine)-cobalt(III) ion at various chloride and acid concentrations

$[H^+]$ (M)	$[Cl^-]$ (M)	40 °C		30 °C	
		k(fast)	*k*(slow)	*k*(fast)	*k*(slow)
1.00	1.00	0.961	3.79	1.61	0.670
	0.75	0.926	3.04	1.53	0.485
	0.50	0.774	2.20	1.39	0.387
	0.10	0.643	1.14	1.20[b]	0.166
	0.05	0.606	1.00	0.891	0.169
0.50	1.00	2.45	4.69		
	0.75	1.53	3.65		
	0.50	1.22	2.66		
	0.10	1.18	1.7		
	0.05	1.32	1.83		
0.10	1.00	3.71	11.0		
	0.75	4.58	8.27		
	0.50	3.17	7.38		
	0.10	1.76[b]	6.88		
	0.05	2.29[b]	8.27		
0.05	1.00	6.95	1.65	11.6	2.94
	0.75	6.32	1.32	11.2	2.55
	0.50	5.10	1.27	10.1	2.36
	0.10	4.52[b]	1.46	6.34[b]	2.55
	0.05	6.21[b]	1.60	9.90[b]	2.82
0.02	1.00	12.8	2.94		
	0.75	9.32	2.93		
	0.50	8.05	2.91		
	0.10	5.56[b]	3.75		
	0.05	5.92[b]	3.68		
0.01	1.00	16.4	5.57		
	0.75	11.6	5.47	28.7	10.3
	0.50	11.1[b]	5.52	24.6	8.74
	0.10	5.54[b]	5.59	20.4[b]	12.4
	0.05	9.97[b]	7.52	20.6[b]	14.6

[a] Unless otherwise noted standard deviations within the NLLS treatment have reasonable values. [b] One of the standard deviations of the NLLS's parameters had a large value.

TABLE 3. Rate constants[a] ($10^4 \times k_{obs}$ (s^{-1})) for decomposition of the *trans*-diaquatetrakis(pyridine)cobalt(III) ion at various cobalt concentrations (ionic strength = 1.00 M)

$[H^+]$ (M)	$[Cl^-]$ (M)	Cobalt	*k*(fast)	*k*(slow)
0.10	1.00	0.00597[b]	46.8	9.22
0.10	1.00	0.000162[b]	35.8	11.1
0.10	1.00	0.000166[b]	38.3	10.6
0.05	0.05	0.000438[c,d]	7.35	2.53
0.05	0.05		9.90[d]	2.82
0.05		0.000410[c,d]	7.40	2.81
0.05			7.43[d]	3.46

[a] Unless otherwise noted standard deviations within the NLLS treatment have reasonable values. [b] The cobalt concentration refers to added $Co(py)_4(H_2O)_2^{3+}$ complex and 40 °C. [c] The cobalt concentration refers to added Co^{2+}(aq) and 30 °C. [d] One of the standard deviations of the NLLS's parameters had a large value.

[23] and suggests an acid dependence of k_{fast} as shown below.

$$k_{fast} = a/(b + [H^+]) \tag{3}$$

The data in Table 2 at any constant hydrogen ion concentration indicates that k_{fast} shows a linear chloride ion dependence with a finite intercept and this is illustrated in Fig. 4. A function of the form

TABLE 4. Mechanistic constants for the fast step[a]

Temperature (°C)	$10^4 \times k_2K_1$ (M s^{-1})	$10^4 \times k_2$ (s^{-1})	$10^4 \times k_3K_1$ (s^{-1})	$10^4 \times k_3$ (M s^{-1})	K_1	k_2/k_3
30	1.07 ± 0.03	16.7 ± 3.1	0.71 ± 0.05	7.7 ± 3.6	0.078	1.50
40	5.24 ± 0.50	74.2 ± 45.0	4.98 ± 1.71	27 ± 24	0.13	1.05

$\Delta H_{21}^{\pm} = 113$ kJ/mol $\Delta S_{21}^{\pm} = 53$ J/mol K $\Delta H_{31}^{\pm} = 144$ kJ/mol $\Delta S_{21}^{\pm} = 150$ J/mol K

[a] Activation parameters have not been tabulated for the individual rate constants because of the large uncertainties.

$$k_{\text{fast}} = f + g[\text{Cl}^-] \tag{4}$$

is suggested and implies parallel reaction paths.

