balt since copper could be reduced to Cu(I). However, the only difference noted was that the approximate relative intensity of the [Cu(SALX)]$^-$ ions was greater than that for [Ni(SALX)]$^-$ and [Co(SALX)]$^-$.

Registry No. H_2SALHTDA, 52279-42-2; Co(SALHTDA), 17084-78-5; Ni(SALHTDA), 52358-03-9; Cu(SALHTDA), 52279-50-2; H_2SALDAPE, 52279-43-3; Co(SALDAPE), 52279-51-3; Ni(SALDAPE), 52279-52-4; Cu(SALDAPE), 52279-53-5; H_2SALDAPS, 52279-44-4; Co(SALDAPS), 52279-54-6; Ni(SALDAPS), 52279-55-7; Cu(SALDAPS), 52358-04-0; H_2SALDPT, 52279-45-5; Co(SALDPT), 15306-22-6; Ni(SALDPT), 15391-40-9; Cu(SALDPT), 15391-22-7.

Contribution from the Research School of Chemistry, The Australian National University,
Canberra, 2600, Australia, and Chemistry Department I, University of Copenhagen, Copenhagen, Denmark

Hydrolysis and Nitrosation of the $(NH_3)_5CoNCO^{2+}$ Ion. Evidence for $(NH_3)_5CoNHCOOH^{2+}$ and $(NH_3)_5Co^{3+}$ Intermediates

D. A. BUCKINGHAM, D. J. FRANCIS, and A. M. SARGESON*

Received April 8, 1974 AIC40231T

$(NH_3)_5CoNCO^{2+}$ hydrolyzes (1 *M* H^+) by consecutive reactions to yield first $(NH_3)_5CoNH_2CO_2H^{3+}$ ($-d[\text{cyanato}]/dt = k_1K_1[H^+][\text{cyanato}]$) and then by three parallel paths to form $(NH_3)_5CoOH_2^{3+}$, $(NH_3)_5CoO_2CNH_2^{2+}$, and $Co(NH_3)_6^{3+}$ ($-d[\text{carbamate}]/dt = [(k_2' + k_2'')[H^+] + k_3K_2][\text{carbamate}]/(K_2 + [H^+])$). The aqua- and O-bonded carbamato complexes arise from the k_2 paths and the hexaammine arises from the deprotonated N-bonded carbamate intermediate (k_3). Essentially the rate-determining step for the nitrosation reaction is the same as that for acid hydrolysis. Subsequently in a somewhat faster step NO^+ adds to the N-deprotonated carbamate intermediate to generate N_2 and CO_2 and the $Co(NH_3)_5^{3+}$ intermediate. The latter is characterized by the competition ratio for H_2O, Cl^-, and NO_3^- and is shown to be the same as that observed in previous examples of induced aquation.

Introduction

The existence and nature of the five-coordinate intermediate $(NH_3)_5Co^{3+}$ has been the subject of several investigations.[1-6] Common competition ratios between nucleophiles in solution have been observed from several sources of this intermediate[2-6] but there is a need for additional support for its existence. The recent preparation by Balahura and Jordan[7] of $[(NH_3)_5CoNCO](ClO_4)_2$ leads to the possibility that coordinated NCO^- would be susceptible to nitrosation by NO^+ like free NCO^- ion, to produce coordinated N_2 and CO_2.[8] Such species are good leaving groups in cobalt(III) amine chemistry[2,3] and the reactive intermediate $[(NH_3)_5Co]^{3+}$ could be expected. This paper gives evidence to support the existence of such an intermediate in the form of its competition properties for nucleophiles such as H_2O, Cl^-, NO_3^-, and HNO_2.

During some preliminary acid hydrolysis experiments of the $(NH_3)_5CoNCO^{2+}$ ion unusual kinetics and products were observed. This reaction was therefore reexamined[7] in more detail and the new results also form a major part of the paper.

Experimental Section

Preparation of $[(NH_3)_5CoNCO](ClO_4)_2$. The following method was developed to improve the yields of the isocyanato complex reported by Balahura and Jordan.[7] The addition of molecular sieves or triethylamine to the reaction mixture had no effect on the yield. The use of trimethyl or triethyl phosphate as the reaction solvent resulted in appreciably lower yields of the isocyanato complex. Reaction temperature, reaction time, and order of reagent addition appeared to be the most critical factors.

Finely ground, reagent grade urea (15 g) was dissolved in *N,N*-dimethylacetamide (100 ml) and the solution heated to 135°. $[(NH_3)_5CoOH_2](ClO_4)_3$ (12 g) was added to the stirred solution and kept at 135° for 25 min. 2-Butanol (1 l.) was added to the warm solution to precipitate the crude product which was then fractionally recrystallized from water by addition of $NaClO_4$. Six fractions were collected and further fractionated to yield three products, $[(NH_3)_5CoNCO](ClO_4)_2$ (8.1 g, 80%), $[(NH_3)_6Co](ClO_4)_3$, and a pink material which was not characterized but was presumed to be $[(NH_3)_5CoOC(NH_2)_2](ClO_4)_3$.[7] *Anal.* Calcd for $[(NH_3)_5CoNCO](ClO_4)_2$: C, 3.12; H, 3.94; N, 21.83; Co, 15.28. Found: C, 3.1; H, 3.9; N, 21.8; Co, 15.3. The uv-visible spectrum (in H_2O, ϵ_{504} 134.8, ϵ_{356} 88.3 M^{-1} cm^{-1}) and the infrared spectrum (ν_3(C–N) 2262 cm^{-1} in KBr disk) of the complex agreed with those reported previously.[7] The pure complex yielded only one 2+ band on elution from Dowex 50W-X2 (Na^+ form) cation-exchange resin with 1.0 *M* $NaClO_4$ (pH ~5) and only one 3+ band after reaction in HCl (0.08 *M*) for 30 min followed by elution from Dowex 50W-X2 (H^+) with 3 *M* HCl. The 3+ band was characterized from its uv-visible spectrum to be $(NH_3)_6Co^{3+}$ ion in agreement with the earlier study.[7]

Product Analysis. Acid Hydrolysis. In a typical experiment, acid (50 ml, $\mu = 2.0$, $HClO_4$, HCl, or HNO_3) and an aqueous solution of $[(NH_3)_5CoNCO](ClO_4)_2$ (0.2 g in 50 ml) were simultaneously added to a beaker and stirred for 10 min at 25°. The reaction solution was then diluted (about three times) and neutralized to pH 6 with NaOH. The solution was rapidly sorbed on a Dowex 50W-X2 (Na^+ form) cation-exchange resin and washed with distilled water. The products were eluted separately: 2+ ions with 1 *M* $NaClO_4$ (pH ~5), $(NH_3)_5CoOH^{2+}$ with 1.0 *M* $NaClO_4$ (pH 10), and $(NH_3)_6Co^{3+}$ with 3 *M* HCl. By lowering the pH to 2 with 1.0 *M* $HClO_4$, the $(NH_3)_5CoOH^{2+}$ was converted to $(NH_3)_5CoOH_2^{3+}$ thereby preventing decomposition of the hydroxo species. Concentrations were determined by uv-visible and/or atomic absorption spectroscopy. The above procedure took less than 60 min from reaction initiation and was necessary to minimize hydrolysis of minor products. Unless the reaction solution was neutralized and rapidly sorbed, complete hydrolysis of the initial 2+ ion to $(NH_3)_5CoOH_2^{3+}$ occurred in the time (~24 hr) required to sorb, elute, and analyze the fractions. Partial anation of the $(NH_3)_5CoOH_2^{3+}$ to $(NH_3)_5CoX^{2+}$ ($X^- = Cl^-, Br^-, NO_3^-$) also occurred in these long experiments.

---

* To whom correspondence should be addressed at The Australian National University.

(1) Presented at the Fourth Conference of the Division of Coordination and Metal-Organic Chemistry of the Royal Australian Chemical Institute, Camden, N.S.W., Australia, May 23-26, 1972.

(2) A. Haim and H. Taube, *Inorg. Chem.*, 2, 1199 (1963).

(3) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, 6, 1027 (1967).

(4) J. Sullivan (Argonne National Laboratory), private communication.

(5) F. A. Posey and H. Taube, *J. Amer. Chem. Soc.*, 79, 255 (1957).

(6) J. S. Valentine and D. Valentine Jr., *J. Amer. Chem. Soc.*, 93, 1111 (1971).

(7) R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 9, 1567 (1970).

(8) The reaction of KNCO with acidic $NaNO_2$ produced N_2 and CO_2 which were identified by gas chromatography.

Large-scale (1 g) product distribution experiments were carried out at $\mu = 3.0$ ($NaClO_4$) in 1, 2, and 3 *M* $HClO_4$ and in 3 *M* HCl. The above general procedure was used except that for some early experiments the diluted reaction solution was not neutralized before sorption on the cation-exchange resin.

In some experiments in which large concentrations of $NaNO_2$ were used, the 2+ products were tested for the presence of $(NH_3)_5CoNO_2^{2+}$ by mixing an aliquot of the 2+ product with an equal amount of 0.1 *M* NaOH. After 10 min when $(NH_3)_5CoCl^{2+}$ or $(NH_3)_5CoNO_3^{2+}$ were hydrolyzed, the solution was acidified to pH 3 with $HClO_4$ and diluted 10-fold with water. After sorption on a Dowex 50W-X2 (H^+ form) cation-exchange resin any $(NH_3)_5CoNO_2^{2+}$ was eluted with pH 5, 1.0 *M* $NaClO_4$. The $(NH_3)_5CoNO_2^{2+}$ was characterized by comparison of its uv-visible spectrum with that of an authentic sample. In all cases, the amount of $(NH_3)_5CoNO_2^{2+}$ detected was <1% of the total reaction product.

Samples of $[(NH_3)_5CoCl](ClO_4)_2$, $[(NH_3)_5CoOH_2](ClO_4)_3$, and $[(NH_3)_6Co](ClO_4)_3$ were repeatedly recrystallized from $NaClO_4$ until analytically pure, and the uv-visible spectra were obtained. *Anal.* Calcd for $[(NH_3)_5CoCl](ClO_4)_2$: N, 18.51; H, 4.00; Co, 15.57. Found: N, 18.2; H, 4.0; Co, 15.5 (ϵ_{532} 49.5 M^{-1} cm^{-1}, pH 5, 1 *M* $NaClO_4$). Calcd for $[(NH_3)_5CoOH_2](ClO_4)_3$: N, 15.21; H, 3.73; Co, 12.80. Found: N, 15.3; H, 3.8; Co, 12.8 (ϵ_{492} 47.9 M^{-1} cm^{-1}, pH 5, 1 *M* $NaClO_4$). Calcd for $[(NH_3)_6Co](ClO_4)_3$: N, 18.29; H, 3.96; Co, 12.82; Cl, 23.14. Found: N, 18.3; H, 4.1; Co, 13.3; Cl, 23.1 (ϵ_{479} 57.6 M^{-1}cm^{-1}, 3 *M* HCl). Previously published extinction coefficients were used for $[(NH_3)_5CoBr](ClO_4)_2$ (ϵ_{550} 55.5 M^{-1} cm^{-1} in 1 *M* $NaClO_4$) and $[(NH_3)_5CoNO_3](ClO_4)_2$ (ϵ_{502} 56.3 M^{-1} cm^{-1} in 1 *M* $NaClO_4$).

The variation of product distribution with reaction time (3 *M* HCl) was tested by quenching the reaction at various times with water (10 times the reaction volume). The solutions were then treated as above and the $(NH_3)_6Co^{3+}$ and $(NH_3)_5CoOH_2^{3+}$ ions were characterized by their uv-visible spectra and their elution properties.

Initially the product $(NH_3)_5CoO_2CNH_2^{2+}$ was characterized by its uv-visible spectrum as well as by a larger scale experiment (1 g) in which the eluent containing the 2+ product was diluted and sorbed on a small column (8 × 1 cm) containing Dowex 50W-X2 resin (200-400 mesh) and eluted rapidly with 2.0 *M* $NaNO_3$. Upon cooling, fine red crystals (0.025 g) precipitated. These crystals were filtered, washed with methanol, and air-dried. An authentic sample of $[(NH_3)_5CoO_2CNH_2](NO_3)_2$ was prepared[9,10] by recrystallizing the carbamato perchlorate from water with sodium nitrate. *Anal.* Calcd for $[(NH_3)_5CoO_2CNH_2](NO_3)_2$: C, 3.66; H, 5.23; N, 34.15. Found for 2+ product: C, 3.9; H, 5.5; N, 33.9. Found for authentic sample: C, 3.9; H, 5.5; N, 34.3. The infrared spectra of both the 2+ product and authentic $[(NH_3)_5CoO_2CNH_2](NO_3)_2$ (KBr disks) were recorded with a Perkin-Elmer 457 Grating infrared spectrophotometer.

Nitrosation. A solution of $[(NH_3)_5CoNCO](ClO_4)_2$ (0.04 g) and $NaNO_2$ (0.02-0.69 g) in 50 ml of H_2O was rapidly mixed with a 50-ml solution containing $HClO_4$ and $LiClO_4$ ($\mu = 2.0$). Upon completion of the reaction, the solution was sorbed on a Dowex 50W-X2 (H^+ form) cation-exchange resin (10 × 1 cm). Elution with 1 *M* $NaClO_4$ (pH ~5), 1 *M* $NaClO_4$ (pH ~10), and 3 *M* HCl yielded only two products, $(NH_3)_5CoOH_2^{3+}$ (after acidification of pH 10 eluent) and $(NH_3)_6Co^{3+}$, which were characterized by their uv-visible spectra and their behavior on the cation-exchange resin. The separated products were collected and their concentrations determined as previously described.

A flask containing $[(NH_3)_5CoNCO](ClO_4)_2$ (0.1 g), $NaNO_2$ (0.7 g), and distilled water (20 ml) was sealed with a septum cap and helium was bubbled through the solution to flush out other gases. A sample of the gas above the solution injected into a Gallemkamp CL-190 gas chromatograph (helium carrier gas, 2-butyl phthalate on Chromosorb P/80-100 mesh) showed no N_2 or CO_2 peaks. Ten minutes after the addition of 2.0 *M* $HClO_4$ (4.0 ml), the gas was again sampled and showed large concentrations of CO_2 and N_2.

Competition. A solution of acid, 50 ml ($\mu = 2.0$, HCl or HNO_3), and a solution containing $[(NH_3)_5CoNCO](ClO_4)_2$ (50 ml, 0.2 g) and $NaNO_2$ were simultaneously added to a beaker and stirred for 10 min. After dilution (four times), urea (0.8 g) was added to consume excess NO^+ and the solution was degassed by suction. After rapid (<60 min) sorption on a Dowex 50W-X2 (Na^+ form) cation-exchange resin, the products were eluted and collected, and their concentrations were determined as described previously. The samples of $[(NH_3)_5CoCl](ClO_4)_2$, $[(NH_3)_5CoOH_2](ClO_4)_3$, $[(NH_3)_5CoNO_3](ClO_4)_2$, $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$,[9,10] and $[(NH_3)_6Co](ClO_4)_3$ were prepared by standard procedures.

Tracer Studies. Acid Hydrolysis. $[(NH_3)_5CoNCO](ClO_4)_2$ (0.1 g) was dissolved in ^{18}O-enriched water (10 ml, 1.58 atom % ^{18}O). The CO_2 sampling and collection system was the same as that described elsewhere[11] except that the helium, which was used as the carrier gas, entered the bubbler from the bottom through a sintered-glass frit. The solution was deaerated with helium for 10 min and 6 *M* $HClO_4$ was added through a septum cap on the side arm. The resultant CO_2 was removed from the gas stream by freezing with liquid nitrogen. After 10 min, the CO_2 was collected. A 1-ml sample of the reaction solution was degassed and its ^{18}O content was analyzed after equilibration with normal CO_2 (~2-5 mmol). The ^{18}O content of CO_2 samples was measured on an Atlas MAT GD-150 mass spectrometer.

Nitrosation. $[(NH_3)_5CoNCO](ClO_4)_2$ (0.3 g) and $NaNO_2$ (0.24 g) were dissolved in ^{18}O-enriched water (20.0 ml, 1.56 atom % ^{18}O). The solution was deaerated with helium and CF_3SO_3H (2.26 ml, 3 M Co.) was added. After 10 min the solution (1 ml) was sampled to determine the solvent enrichment while the remainder was immediately added to ice-cold concentrated HBr (25 ml). A mixture of $[(NH_3)_5CoOH_2]Br_3$ and $[(NH_3)_6Co]Br_3$ rapidly precipitated. After filtering and washing with methanol, the solid was analyzed for its ^{18}O content by the Anbar and Guttman method,[12] using an Atlas Mat MAT M-86 mass spectrometer to measure the ^{18}O content of CO_2 samples. The CO_2 from the nitrosation reaction was contaminated by large quantities of oxides of nitrogen. Efficient separation of the gases was not achieved and this prevented the measurement of the ^{18}O content of the CO_2. The purple product mixture obtained after heating the initial product at 80° *in vacuo* was dissolved in water (pH 4) and sorbed on a Dowex 50W-X2 (Na^+ form) cation-exchange resin, and the product distribution was determined as previously described.

Kinetics. Acid Hydrolysis. An aqueous solution containing $[(NH_3)_5CoNCO](ClO_4)_2$ and supporting electrolyte ($NaClO_4$, $LiClO_4$, NaCl, or NaBr) was mixed with an aqueous solution of acid ($HClO_4$, HCl, or HBr) of known concentration in a rapid-mixing device[13] attached to a Cary 14 or a Cary 16K spectrophotometer. The variation of absorbance (at 504, 330, 274, 250, 235, 228, or 226 nm) with time was followed at 25.0°. The acid concentration was at least 10 times that of the complex concentration.

Nitrosation. A solution containing known amounts of $NaNO_2$, $[(NH_3)_5CoNCO](ClO_4)_2$, and $LiClO_4$ was mixed with an acid solution and the kinetics followed as above.

Results

Acid Hydrolysis Products. The products of the acid hydrolysis reaction of $[(NH_3)_5CoNCO](ClO_4)_2$ were $(NH_3)_6Co^{3+}$, $(NH_3)_5CoO_2CNH_2^{2+}$, and $(NH_3)_5CoOH_2^{3+}$. The data in Table I indicate that the amounts of $(NH_3)_5CoO_2CNH_2^{2+}$ and $(NH_3)_5CoOH_2^{3+}$ increase with $[H^+]$ (no. 4, 12-16, 22, 23), increase with ionic strength of NaCl (no. 5-10, 20, 23), and are dependent on the acid used (HCl ~ HNO_3 ~ HBr > $HClO_4$).

The $(NH_3)_5CoO_2CNH_2^{2+}$ product was characterized by its infrared spectrum (Figure 1), its elemental analysis, and its uv-visible spectrum in pH 5, 1 *M* $NaClO_4$ (ϵ_{510} 74.7, ϵ_{356} 64.5 M^{-1} cm^{-1}; for authentic $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$,[13,14] ϵ_{508} 77.5 and ϵ_{356} 60.8 M^{-1} cm^{-1}). Also the 2+ product hydrolyzed slowly in 1.0 *M* $HClO_4$ to yield $(NH_3)_5CoOH_2^{3+}$ and was nitrosated rapidly with $HClO_4$ (pH 2) and $NaNO_2$ to produce $(NH_3)_5CoOH_2^{3+}$ as well as rapidly evolving N_2 and CO_2. This behavior is consistent with the properties of the authentic O-bonded carbamato complex.[3,10]

The $(NH_3)_6Co^{3+}$ product was characterized by its uv-visible

---

(9) M. Linhard and H. Flygare, *Z. Anorg. Allg. Chem.*, **251**, 25 (1943).