From the results of the repetitive scan experiments and the dependence of the rates on chloride ion and hydrogen ion concentrations, the following scheme is proposed for the fast step.

$$\text{Co(py)}_4(\text{H}_2\text{O})_2{}^{3+} \overset{K_1}{\rightleftharpoons} \text{Co(py)}_4(\text{H}_2\text{O})(\text{OH})^{2+} + \text{H}^+$$

$$\text{Co(py)}_4(\text{H}_2\text{O})(\text{OH})^{2+} + \text{H}_2\text{O} \xrightarrow{k_2} \text{Co(py)}_3(\text{H}_2\text{O})_2(\text{OH})^{2+} + \text{py}$$

$$\text{Co(py)}_4(\text{H}_2\text{O})(\text{OH})^{2+} + \text{Cl}^- \xrightarrow{k_3} \text{Co(py)}_3(\text{H}_2\text{O})(\text{OH})\text{Cl}^+ + \text{py}$$

The observed rate constant for the fast step may be related to the mechanism by $k_{\text{fast}} = (k_2K_1 + k_3K_1[\text{Cl}^-])/(K_1 + [\text{H}^+])$. At constant $[\text{H}^+]$, a plot of k_{fast} versus $[\text{Cl}^-]$ should be linear as observed in Fig. 4 with a slope $= k_3K_1/(K_1 + [\text{H}^+])$ and an intercept $= k_2K_1/(K_1 + [\text{H}^+])$. Rearranging the above equation for the slope yields $1/\text{slope} = [\text{H}^+]/k_3K_1) + 1/k_3$ and indicates that when the reciprocal of the slopes are plotted versus $[\text{H}^+]$ (Fig. 5), the new intercept is $1/k_3$ and the new slope is $1/k_3K_1$ hence k_3 and K_1 are obtained. These values are listed in Table 4 but it should be noted that the error associated with the intercept is large so that only the product of k_3 and K_1 may be given with much certainty.

Rearranging the equation for the intercept of the k_{fast} versus $[\text{Cl}^-]$ plots produces $1/\text{intercept} = [\text{H}^+]/(k_2K_1) + 1/k_2$ and indicates that similar information may be obtained by plotting the reciprocal of the intercepts versus $[\text{H}^+]$ as shown in Fig. 6 but now the intercept of this plot is $1/k_2$ and the slope is $1/k_2K_1$. The values calculated for k_2 and K_1 are listed in Table 4 as is the ratio k_2/k_3. The fact that the ratio k_2/k_3 is approximately unity implies neither water nor chloride ion is strongly favored as an entering group and is consistent with an intimate mechanism that is primarily dissociative.

The mechanistic equilibrium constant K_1 corresponds to the first acid dissociation constant for the *trans*-diaquatetrakis(pyridine)cobalt(III) ion and its value 4.2×10^{-2} M has been obtained [8] by direct pH measurements of solution of the complex in 1.0 M NaNO_3 at 25 °C. This value is in agreement with

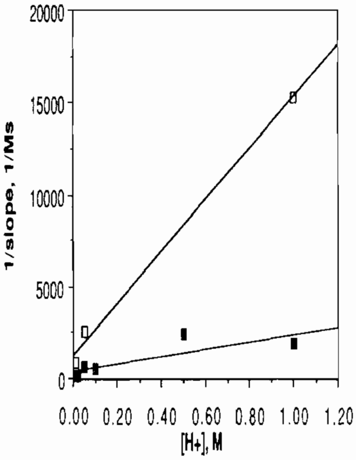

Fig. 5. Plots of $(\text{slope})^{-1}$ vs. $[\text{H}^+]$. At 30 °C the slopes are from the k_{fast} vs. $[\text{Cl}^-1]$ plot shown in Fig. 4 (■ $T = 40$ °C; □ $T = 30$ °C).