(10) A. M. Sargeson and H. Taube, *Inorg. Chem.*, **5**, 1094 (1966). It should be note that ϵ_{505} is 77.5 and not 60 as reported in this reference.

(11) D. J. Francis and R. B. Jordan, *Inorg. Chem.*, **11**, 4617 (1972).

(12) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isotop.*, **5**, 223 (1959).

(13) Y. Inoue and D. D. Perrin, *J. Phys. Chem.*, **66**, 1689 (1962).

(14) L. L. Rines, J. A. Plambeck and D. J. Francis, "ENNLSQ Reprogrammed," Program Library, Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada, 1970.

Table I. Product Distribution for the Acid Hydrolysis of $[(NH_3)_5CoNCO](ClO_4)_2$ at 25°

Acid	No.	$[H^+]$, *M*	μ, *M*	% $(NH_3)_6$-Co^{3+}	% $(NH_3)_5CoO_2$-CNH_2^{2+} (A)	% $(NH_3)_5$-$CoOH_2^{3+}$ (B)	% A + % B	Time of soln at pH <1
$HClO_4$	1	1	1	95.3	*b*		4.7	60 min
$HClO_4$	2	1	1	95.9	*b*		4.1	>6 hr
$HClO_4$	3	1	1	94.5	*b*		5.5	>6 hr
$HClO_4$	4	1	1	95.5	1.7	2.8	4.5	~30 min
HCl	5	1	1	91.1	0.5	8.4	8.9	>6 hr
HCl	6	1	1	92.2	5.3	2.5	7.8	60 min
HCl	7	1	1	92.0	5.2	2.8	8.0	~2 hr[a]
HCl	8	0.9	1	92.9	5.3	1.8	7.1	20 min
HCl	9	0.9	0.9	93.3	5.5	1.1	6.6	33 min
HCl	10	0.5	1	97.2	0.7	2.1	2.8	>6 hr
HNO_3	11	1	1	92.0	2.4	5.6	8.0	~6 hr
$HClO_4$	12	3	3	90.1	*b*		9.9	>12 hr
$HClO_4$	13	3	3	91.6	*b*		8.4	>12 hr
$HClO_4$	14	2	3[e]	95.2	*b*		4.8	>12 hr
$HClO_4$	15	1	3[e]	95.9	*b*		4.1	>12 hr
$HClO_4$	16	1	3[e]	96.9	*b*		3.1	>12 hr
HCl	17	6	6	31.9	43.5[d]	24.6	68.1	>12 hr
HCl	18	3	3	64.7	4.0[d]	31.3	35.3	>12 hr[a]
HCl	19	3	3	63.1	29.6	7.2	36.8	23 min[a]
HCl	20	3	3	62.5	30.6	6.9	37.5	10 min[a,c]
HCl	21	2	2	78.3	17.1	4.6	21.7	8 min
HCl	22	1	2	87.0	10.6	2.4	13.0	7 min
HBr	23	2	2	90.1	*b*	9.9	9.9	>12 hr

[a] Large-scale (1 g) experiment. [b] The 2+ ions and $(NH_3)_5CoOH^{2+}$ were eluted together with pH 10, 1 *M* $NaClO_4$. [c] Reaction time 4 min; diluted four times; neutralized to pH 7 within 10 min from reaction initiation. [d] Contains some $(NH_3)_5CoX^{2+}$ from sequential aquation–anation of $(NH_3)_5CoO_2CNH_2^{2+}$ in >12 hr. [e] $NaClO_4$.

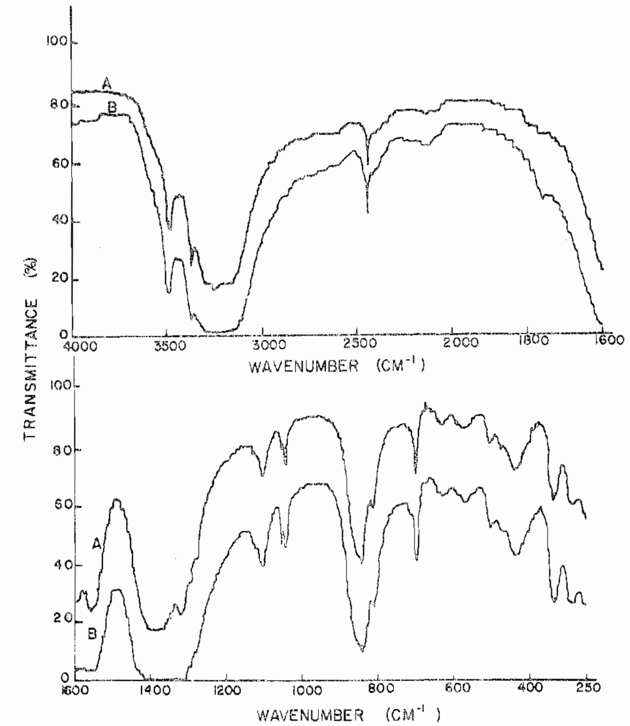


Figure 1. Infrared spectra of the nitrate salt of the 2+ product of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ (B) and of authentic $[(NH_3)_5CoO_2CNH_2](NO_3)_2$ (A) (KBr disks).

spectrum in 3 *M* HCl (λ_{max} 479, 344 nm; for an authentic sample, λ_{max} and 342 nm), its relative insolubility in perchlorate media, and its behavior as a 3+ ion on the ion-exchange resin.

The $(NH_3)_5CoOH_2^{3+}$ product was characterized by its uv-visible spectrum in pH 5, 1 *M* $NaClO_4$ (λ_{max} 492, 345 nm; for an authentic sample, λ_{max} 492 and 347 nm) and by its rapid reversible change from an orange-red 3+ ion at pH 5 to a rose 2+ ion at pH 10.

It was not initially realized that $(NH_3)_5CoO_2CNH_2^{2+}$ was a product of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$. In some early experiments (Table I, no. 2, 3, 5, 11–18) the reaction solution remained at pH <1 for a long time which allowed $(NH_3)_5CoO_2CNH_2^{2+}$ to hydrolyze at least partially to $(NH_3)_5CoOH_2^{3+}$. In some very long experiments (no. 17, 18, 23) anation of the resultant aquo complex to $(NH_3)_5CoCl^{2+}$ occurred. Upon decreasing the time that the reaction solution was at pH <1 to 23–60 min (no. 1, 4, 6, 8, 9, 19–22) $(NH_3)_5CoO_2CNH_2^{2+}$ appeared as a product, but no $(NH_3)_5CoCl^{2+}$ was detected.

Considering the time which the reaction solution was at pH <1 and the known rate constant[3] for the acid hydrolysis of the O-bonded carbamato complex, it can be shown that too much aquo complex was produced (no. 6–9, 19–22) for all of it to be a hydrolysis product of the O-bonded carbamato complex. This possibility was also eliminated by the product distributions from reaction mixtures neutralized at different times, 10 min (no. 20) and 23 min (no. 19). Nor did any significant hydrolysis occur when a sample of $[(NH_3)_5CoO_2CNH_2](ClO_4)_2$ was treated in the same manner. Thus the $(NH_3)_5CoOH_2^{3+}$ recovered is a direct product of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$.

Acid Hydrolysis Tracer Studies. Table II shows that the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ in ^{18}O-enriched water gives CO_2 containing one oxygen from the solvent and one oxygen from the coordinated cyanate ion.

Acid Hydrolysis Kinetics. Pseudo-first-order rate constants, k_a^{504}, were obtained spectrophotometrically from plots of log $(A_t - A_\infty)$ against time, linear over at least 3 half-lives, at 504 nm ($[H^+] = 0.06$–1.0 *M*, $[Co] = 1 \times 10^{-3}$ *M*, $\mu = 1.0$ ($LiClO_4$)). The observed rate constants, k_a^{504}, varied with $[H^+]$ (0.06–0.5 *M*), Figure 2, and fit eq 1.

$$k_a = k[H^+] \qquad (1)$$

At $[H^+] > 0.5$ *M*, slight curvatures in the plots of log $(A_t - A_\infty)$ against time were observed as well as a deviation of the plot k_a^{504} *vs.* $[H^+]$ from eq 1, Figure 2. This was the first indication of a consecutive kinetic process. At wave-

Table II. ^{18}O-Tracer Experiments for the Acid Hydrolysis and Nitrosation of $[(NH_3)_5CoNCO](ClO_4)_2$ at 25°

Reactants	Product analyzed	$N_0{}^e$	N_∞	N_0	N	F^f
$(NH_3)_5CoNCO^{2+\,a,c}$	CO_2	0.00213	0.01773	0.00216	0.01033	0.537
$(NH_3)_5CoNCO^{2+\,b,c}$	CO_2	0.00217	0.01598	0.00215	0.00910	0.503
$(NH_3)_5CoNCO^{2+}$, $NO^{+\,d}$	$(NH_3)_5CoOH_2{}^{3+\,g}$	0.00193	0.01465	0.00189	0.01383	0.938
$(NH_3)_5CoNCO^{2+}$, $NO^{+\,d}$	$(NH_3)_5CoOH_2{}^{3+\,g}$	0.00201	0.01518	0.00201	0.01421	0.928

[a] $[H^+] = 0.097\ M\ (HClO_4)$. [b] $[H^+] = 1.0\ M\ (HClO_4)$. [c] R = mass 46/(mass 44 + mass 45), GD-150. [d] R = mass 46/mass 44, MAT M-86, $[H^+] = 0.99\ M\ (CF_3SO_3H)$, $[HNO_2] = 0.16\ M$. [e] N = atom fraction $^{18}O = R/(2 + R)$; N, N_0, and N_∞ refer to values determined from the product, normal isotopic ratio CO_2, and reaction solvent, respectively. [f] F = fraction enrichment $= (N - N_0)/(N_\infty - N_0)$. [g] *Via* CO_2 derived by the Anbar–Guttman method.[12]

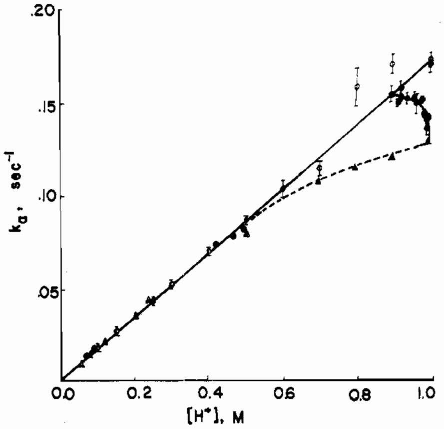


Figure 2. Variation of k_a with $[H^+]$ for the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ at 504 nm (▲) and 226 nm (○) and for the reaction of NO^+ with $(NH_3)_5CoNCO^{2+}$ at 504 nm (●), $\mu = 1.0$ ($LiClO_4$), 25.0°. (The open circles represent the weighted averages[14] of replicate runs (10) while the error bars represent two standard deviations[18] of the averages. The straight solid line was calculated from the best fit value of k obtained by fitting the k_a *vs.* $[H^+]$ data to eq 1.) Weighted average $= (\Sigma_{i=1}{}^{n}(Y_i/s_i))/n$ where n, Y_i, and s_i are the number of runs, the ith rate constant, and the standard error of the fit of the ith run, respectively. $\sigma = ((\Sigma_{i=1}{}^{n}\Delta_i{}^2)/(n = 1))^{1/2}$ where n and Δ_i are the number of data points and the absolute value of the difference between the ith observed value and the average value, respectively.

lengths below 250 nm the absorbance *vs.* time curve was similar to Figure 3, which gives a typical run and which can be represented by

$$A_t = A_0 + A_1e^{-k_at} + A_2e^{-k_bt} \tag{2}$$

and corresponds to the reaction[15,16] type

$$A \xrightarrow{k_a} B \xrightarrow{k_b} C \tag{3}$$

These kinetic data were fitted to eq 2 by a method[17,18] which allowed a more accurate solution for k_a and k_b by eliminating the parameters A_0, A_1, and A_2 from the fitting procedure. Values of the rate constants and the standard error of the fit for a typical set of data at 0.60 M H^+ (226 nm, $\mu = 1.0$ ($LiClO_4$), 25°) were $k_b = 0.158$ sec^{-1} and $k_a = 0.102$ sec^{-1}, SE $= 0.24 \times 10^{-3}$ (SE $= (\Delta/N - NR)^{1/2}$ where $\Delta = A_t{}^{\text{exptl}} - A_t{}^{\text{calcd}}$, N is the number of data points (A_t, t), and NR is the number of rate constants (2)). These data are given to show the efficiency of the technique in separating similar consecutive rate constants. The observed rate constants $k_a{}^{226}$ and $k_b{}^{226}$ varied with $[H^+]$ and were fitted to eq 1 and 4, respectively, using a least-squares computer

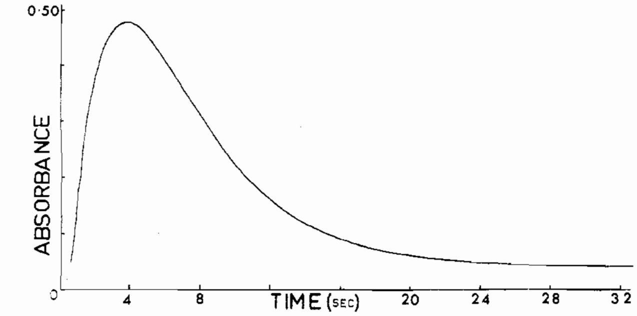


Figure 3. Absorbance *vs.* time at 226 nm for $(NH_3)_5CoNCO^{2+}$ ($5.48 \times 10^{-4}\ M$) in 1.00 $HClO_4$ at 25.0°.

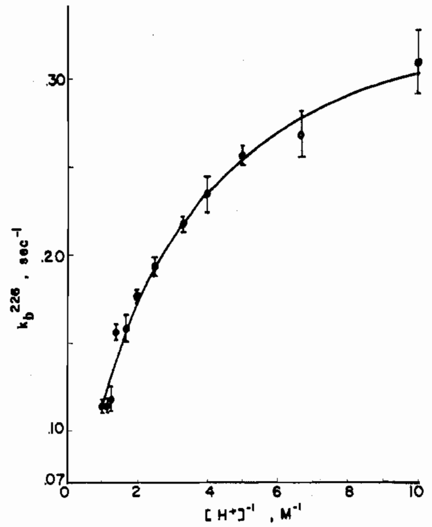


Figure 4. Variation of $k_b{}^{226}$ with $[H^+]$ for the subsequent reaction of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ at 226 nm, $\mu = 1.0$ ($LiClO_4$), and 25.0°. (The open circles represent the weighted averages[14] of replicate runs (10) while the error bars represent two standard deviations[18] of the averages. The solid line was calculated from the best fit values of k_2, k_3, and K_2 obtained by fitting the $k_b{}^{226}$ *vs.* $[H^+]$ data to eq 4.

$$k_b{}^{226} = \frac{k_2[H^+] + k_3K_2}{K_2 + [H^+]} \tag{4}$$

program[14] to yield best fit values of k, k_2, k_3, and K_2 of $0.174 \pm 0.005\ M^{-1}$ sec^{-1}, 0.001 ± 0.016 sec^{-1}, 0.376 ± 0.014 sec^{-1}, and $0.424 \pm 0.038\ M$, respectively.[19] Figures 2 and 4 show the dependence of $k_a{}^{226}$ on $[H^+]$ and the dependence of $k_b{}^{226}$ on $[H^+]$ respectively, as well as the solid lines calculated from the best fit values of k, k_2, k_3, and K_2. The significance of k_2, k_3, and K_2 is discussed later.

For kinetic data of the form given in Figure 3, it is not

---

(15) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1953, p 166.

(16) A_0, A_1, and A_2 are constants comprising k_1, k_2, and the molar extinction coefficients of the species A, B, and C.

(17) M. R. Osborne, "A Method for Fitting Exponentials to Data," Technical Report No. 31, Australian National University Computer Centre, Canberra, Australia, 1969.

(18) A subroutine was added to the computer program[17] which calculated A_0, A_1, and A_2 and then computed "best fit" values of A_t from the five calculated parameters.

(19) Ninety-five per cent confidence limits.

possible directly to assign k_a to the first reaction[20] and k_b to the second reaction (or *vice versa*) without additional experimental evidence. Fortunately, the kinetic data at 504 nm allow an assignment to be made. The data for the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ at 504 nm show a linear plot of log $(A_t - A_\infty)$ *vs.* t over a range of $[H^+]$ (0.060–0.50 M). The conditions (see Appendix) under which the system given by eq 3 will show a linear plot of log $(A_t - A_\infty)$ *vs.* t are as follows: (1) $0.1 > k_a/k_b$ or $k_a/k_b > 10$; (2) $\epsilon_b = \epsilon_c$, k_a is measured; (3) $k_a/k_b = (\epsilon_c - \epsilon_a)/(\epsilon_b - \epsilon_a)$, where ϵ_a, ϵ_b, and ϵ_c are the molar absorptivities of the species A, B, and C at some common wavelength. Since the data at 226 nm show a different $[H^+]$ dependence for k_a^{226} and k_b^{226}, the requirement that the ratio of the rate constants be a constant (condition 3), over the observed $[H^+]$, is not observed. From the data at 226 nm, it can be seen that condition 1 (rate constant ratio >10) only applies at $0.1 < [H^+] >> 1$ M. Yet condition 2 cannot exactly apply since above $[H^+] > 0.5$ M, a slight curvature in the log plots occurs. However if $\epsilon_b \neq \epsilon_c$ but $(\epsilon_b - \epsilon_c)$ is very small, the combination of a fairly large rate constant ratio and this small difference in ϵ_b and ϵ_c is sufficient to keep the third term in eq 2 negligible. As $[H^+]$ increases, the rate constant ratio decreases until eventually the third term becomes significant (at about 0.5 M H^+). The fact that, at any $[H^+]$, a shift in wavelength is sufficient to cause a loss of linearity is also good evidence that condition 2 is largely responsible for the linearity at 504 nm. Because condition 2 has been imposed to explain a negligible second exponential term, the resultant k_a^{504} value *must* correspond to the first reaction. It should be noted that neither of the conditions $\epsilon_a = \epsilon_b$ nor $\epsilon_a = \epsilon_c$ leads to a linear plot of log $(A_t - A_\infty)$ *vs.* time. Clearly the data at 504 and 226 nm give the same rate constant for the first process.

The deviation of the k_a^{504} *vs.* $[H^+]$ plots from eq 1 at $[H^+] > 0.5$ M occurs when the experimental error in the data of the log $(A_t - A_\infty)$ *vs.* time plot masks the very slight curvature in the plot expected when the values of k_a and k_b and ϵ_a and ϵ_b are only slightly different. The resultant "apparent" straight line yields a value for the specific rate constant which lies between the true values of k_a and k_b, hence the low value for k_a^{504}.

The kinetics of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ were also followed at an ionic strength of 3.0 ($LiClO_4$ or $NaClO_4$. The absorbance *vs.* time data (274, 264, 250, 235, and 220 nm) were analyzed by the same method as the lower ionic strength data. For the first reaction, the observed rate constant, k_a, in $LiClO_4$ media, varied directly with $[H^+]$ and was fitted[15] to eq 1 to give $k = 0.314$ M^{-1} sec^{-1}, at 25°. However, when $NaClO_4$ was used as a supporting electrolyte, a nonlinear plot of k_a *vs.* $[H^+]$ occurred. This was attributed to changes in activity coefficient of the complex as Na^+ was substituted for H^+ and will not be considered further. Figure 5 shows the variation of k_a with $[H^+]$ ($\mu = 3.0$, $NaClO_4$ or $LiClO_4$) as well as the solid line calculated from the best fit value of k ($\mu = 3.0$, $LiClO_4$). For the second reaction, in both $NaClO_4$ and $LiClO_4$ media, the observed rate constant, k_b, varied inversely with $[H^+]$ as

$$k_b = k_2 + k_3'/[H^+] \qquad (5)$$

and was fitted[15] to eq 5 to yield best fit values of the specific rate constants k_2 and k_3' of 0.019 sec^{-1} and 0.066 M sec^{-1} ($LiClO_4$) and 0.029 sec^{-1} and 0.052 M sec^{-1} ($NaClO_4$), respectively. Figure 6 shows the variation of k_b with $[H^+]$ ($\mu = 3.0$, $NaClO_4$ or $LiClO_4$) as well as the solid lines calculated from the best fit values of k_b.