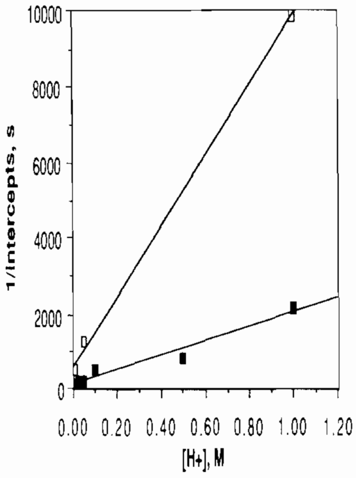

Fig. 6. Plots of $(\text{intercepts})^{-1}$ vs. $[\text{H}^+]$. At 30 °C the intercepts are from the k_{fast} vs. $[\text{Cl}^{-1}]$ plot shown in Fig. 4. (■ $T = 40$ °C; □ $T = 30$ °C).

our kinetically determined value of 7.8×10^{-2} M at 30 °C and serves to support our proposed mechanism for the fast step.

The values of $\Delta H^{\pm}$ and $\Delta S^{\pm}$ listed in Table 4 are for the composite rate constants k_2K_1 and k_3K_1. The constant k_3 may itself be a composite rate constant since we have neglected any ion pairing between the complex cation and the chloride ion. Since they are composite rate constants and arise from measurements at only two temperatures, their interpretation is hampered. We simply note that the values of $\Delta H_{31}{}^{\pm}$ (144 kJ/mol) and $\Delta S_{31}{}^{\pm}$ (150 J/mol K) are close to the composite constants reported [24] for the first anation step of *cis*-$Co(NH_3)_4(H_2O)_2{}^{3+}$ by NCS^- ($\Delta H^{\pm} = 143 \pm 7$ kJ/mol and $\Delta S^{\pm} = 141 \pm 11$ J/mol K).

The Slow Step

At both temperatures, k_{slow} exhibits a linear reciprocal hydrogen ion dependency with small intercepts at high chloride concentrations and negligible intercepts at low chloride concentrations. These plots suggest an acid–base equilibrium and a function of the form

$$k_{slow} = c + (d/[H^+])$$

At high chloride concentrations (measurable intercepts) both the protonated and deprotonated forms are kinetically active. At low chloride concentrations (negligible intercepts) only the deprotonated species is reactive.

The plots of k_{slow} versus chloride ion concentration shown in Fig. 7 indicate a complex relationship. It appears that there are limiting forms at the extremes of $[Cl^-]$ and we assume that there are several parallel paths for the mechanism associated with k_{slow}.

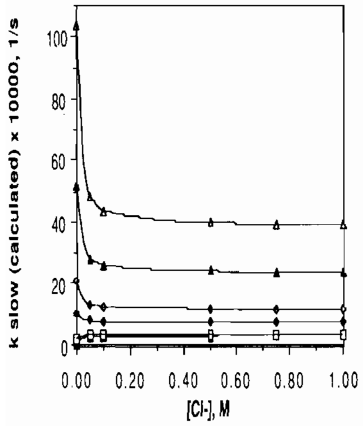

Fig. 7. Plot of k_{slow} vs. $[Cl^-]$ at 40 °C for the slow step in the decomposition of *trans*-$Co(py)_4(H_2O)_2{}^{3+}$ in acidic chloride solutions (■ = 1.00 M $[H^+]$; □ = 0.50 M $[H^+]$; ◆ = 0.10 M $[H^+]$; ◇ = 0.05 M $[H^+]$; ▲ = 0.02 M $[H^+]$; △ = 0.01 M $[H^+]$).