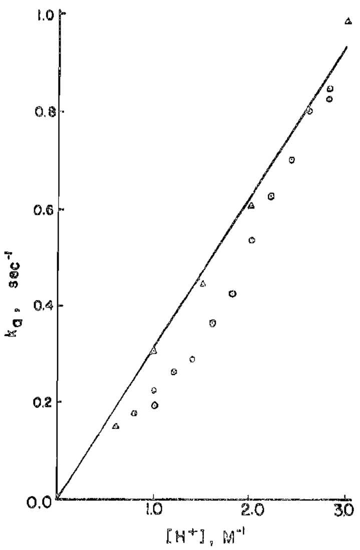


Figure 5. The first reaction (25°) in the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$, showing the variation of k_a with $[H^+]$: △, $\mu = 3$ ($LiClO_4$); ○, $\mu = 3$ ($NaClO_4$). (The solid line was calculated from the best fit value of k obtained by fitting the k_a *vs.* $[H^+]$ data ($LiClO_4$) to eq 1.)

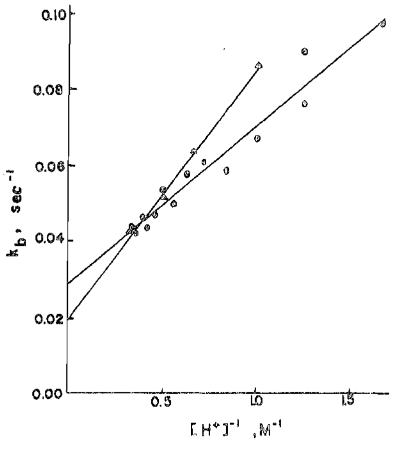


Figure 6. The subsequent reaction (25°) in the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$, showing the variation of k_b with $[H^+]$: △, $\mu = 3$ ($LiClO_4$); ○, $\mu = 3$ ($NaClO_4$). (The solid lines were calculated from the best fit values of k_2 and k_3 obtained by fitting the k_b *vs.* $[H^+]$ data to eq 5).

Table III. Consecutive Rate Constants[a] for the Acid Hydrolysis of $[(NH_3)_5CoNCO](ClO_4)_2$ in HCl, $HClO_4$, HBr, and HNO_3 at 25.0°

Acid	λ, nm	μ, M	$[H^+]$, M	k_a, sec^{-1}	k_b, sec^{-1}
$HClO_4$	274	3	3.0	0.99[b]	0.045[b]
HNO_3	330	3	3.0	1.0	0.019
HCl	285	3	3.0	2.0	0.031
HCl	274	3	3.0	1.9	0.029
HCl	250	3	3.0	1.9	0.024
HCl	274	2	2.0	0.88	0.042
HBr	274	2	2.0	0.76	0.055

[a] Obtained by plotting log $(A_t - A_\infty)$ *vs.* time (curved) and then calculating k_b from the last linear portion of the curve and k_a from a plot of log Δ *vs.* time where Δ is the difference between $(A_t - A_\infty)$ and the extrapolated linear portion of the curve. [b] Obtained by computer fitting[15] of eq 2.

The kinetics of the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ were also followed at various wavelengths in HCl, HBr, and

---

[20] N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, 66, 2110 (1970).

Table IV. Variation in Product Distribution[a] with Quenching Time[b] for the Acid Hydrolysis of $[(NH_3)_5CoNCO](ClO_4)_2$ in 3.0 *M* $HClO_4$ at 25.0°

Quench time	% $(NH_3)_6Co^{3+}$	% $(NH_3)_5CoO_2CNH_2^{2+}$ + % $(NH_3)_5CoOH_2^{3+}$	% A → B[c]	% B → C[d]
1.8 sec	99.0	1.0	82.6	7.4
4.7 sec	98.0	2.0	99.0	20.6
10 min	91.6	8.4	100.0	100.0

[a] Products separated by ion-exchange chromatography and concentrations analyzed by uv-visible and atomic absorption spectroscopy (see Experimental Section). [b] Quenching by dilution to $[H^+] = 0.1$ *M* where unreacted $(NH_3)_5CoNCO^{2+}$ goes completely to $(NH_3)_6Co^{3+}$. [c] $k_a = 0.99$ sec^{-1}. [d] $k_b = 0.045$ sec^{-1}.

Table V. Observed Rate Constants for the Nitrosation of $(NH_3)_5CoNCO^{2+}$ in $HClO_4$ at 25.0°, $\mu = 1.0$ ($LiClO_4$)

$[H^+]$,[a] *M*	$[HNO_2]$,[b] *M*	$10^2k_a^{NO}$,[c] sec^{-1}	10^2k^{NO}-(calcd),[g] sec^{-1}
0.0706	0.0288	1.32	1.24
0.0932	0.0062	1.57	1.63
0.0942	0.0051	1.64	1.65
0.4207	0.0762	7.47	7.37
0.4671	0.0297	7.82	8.18
0.4912	0.0056	7.83	8.60
0.4942	0.0026	8.20	8.64
0.8941	0.0994	15.5	15.6
0.9171	0.0764[d]	15.1	16.1
0.9177	0.0758	15.4	16.1
0.9180	0.0755	15.4	16.1
0.9201	0.0734[e]	15.8	16.1
0.9287	0.0713	15.1	16.2
0.9287	0.0713	14.7[f]	16.2
0.9641	0.0294	15.1	16.9
0.9729	0.0206	15.4	17.0
0.9834	0.0101	14.5	17.2
0.9870	0.0065	14.1	17.3
0.9884	0.0051	14.3	17.3
0.9910	0.0025	13.7	17.4

[a] $[H^+]$ calculated from eq 7. [b] $[HNO_2]$ calculated from eq 7. [c] Measured at 504 nm. [d] $LiNO_2$ used. [e] All solutions kept O_2 free. [f] Measured at 274 nm. [g] Calculated from eq 6 and the best fit value of k_a^{NO}.

HNO_3. The absorbance *vs.* time data were separated graphically[21] to yield values of k_a and k_b which are shown in Table III, along with a result from the $HClO_4$ data. This qualitative comparison indicates some specific ion catalysis with Cl^- and Br^- (k_a; HCl ~ HBr > $HClO_4$ ~ HNO_3) for the first reaction while the second reaction also seems to be sensitive to the anion used.

Time-Dependent Acid Hydrolysis Product Distribution. Since the acid hydrolysis of $(NH_3)_5CoNCO^{2+}$ at 0.1 *M* $[H^+]$ quantitatively produces $(NH_3)_6Co^{3+}$, any other products detected, after diluting a reaction mixture from 3.0 to 0.1 *M* H^+, must arise prior to dilution. Table IV gives the relative amount of carbamato plus aquo complex detected by this method at various reaction times. The 4.7-sec experiment shows that ~20% of the minor products $(NH_3)_5CoO_2CNH_2^{2+}$ and $(NH_3)_5CoOH_2^{3+}$ were produced during the time required for the subsequent reaction to have gone 20% toward completion. Thus it is evident that the carbamato and aquo products are produced during the subsequent reaction. Since the relative amount of $(NH_3)_6Co^{3+}$ formed varies with $[H^+]$ (Table I, no. 12–16), the production of $(NH_3)_6Co^{3+}$ can be associated with the k_3 path which also varies as $[H^+]^{-1}$ and the production of both $(NH_3)_5CoOH_2^{3+}$ and $(NH_3)_5CoO_2CNH_2^{2+}$ can be attributed to the k_2 path, which is independent of $[H^+]$ in the subsequent reaction rate law (4).

Nitrosation Tracer Study. Table II shows that the reaction of NO^+ with $(NH_3)_5CoNCO^{2+}$ in ^{18}O-enriched water gives $(NH_3)_5CoOH_2^{3+}$ which derives 0.93 of its oxygen atoms from the solvent and 0.07 of its oxygen atoms from the original NCO ligands. Although N_2 and CO_2 were detected as products, the measurement of the ^{18}O enrichment in CO_2 was not achieved. Contamination with nitrogen oxides prevented a reliable assessment of this enrichment and numerous attempts selectively to trap the gases failed.

Nitrosation Kinetics. The isocyanato complex was nitrosated with $NaNO_2$ in excess acid. The absorbance *vs.* time data at 504 nm were analyzed in the same way as for the acid hydrolysis data to yield a rate law (6) of the same form,

$$k_a^{NO} = k[H^+] \tag{6}$$

Table V. Clearly the rates are independent of $[HNO_2]$. Moreover, the derived rate constant $k = 0.174\ M^{-1}$ sec^{-1} is the same as that observed for acid hydrolysis and we conclude therefore that the preliminary and very largely rate-determining step for the nitrosation reaction is hydrolysis of the coordinated NCO^- ion. The values of $[H^+]$ and $[HNO_2]$ in Table V were calculated from

$$2[H^+] = (H_T - [NO_2^-] - K) + (([NO_2^-] + K - H_T) + 4KH_T)^{1/2}$$
$$[HNO_2] = H_T - [H^+] \tag{7}$$

where H_T, $[NO_2^-]$, and K were the initial H^+ concentration, the initial sodium nitrite concentration, and the dissociation constant for HNO_2 (5×10^{-4}),[2] respectively.

At wavelengths below 250 nm, crude absorbance *vs.* time plots similar to Figure 2 were again observed ($[H^+] = 0.98$, 1.01, and 2.92 *M* and $[HNO_3] = 0.0196$, 0.0059, and 0.0119 *M*, respectively). However, the high absorbance of acidic $NaNO_2$ solutions at these wavelengths prevented any reasonable quantitative analysis of the data. Figure 2 and Table V show that, unlike the acid hydrolysis data at 504 nm, the nitrosation rate constant, k_a^{NO}, only deviates from the linear behavior of eq 1 at $[H^+] > 0.9$ *M* and only then when $[HNO_2] < 0.10$ *M*. As the $[HNO_2]$ decreases, the value of k_a^{NO} decreases to the value of k_a^{504} at zero $[HNO_2]$. This indicates that, compared to the acid hydrolysis case, the ratio of the rate constants (k_b/k_a) does not decrease to <10 until $[H^+] \simeq 0.9$ *M and* $[HNO_2] \leqslant 0.1$ *M*. Since k_a has been shown not to be dependent on $[HNO_2]$, then k_b must be. Thus there is indirect evidence for a term in $[HNO_2]$ in the rate law for the second reaction.

Nitrosation Product Analysis. An additional indication of a $[HNO_2]$ term in the second reaction rate law is given by the data in Table VI, which show that for the nitrosation reaction the product ratio

$$R_{aquo} = [(NH_3)_5CoOH_2^{3+}]/[(NH_3)_6Co^{3+}] \tag{8}$$

is a function of both $[H^+]$ and $[HNO_2]$ according to the expression

$$\frac{R_{aquo}}{[H^+][HNO_2]} = \frac{a}{[HNO_2]} + b \tag{9}$$

---

(21) H. A. C. McKay, *J. Amer. Chem. Soc.*, 65, 702 (1943).

Table VI. Product Distribution for the Nitrosation of $[(NH_3)_5CoNCO](ClO_4)_2$ at 25.0° and $\mu = 1.0$ ($LiClO_4$)

$[H^+]$,[a] M	$[HNO_2]$,[b] M	% $(NH_3)_5$-$CoOH_2^{3+}$	R_{aquo} = $(NH_3)_5CoOH_2^{3+}$/$(NH_3)_5Co^{3+}$	$[HNO_2]^{-1}$, M^{-1}	R_{aquo}(obsd)/$[H^+][HNO_2]$, M^{-2}	R_{aquo}(calcd)[c]/$[H^+][HNO_2]$, M^{-2}
0.071	0.029	9.7	0.11	34.7	53	49
0.093	0.0062	3.2	0.033	161.0	58	58
0.42	0.076	59.8	1.5	13.1	47	48
0.47	0.030	40.0	0.067	33.7	48	49
0.49	0.0056	14.7	0.17	179.0	63	60
0.90	0.090	80.1	4.0	11.1	49	48
0.92	0.076	75.7	3.1	13.2	45	48
0.94	0.056	71.0	2.5	17.8	47	48
0.95	0.041	65.8	1.9	24.6	50	49
0.96	0.030	60.2	1.5	33.5	52	49
0.97	0.021	48.6	0.95	48.5	47	50
0.99	0.0051	22.7	0.29	195.0	58	61

[a] Calculated from eq 6. [b] Calculated from eq 7. [c] Calculated from eq 9 and the best fit values of *a* and *b*.

Table VII. Product Analysis of the Reaction of NO^+ with $(NH_3)_5CoNCO^{2+}$ in the Presence of a Competitor, Cl^- (1 M), at 25°

		%				
$[H^+]$, M	$[HNO_2]$, M	$(NH_3)_5CoCl^{2+}$	$(NH_3)_5CoOH_2^{3+}$	$(NH_3)_6Co^{3+}$	R,[a] M^{-1}	R_{cor},[b] M^{-1}
0.998	0.00239	8.0	45.6	46.4[c]	0.18	0.22
0.998	0.00239	7.8	47.5	44.7[c]	0.16	0.20
0.479	0.0209	7.2	47.0	45.8[c]	0.15	0.19
0.479	0.0209	7.9	44.1	48.0[c]	0.17	0.22
0.980	0.0304	10.3	66.1	23.1	0.16	0.20
0.911	0.0886	13.0	72.8	14.2[c]	0.18	0.22
0.913	0.0872	12.4	74.8	12.8[c]	0.17	0.20
0.909	0.0908	12.4	79.5	8.1	0.16	0.19
0.910	0.0901	13.0	79.4	7.6	0.16	0.20
0.909	0.0912	16.1	75.2	8.6	0.21	0.26
0.911	0.0895	13.2	71.9	14.9	0.08	0.22
0.98	0.020	18.9	81.1		0.23[d]	0.23

[a] $R = [(NH_3)_5CoCl^{2+}]/[(NH_3)_5CoOH_2^{3+}][Cl^-]$. [b] $R_{cor} = [Cl^{NO}]/[OH_2^{NO}][Cl^-]$ where $[Cl^{NO}] = [Cl^T] - [Cl^{carb}]$, $[Cl^{carb}] = \%\ (NH_3)_5CoO_2CNH_2^{2+\,c} \times R_{carb}/[Cl^-]/(1 + R_{carb}/[Cl])$, $[OH_2^{NO}] = ([OH_2^T] - [OH_2^{H^+}] - [OH_2^{carb}) \times 0.86$, and $[OH_2^{carb}] = \%\ (NH_3)_5CoOH_2^{3+} \times [Cl^-]/R_{carb}/(1 + [Cl^-]/R_{carb})$. $[Cl^T]$ and $[OH_2^T]$ are the experimental percentages of chloro and aquo products while R_{carb} is the competition ratio (0.19) for the nitrosation of the O-bonded carbamate complex.[3] $[OH_2^{H^+}]$ is the experimental percentage of aquo product found for the acid hydrolysis in HCl (Table I, no.7). [c] Percentage of carbamato product found for the acid hydrolysis in HCl (Table I, no. 6, 7). [d] $[Co(NH_3)_5N_3](ClO_4)_2$; 0.2 mmol nitrosated in 1 M HCl.

The data have been fitted[14] to eq 9 to give best fit values for *a* and *b* of 0.071 ± 0.023 M^{-1} and 46.8 ± 2.2 M^{-2}, respectively.

Competition Study. The results of the product analysis of the nitrosation of $(NH_3)_5CoNCO^{2+}$ in the presence of Cl^-, which can compete with OH_2 for the possible five-coordinate intermediate, $(NH_3)_5Co^{3+}$, are given in Table VII. The nitrosation of $(NH_3)_5CoN_3^{2+}$ in the presence of Cl^- was done under the same conditions as the above experiment. The results of the product analysis of that experiment are also given in Table VII. In an experiment using NO_3^- (1 M) as competitor the competition ratio is $[Co(NH_3)_5NO_3^{2+}]/[Co(NH_3)_5OH_2^{3+}][NO_3] = 0.37$. After correction for the aqua complex arising from the paths above which do not lead to competition by anions this value increased to 0.46.

Discussion

Acid Hydrolysis. The rate laws of the reaction of $(NH_3)_5CoNCO^{2+}$ in acidic solutions are consistent with the mechanism

$$(NH_3)_5CoNCO^{2+} + H^+ \overset{K_1}{\rightleftarrows} (NH_3)_5CoNCOH^{3+} \qquad (10)$$

$$(NH_3)_5CoNCOH^{3+} + H_2O \xrightarrow{k_1} (NH_3)_5CoNH_2COOH^{3+} \qquad (11)$$

$$(NH_3)_5CoNH_2COOH^{3+} \overset{K_2}{\rightleftarrows} (NH_3)_5CoNHCOOH^{2+} + H^+ \qquad (12)$$

$$(NH_3)_5CoNH_2COOH^{3+} \xrightarrow{k_2'} (NH_3)_5CoOCONH_2^{2+} + H^+ \qquad (13)$$

$$(NH_3)_5CoNH_2COOH^{3+} + OH_2 \xrightarrow{k_2''} (NH_3)_5CoOH_2^{3+} + NH_3 + CO_2 \qquad (14)$$

$$(NH_3)_5CoNHCOOH^{2+} \xrightarrow{k_3} (NH_3)_5CoNH_2^{2+} + CO_2 \qquad (15)$$

$$(NH_3)_5CoNH_2^{2+} + H^+ \xrightarrow{\text{fast}} (NH_3)_6Co^{3+} \qquad (16)$$

For the first reaction observed, the assumption of a fast protonation followed by a rate-controlling addition of a water molecule leads to a derived rate law of the form

$$k_a = \frac{k_1K_1[H^+]}{1 + K_1[H^+]} \qquad (17)$$

The results require that $1 >> K_1[H^+]$ and $k_a = k_1K_1[H^+] = k[H^+]$. It follows that $K_1 < 0.05$ which is not surprising considering the low basicity of analogous coordinated ions such as azide and thiocyanate. While N appears to be more basic than O in the free NCO^- ion, it seems more likely that once N is coordinated O becomes the more basic atom. Protonation at either N or O however should activate the C atom to nucleophilic attack by H_2O.

Assuming the mechanism (12)-(16) the reaction (k_b) requires a rate law of the form

$$-d[I]/dt = (k_2' + k_2'')[(NH_3)_5CoNH_2CO_2H^{3+}] + k_3[(NH_3)_5CoNHCO_2H^{2+}] \qquad (18)$$

where $[I] = [(NH_3)_5CoNH_2CO_2H^{3+}] + [(NH_3)_5CoNHCO_2H^{2+}]$ and leads to

$$k_b = \frac{(k_2' + k_2'')[H^+] + k_3K_2}{K_2 + [H^+]} \tag{19}$$

This agrees with the rate law observed for the second reaction at $\mu = 1$ ($LiClO_4$) for $[H^+] = 0.1$-1 *M*, Figure 4. Presumably at high H^+ concentrations (1-3 *M*) and high ionic strength ($\mu = 3$ ($LiClO_4$)) H^+ is much greater than K_2 and the rate law reduces to

$$k_b = (k_2' + k_2'') + k_3K_2/[H^+] \tag{20}$$

It appears that at $\mu = 3$, K_2 is significantly less than 0.424 *M*, the value found at $\mu = 1$.