Our approach to proposing a mechanism for the slow step is to treat the fast chloride anation of the triaquatris(pyridine)cobalt(III) ion as a rapid equilibrium and to ignore the relatively rapid loss of pyridine from any of the tris(pyridine)cobalt(III) species that may precede the reduction to $Co^{2+}(aq)$. With these assumptions and the results of the repetitive scan experiments and the dependence of the rates on chloride ion and hydrogen ion concentrations, the following scheme is proposed.

$$Co(py)_3(H_2O)_2(OH)^{2+} + Cl^- \xrightleftharpoons{K_4} Co(py)_3(H_2O)(OH)Cl^+ + H_2O$$

$$Co(py)_3(H_2O)_3{}^{3+} \xrightleftharpoons{K_5} Co(py)_3(H_2O)_2(OH)^{2+} + H^+$$

$$Co(py)_3(H_2O)_2Cl^{2+} \xrightleftharpoons{K_6} Co(py)_3(H_2O)(OH)Cl^+ + H^+$$

$$Co(py)_3(H_2O)_2(OH)^{2+} \xrightarrow{k_7} Co^{2+}(aq) + \text{products}$$

$$Co(py)_3(H_2O(OH)Cl^+ \xrightarrow{k_8} Co^{2+}(aq) + \text{products}$$

$$Co(py)_3(H_2O)_2Cl^{2+} \xrightarrow{k_9} Co^{2+}(aq) + \text{products}$$

$$Co(py)_3(H_2O)_3{}^{3+} \xrightarrow{k_{10}} Co^{2+}(aq) + \text{products}$$

The expected observed rate constant in terms of mechanistic constants has the form

$$k_{slow} = \frac{k_7K_6K_5 + k_8K_6K_5K_4[Cl^-] + k_9K_5K_4[Cl^-][H^+] + k_{10}K_6[H^+]}{K_6K_5 + K_6[H^+] + K_6K_5K_4[Cl^-] + K_5K_4[Cl^-][H^+]} \quad (5)$$

In the absence of chloride, eqn. (5) reduces to $k_{slow} = (k_7K_5 + k_{10}[H^+])/(K_5 + [H^+])$ but the data in Table 2 indicate that a plot of k_{slow} versus reciprocal $[H^+]$ at $[Cl^-] = 0$ is linear with a zero intercept, hence it must be assumed that $K_5 \ll [H^+]$ and $k_{10}[H^+] \ll k_7K_5$, so that in the absence of chloride ion $k_{slow} = k_7K_5/[H^+]$. The values of k_7K_5 at both temperatures may be calculated from the slopes of the k_{slow} versus reciprocal $[H^+]$ plots and are listed in Table 5. The approximation made above should be true at all chloride concentrations, therefore the general form of k_{slow} will be simplified

$$k_{slow} = \frac{k_7K_6K_5 + k_8K_6K_5K_4[Cl^-] + k_9K_5K_4[Cl^-][H^+]}{K_6[H^+] + K_6K_5K_4[Cl^-] + K_5K_4[Cl^-][H^+]} \quad (6)$$

TABLE 5. Mechanistic constants for the slow reaction

Temperature (℃)	$10^4 \times k_7K_5$ (M s^{-1})	$10^6 \times k_7K_6/K_4$ (s^{-1})	$10^2 \times k_8K_6$ (M s^{-1})	$10^4 \times k_9$ (s^{-1})
30	0.169 ± 0.003	a	a	a
40	1.01 ± 0.04	1.18 ± 0.04	1.29 ± 0.04	2.71
$\Delta H_{75}^{\pm}$ = 136 kJ/mol	$\Delta S_{75}^{\pm}$ = 53.2 J/mol K 150 J/mol K			

[a]Constants are not determinable at this temperature from the available data.