The derived product ratio is given by

$$\frac{[(NH_3)_5CoOH_2^{3+}] + [(NH_3)_5CoOOCNH_2^{2+}]}{[(NH_3)_6Co]^{3+}} = \frac{(k_2' + k_2'')[H^+]}{k_3K_2} \tag{21}$$

and the amounts of aquo- and O-bonded carbamato complex produced are essentially proportional to $[H^+]$. In 1 *M* $HClO_4$ the observed product ratio indicates that $k_2 = k_2' + k_2''$ is ~0.008 sec^{-1} which is consistent with the rate constant and tolerance deduced from the kinetic data. The ratio of *O*-carbamato product to aquo product is also sensitive to the anion present and substantially more of the former appears in HCl solutions than in $HClO_4$. This is not especially surprising since both k_a and k_b are sensitive to which anion is present.

The mechanistic proposals are consistent with the ^{18}O-tracer experiments which show only one oxygen atom of the CO_2 product derived from the solvent. Additional support comes from the related hydrolysis of $[(NH_3)_5RhNCO]^{2+}$ where the same rate law was observed for the first process and the intermediate $[(NH_3)_5RhNH_2CO_2H](ClO_4)_3$ was isolated.[22] Analogous processes also occur with the hydrolysis of alkyl isocyanates[23] to unstable carbamates and the attack of free cyanate ion by coordinated OH^- ion in $(NH_3)_5CoOH^{2+}$ to produce the O-bonded carbamatocobalt(III) pentaammine complex ion.[9,10]

For the second reaction the analogy between metal and alkyl carbamates can be continued. The spontaneous decarboxylation of $(NH_3)_5RhNHCOOH^{2+}$ [22] and $(NH_3)_5CoNHCOOH^{2+}$ in acid to give $[(NH_3)_6M]^{3+}$ and CO_2 (M = Rh, Co) has an exact parallel in the rapid decomposition of RNHCOOH to RNH_2 and CO_2.[23] Also, the metal chemistry, where the metal is regarded as a substitute for a proton, might be considered a model for the decomposition of carbamic acid: $NH_2COOH \rightarrow NH_3 + CO_2$. It would appear to eliminate for example H_2O attack at the carbonyl center to generate NH_4^+ and HCO_3^- as a feasible mechanistic path.

The detection and isolation of $(NH_3)_5CoOCONH_2^{2+}$ demonstrates another example of linkage isomerization similar to that seen for N- and O-bonded sulfamate,[24] N- and S-bonded thiocyanate,[25] and N- and O-bonded nitrite ions.[26] The results also imply that isomerization might occur on a small scale during the acid hydrolysis of the $(NH_3)_5RhNCO^{2+}$ and $(NH_3)_5RuNCO^{2+}$ ions.[22] However, in these instances rupture of the metal-nitrogen bond should be less easily achieved than for Co(III). Such an argument would be consistent at least with the general chemistry of cobalt(III)- and rhodium(III)-amine complexes. The carbamate isomer has now been sought by spectral methods in Rh chemistry and was not found.[22]

The rearrangement of the N- to O-bonded carbamate is effected by the fully protonated species. This property has been observed also in the (amide N)-bound peptide species where protonation of the N center leads to a rearrangement to the (carbonyl O)-bound species.[27] The property is also consistent with the fully protonated species being a good leaving group from the Co(III) center. Deprotonation at the carbamate N center stabilizes the Co-N bond and relatively CO_2 becomes a better leaving group. Presumably, decomposition of $(NH_3)_5CoNHCOOH^{2+}$ parallels the acid independent path for the decomposition of $(NH_3)_5RhNHCOOH^{2+}$.[22] For carbamic acid and the *N*-alkylcarbamic acids as well as for $(NH_3)_5CoNHCOOH^{2+}$ and $(NH_3)_5RhNHCOOH^{2+}$ it is likely that CO_2 is the leaving group and proton transfer from the carboxylate moiety to the N center therefore is effected by H_2O and may precede or be synchronous with its loss.

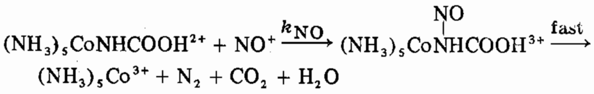
Nitrosation. The nitrosation kinetic and product analysis data are consistent with the following mechanism in addition to eq 10-16.

$$H^+ + NO_2^- \underset{}{\overset{K_{N1}}{\rightleftharpoons}} HNO_2 \tag{22}$$

$$H^+ + HNO_2 \overset{K_{N2}}{\rightleftharpoons} H_2NO_2^+ \tag{23}$$

$$H_2NO_2^+ \underset{k_y}{\overset{k_x}{\rightleftharpoons}} H_2O + NO^+ \tag{24}$$

$$(NH_3)_5CoNH_2COOH^{3+} \overset{K_2}{\rightleftharpoons} (NH^3)^5CoNHCOOH^{2+} + H^+ \tag{25}$$



$$(NH_3)_5CoNHCOOH^{2+} + NO^+ \xrightarrow{k_{NO}} (NH_3)_5Co\overset{NO}{\overset{|}{N}}HCOOH^{3+} \xrightarrow{fast} (NH_3)_5Co^{3+} + N_2 + CO_2 + H_2O \tag{26}$$

$$\left.\begin{aligned} &(NH_3)_5Co^{3+} + H_2O \xrightarrow{fast} (NH_3)_5CoOH_2^{\,3+} \\ &(NH_3)_5Co^{3+} + Cl^- \xrightarrow{fast} (NH_3)_5CoCl^{2+} \end{aligned}\right\} \tag{27}$$

The derived rate law for the disappearance of $(NH_3)_5CoNHCO_2H^{2+}$ (I) by both nitrosation and hydrolysis assuming a steady-state concentration of NO^+ is

$$-\frac{d[I]}{dt} = \left(\frac{(k_2' + k_2'')[H^+] + k_3K_2}{K_2 + [H^+]} + \frac{k_{NO}k_xK_2K_{N2}[H^+][HNO_2]}{k_{NO}K_2[I] + k_y(K_2 + [H^+])}\right)[I] \tag{28}$$

where $[I] = [(NH_3)_5CoNH_2CO_2H^{3+}] + [(NH_3)_5CoNHCO_2H^{2+}]$. If $k_{NO}K_2[I] << k_y(K_2 + [H^+])$, then the rate law reduces to

$$-\frac{d[I]}{dt} = \left(\frac{(k_2' + k_2'')[H^+] + k_3K_2}{K_2 + [H^+]} + \frac{k_{NO}k_xK_2K_{N2}[H^+][HNO_2]}{k_y(K_2 + [H^+])}\right)[I] \tag{29}$$

Although the observed rate for the nitrosation is very largely the acid-catalyzed hydration of coordinated NCO^-, there is evidence for a dependence on HNO_2 for the rate of subse-

---

[22] P. C. Ford, *Inorg. Chem.*, 10, 2153 (1971), and private communication.

[23] See J. H. Saunders and K. C. Frisch, "Polyurethanes," Part I, Interscience, New York, N. Y., 1965, p 180.

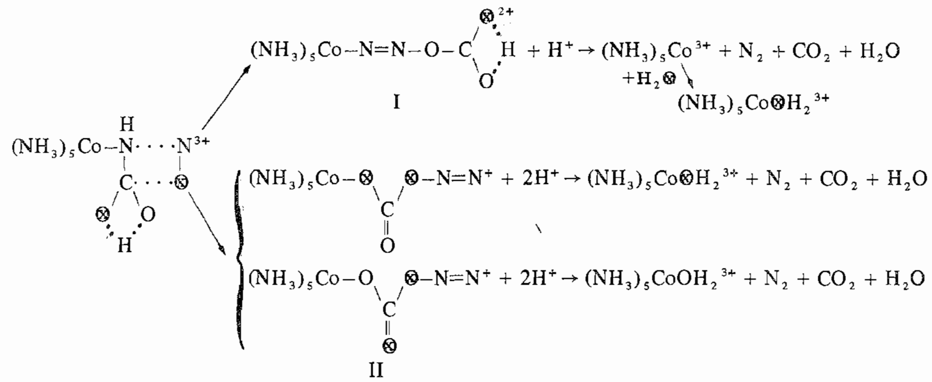
[24] E. Sushynski, A. Van Roodselaar, and R. B. Jordan, *Inorg. Chem.*, 11, 1887 (1972).

[25] D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 9, 655 (1970).

[26] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 291.

[27] H. C. Freeman, *Advan. Protein Chem.*, 22, 257 (1967).

Scheme I



quent steps. The latter data were not good enough to determine if there was also a term in $[H^+]$ but the nitrosation product ratio does provide evidence for such a term. Since only the k_3 path leads to $Co(NH_3)_6{}^{3+}$

$$R_{aquo} = (k_2' + k_2'' + k_{NO}k_xK_2K_{N2}[HNO_2]/k_y)[H^+]/k_3K_2 \qquad (30)$$

or

$$\frac{R_{aquo}}{[H^+][HNO_2]} = \frac{k_2' + k_2''}{k_3K_2[HNO_2]} + \frac{k_{NO}k_xK_{N2}}{k_yk_3} \qquad (31)$$

A plot of $R_{aquo}/[H^+][HNO_2]$ against $[HNO_2]^{-1}$ shows significant differences at high and low H^+.

The value k_{NO} can be determined from the last term in equation 31. Values for b (eq 9), k_3, and k_xK_{N2}/k_y[28] of $4.7\ M^{-2}$, $0.38\ M^{-1}$, and $3 \times 10^{-7}\ M^{-1}$, respectively, yield a value of k_{NO} of $\sim 6 \times 10^7\ M^{-1}\ sec^{-1}$. A value of $2.2 \times 10^3\ M^{-1}\ sec^{-1}$ for k_xK_{N2} was obtained by Anbar and Taube[29] using ^{18}O-exchange data which allow a value of $\sim 7 \times 10^9\ sec^{-1}$ for k_y. It can now be shown that $k_{NO}K_2 \cdot [I] << k_y(K_2 + [H^+])$ is valid ($[H^+] = 0.0706\ M$, $K_2 = 0.42\ M$, $[I] = 1 \times 10^{-3}\ M$).