At all chloride concentrations, plots of k_{slow} versus reciprocal $[H^+]$ are linear, so it must be assumed that $K_6K_5K_4[Cl^-] \ll (K_6[H^+] + K_5K_4[Cl^-][H^+])$ hence k_{slow} may be approximated as

$$k_{\text{slow}} = \frac{k_7K_6K_5 + k_8K_6K_5K_4[Cl^-] + k_9K_5K_4[Cl^-][H^+]}{(K_6 + K_5K_4[Cl^-])[H^+]} \tag{7}$$

$$k_{\text{slow}} = \frac{k_7K_6K_5 + k_8K_6K_5K_4[Cl^-]}{(K_6 + K_5K_4[Cl^-])[H^+]} + \frac{k_9K_5K_4[Cl^-]}{K_6 + K_5K_4[Cl^-]} \tag{8}$$

The slopes from the plots of k_{slow} versus reciprocal $[H^+]$ are described by

$$\text{slopes} = \frac{k_7K_6K_5 + k_8K_6K_5K_4[Cl^-]}{K_6 + K_5K_4[Cl^-]} \tag{9}$$

At 40 ℃, the plot of the slopes obtained versus reciprocal $[Cl^-]$ is found to be linear with a finite intercept. This observation suggests that $K_6 \ll K_5K_4[Cl^-]$ so that eqn. (9) reduces to

$$\text{slopes} = \frac{k_7K_6}{K_4[Cl^-]} + k_8K_6 \tag{10}$$

The slope from a plot of slope versus reciprocal $[Cl^-]$ is k_7K_6/K_4. These values are listed in Table 5. The assumption gleaned from the observation of linear plots of slope versus reciprocal $[Cl^-]$ suggests that the intercepts obtained from the plot of k_{slow} versus reciprocal $[H^+]$ should not vary with $[Cl^-]$. Of the five values only three had non-zero intercepts within experimental uncertainty hence the intercepts are not known as well as the five slopes. The assumption that $K_6 \ll K_5K_4[Cl^-]$ is retained and the value of k_9 in Table 5 is estimated as the average of three intercepts.

The preceding data treatment is true at 40 ℃ where the bulk of the kinetic studies were performed. At 30 ℃, no linear plot could be found to relate the slopes or the intercepts of the plot of k_{slow} versus reciprocal $[H^+]$ with $[Cl^-]$ concentrations. This suggests that the approximations that were made at 40 ℃ are not valid at 30 ℃. The only constant determined for the slow step at 30 ℃ is the product k_7K_5.

From the values of specific and composite rate constants determined at 40 ℃, it was possible to calculate via eqn. (5) k_{slow} at various $[H^+]$ and $[Cl^-]$ concentrations. The calculated value exhibits the same form as the experimental data in Fig. 7.

If approximations are made, we obtain estimates of the relative magnitudes of the reduction constants k_7, k_8, k_9 and k_{10}. The constant K_5 is an acid dissociation constant for $Co(py)_3(H_2O)_3{}^{3+}$. If we estimate K_5 as being equal to K_1 (the acid dissociation constant for $Co(py)_4(H_2O)_2{}^{3+}$) shown in Table 4, then the value of k_6 is 8.0×10^{-4} s^{-1}. The value of K_6 has been determined [16] at 25 ℃ as 4.0×10^{-3} M, and this will serve as the estimate for K_6 at 40 ℃. Thus k_8 is approximated as 1.3×10^{-2} s^{-1}. The value of k_9 is given in Table 5 as 2.7×10^{-4} s^{-1}. The magnitude of k_{10} is negligible compared to k_7. From these values it can be seen that the chloro complexes are reduced at a faster rate than their corresponding aqua complexes ($k_8 > k_7$ and $k_9 > k_{10}$), and that the hydroxy complexes are reduced at a faster rate than their corresponding aqua complexes ($k_7 > k_{10}$ and $k_8 > k_9$).

The values of $\Delta H^{\pm}$ (136 kJ/mol) and $\Delta S^{\pm}$ (112 J/mol K) calculated for the composite rate constant k_7K_5 are approximately those previously reported [6] for the reduction of the *mer*-$Copy_3(H_2O)_3{}^{3+}$ or *cis*-$Copy_2(H_2O)_4{}^{3+}$ complexes: $\Delta H^{\pm} = 135 \pm 2$ kJ/mol and $\Delta S^{\pm} = 113 \pm 8$ J/mol K. The agreement between the two sets of activation parameters supports our slow step mechanism and suggests that the $Co(py)_3(H_2O)_3{}^{3+}$ species undergoes a rapid loss of pyridine before the actual reduction step.

Lastly, one may anticipate additional redox pathways (inner and outer sphere) as the Co^{2+}(aq) product forms. Since both the chloro and non-chloro complexes undergo reduction at similar rates and the addition of a large excess of Co^{2+}(aq) does not alter these rates, the paths are not available and reduction occurs by an internal process that involves the oxidation of ligands water and chloride.

Conclusions

Two obvious reactions occur when *trans*-Copy$_4$(H$_2$O)$_2$$^{3+}$ ion is placed in acidic chloride solution. The faster involves replacement of coordinated pyridine by water or chloride ion in parallel paths. The slower consists of spontaneous reduction of Co(py)$_3$(H$_2$O)$_2$Cl^{2+} and Copy$_3$(H$_2$O)$_3$$^{3+}$ with the chloro complex decomposing at a faster rate than the aqua complex.

Acknowledgement

D.A.G. wishes to acknowledge the State University of New York, Oswego Alumni Association, for partial support of this project via a Barnes Graduate Scholarship.

References

1 R. Llewellyn, J. O'Connor and A. L. Odell, *J. Chem. Soc. A*, (1964) 196.
2 W. L. Reynolds and E. S. Barber, *Int. J. Chem. Kin.*, *7* (1975) 443.
3 W. L. Reynolds, I. Murati and S. Asperger, *J. Chem. Soc. A*, (1974) 719.
4 M. Martinez and M. Ferrer, *Transition Met. Chem.*, *9* (1984) 395.
5 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 2nd edn., 1967, pp. 127–128, 141, 164, 170–171, 203.
6 K. E. Hyde and G. M. Harris, *J. Phys. Chem.*, *82* (1978) 2204.
7 T. Laier, C. E. Schaffer and J. Springborg, *Acta Chem. Scand. Ser., A*, *34* (1980) 343.
8 J. Springborg and C. E. Schaffer, *Acta Chem. Scand.*, *27* (1973) 3312.
9 W. D. Stanley, S. Lum and C. S. Garner, *J. Inorg. Nucl. Chem.*, *35* (1973) 3587.
10 S. Lum, W. D. Stanley and C. S. Garner, *J. Inorg. Nucl. Chem.*, *35* (1973) 1293.
11 S. T. Mallen, The State University of New York, College at Oswego, unpublished results.
12 R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nucl. Chem.*, *1* (1975) 341.
13 F. Basolo, J. G. Bergmann, R. E. Meeker and R. G. Pearson, *J. Am. Chem. Soc.*, *78* (1956) 2676.
14 C. N. Elgy and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, (1980) 2405.
15 V. D. Panasyuk and S. A. Shevchenko, *Ukr. Khim. Zh.*, *29* (25) (1963) 1142.
16 N. Loan, *M.S. Thesis*, The State University of New York, College at Oswego, 1983.
17 J. Glerup, C. E. Schaffer and J. Springborg, *Acta Chem. Scand., Ser. A*, *32* (1978) 673.
18 G. Yogis, *M.S. Thesis*, The State University of New York, College at Oswego, 1987.
19 V. D. Panasyuk and S. A. Shevchenko, *Visn. Kiivs'k Univ., Ser Astron., Fix. ta Khim.*, *5* (2) (1962) 99.
20 B. N. Figgis, *Introduction to Ligand Fields*, Wiley-Interscience, New York, 1966, p. 225.
21 T. O'Donnell, The State University of New York, College at Oswego, unpublished results.
22 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 1981, pp. 22, 67, 117.
23 K. S. Gupta and Y. K. Gupta, *J. Chem. Educ.*, *61* (1984) 972.
24 M. C. Ghosh and P. Banerjee, *J. Coord. Chem.*, *13* (1984) 237.