The value of $k_2' + k_2''$ ($0.011 \pm 0.005\ sec^{-1}$) calculated from the value of a (eq 9) and the kinetic values is considerably more accurate than that determined from kinetic data in the acid hydrolysis study. Also it agrees reasonably with the value estimated from the product ratio ($0.008\ sec^{-1}$) for the hydrolysis reaction. The production of N_2 from the nitrosation reaction also indicates that NO^+ adds at the deprotonated N center, and the ^{18}O-tracer experiments indicate two paths for the decomposition of the nitrosated intermediate. Since H_2O and HNO_2 exchange rapidly,[29] NO^+ will be representative of the solvent oxygen isotope distribution. In all, 93% of the aquo product also shows this distribution and 7% has an oxygen atom from the parent isocyanato complex. Two modes of rearrangement of the nitrosated N-bonded carbamato intermediate appear to be pertinent (Scheme I), one giving coordinated azocarbonate bonded through the N atom (I) and the other giving azocarbonate bonded through an O atom, (II). Clearly in these species two of the O atoms will be enriched in ^{18}O to the solvent level. Also the two oxygen atoms not bound to nitrogen in the first intermediate are equivalent. In the second intermediate however they are not equivalent. Decomposition of the two types of azocarbonate complexes leads to the intermediate $(NH_3)_5Co^{3+}$ (86%) by loss of water, CO_2, and then N_2 in one path and by loss of N_2 and then CO_2 to give the aquo complex[30] in the other path. This type of behavior was also observed in the nitrosation of the carbamate esters.[31] Moreover, the rearrangement proposed to accommodate the lack of enrichment in some of the aquo product is analogous to that observed in the acid hydrolysis reaction, namely, the isomerization of N-bonded carbamate to O-bonded carbamate.

If the intermediate $(NH_3)_5Co^{3+}$ (86%) is produced, then it should compete for nucleophiles other than H_2O in the solvent. This property has been sought and found largely for nitrosation in HCl solutions where the principal competitors are H_2O and Cl^-. In the assessment of the competition ratio, a correction must be made for that part of the nitrosation of $(NH_3)_5CoNHCOOH^{2+}$ which leads directly to $(NH_3)_5CoOH_2{}^{3+}$ (14%) and for $(NH_3)_5CoOH_2{}^{3+}$ which arises from the competing hydrolysis reaction. The aquo complex arising directly from nitrosation of $(NH_3)_5CoOCONH_2{}^{2+}$ can be neglected ($\lesssim$0.3% in 1 M H^+). The aquo product arising directly from acid hydrolysis was evaluated by relation to the amount of hexaammine produced and the product ratio for the simple acid hydrolysis study. The competition ratios for H_2O and Cl^- recorded in Table VII agree within the error with those obtained for nitrosation of $Co(NH_3)_5N_3{}^{2+}$[2,3] and $Co(NH_3)_5OCONH_2{}^{2+}$,[3] for Co^{3+} oxidation of $(NH_3)_5CoN_3{}^{2+}$[4] and for the competition for the intermediate induced by photolysis of $(NH_3)_4Co(NH_2)(O_2)Co(NH_3)_4{}^{4+}$.[6] A similar result was obtained for H_2O and NO_3^- as competitors ($R = 0.46$ compared with the previous value $R = 0.49$[3]). This is a fairly sensitive test for the $Co(NH_3)_5{}^{3+}$ species since NO_3^- competes twice as well as Cl^-.

The results support the proposition that a common intermediate is generated in all these reactions. Note also that a trace of $(NH_3)_5CoNO_2{}^{2+}$ ion is produced in the nitrosation reactions.[10] Capture of the N atom is consistent with the presence of the intermediate and is inconsistent with the reaction between HNO_2 and $(NH_3)_5CoOH_2{}^{3+}$ which yields $(NH_3)_5CoONO^{2+}$.[26]

The reactions of coordinated NCO^- ion recorded here also have some parallel in preparative studies conducted by Ablov.[32] Aqueous solutions (pH 2-7) of *trans*-$[CoI(NCO)(DH)_2]$ (DH = dimethylglyoxime) produce both *trans*-$[CoI(NH_3)(DH)_2]$ and *trans*-$[CoI(OH_2)(DH)_2]$; at higher acid concentrations more of the aquo complex is formed. How-

---

(28) T. A. Turney and G. A. Wright, *J. Chem. Soc.*, 2415 (1958).

(29) M. Anbar and H. Taube, *J. Amer. Chem. Soc.*, 76, 6243 (1954).

(30) J. P. Hunt, A. C. Rutenberg, and H. Taube, *J. Amer. Chem. Soc.*, 74, 268 (1952).

(31) R. Huisgen and H. Reimlinger, *Justus Liebigs Ann. Chem.*, 599, 11 (1956).

(32) A. V. Ablov, N. M. Samus, and A. A. Popova, *Russ. J. Inorg. Chem.*, 16, 215 (1971).

ever, the reaction of dilute HNO_2 and *trans*-$[Co(OH_2)(NCO)(DH)_2]$ resulted in the formation of only *trans*-$[Co(NO_2)(NH_3)(DH)_2]$. Presumably the HNO_2 concentration was too low to compete effectively with the hydrolysis path.

In summary, this study provides evidence that the reactions of coordinated cyanate parallel the reactions of organic isocyanates, that carbamic acid can be stabilized relative to the free acid by coordination to a metal ion, that nitrosation of the coordinated cyanate proceeds *via* a carbamate intermediate, and that linkage isomerization occurs with coordinated carbamate. Also there is additional evidence for the $(NH_3)_5Co^{3+}$ intermediate.

Acknowledgment. A. M. S. expresses his gratitude to Professor Jannick Bjerrum, Claus Schaffer, and the University of Copenhagen for their hospitality in Chemistry Department I, during which some preliminary (nitrosation) experiments were conducted, and to Solveig Kallesoe for assistance at that time. We are also indebted to the Microanalytical Unit at the Australian National University and F. Bergerson and G. Turner, CSIRO, Canberra, for some ^{18}O analyses.

Appendix

The purpose of this Appendix is to show conditions under which systems of two consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (A1)$$

will give a linear plot of log $(A_t - A_\infty)$ *vs.* t, where A_t, A_∞, and t have been defined previously.

For eq A1 the concentrations of the species are given by

$$[A] = A_0 e^{k_1 t} \qquad (A2)$$

$$[B] = \frac{A_0 k_1}{k_2 - k_1}(e^{-k_1 t} - e^{k_2 t}) \qquad (A3)$$

$$[C] = A_0[1 + \frac{1}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})] \qquad (A4)$$

where A_0 is the initial concentration of A.

The absorbance of the reaction solution at time t is given by

$$A_t = \epsilon_a l[A] + \epsilon_b l[B] + \epsilon_c l[C] \qquad (A5)$$

where ϵ_a, ϵ_b, and ϵ_c are the molar extinction coefficients of species A, B, and C, respectively, and l is the spectrophotometer cell length in centimeters. Subsituting eq A2, A3, and A4 into eq A5 and collecting terms in $e^{-k_1 t}$ and $e^{-k_2 t}$ results in

$$A_t - A_\infty = lA_0[\frac{(k_2\epsilon_a - k_1\epsilon_a + k_1\epsilon_b - k_2\epsilon_c)}{k_2 - k_1}e^{-k_1 t} + \frac{k_1}{k_2 - k_1}(\epsilon_c - \epsilon_b)e^{-k_2 t}] \qquad (A6)$$

where

$$A_\infty = \epsilon_c l A_0 \qquad (A7)$$

Rearranging and factoring the first term gives

$$A_t - A_\infty = \frac{lA_0}{k_2 - k_1}[(k_2 - k_1)(\epsilon_a - \epsilon_c) - k_1(\epsilon_c - \epsilon_b)]e^{-k_1 t} + \frac{lA_0 k_1}{k_2 - k_1}(\epsilon_c - \epsilon_b)e^{-k_2 t} \qquad (A.8)$$

Inspection of eq A8 shows the following conditions allow a near-linear plot of log $(A_t - A_\infty)$ *vs.* t: (1) $k_1 >> k_2$ or $k_2 >> k_1$; (2) $\epsilon_b = \epsilon_c$; (3) $k_1/k_2 = (\epsilon_c - \epsilon_a)/(\epsilon_b - \epsilon_a)$.

Registry No. $(NH_3)_5CoNCO^{2+}$, 19998-52-8; $(NH_3)_5CoNH_2CO_2H^{3+}$, 52133-51-4; $(NH_3)_5CoO_2CNH_2{}^{2+}$, 19173-65-0; $(NH_3)_5CoNHCO_2H^{2+}$, 52133-52-5; $[(NH_3)_5CoNCO](ClO_4)_2$, 27427-52-7.

Contribution from the Department of Chemistry,
Kent State University, Kent, Ohio 44242

Electron Transfer through Organic Structural Units. XVI. Reductions of Carboxylatopentaamminecobalt(III) Complexes with Europium(II)[1]

FU-REN FRANK FAN and EDWIN S. GOULD*

Received March 6, 1974 AIC401542

The specific rates of reduction of 53 pentaamminecobalt(III) complexes (containing a variety of carboxylato groups) with Eu^{2+} and Cr^{2+} are compared. The Eu(II) rates span a range of almost 10^7, but over half fall in the interval 0.8–2.0 M^{-1} sec^{-1}. Specific rates much less than unity are encountered with complexes bearing bulky ligands. For oxidants in this category, rates with the two reducing centers fit the relationship $\log k_{Eu} = 0.67 \log k_{Cr} + 0.54$, the slope of the regression line being significantly less than unity, the value observed for outer-sphere reductions. Reductions with Eu^{2+} are disproportionately accelerated by neighboring hydroxy, alkoxy, fluoro, and sulfonate groups, in contrast to the reactions of Cr^{2+}, for which rate enhancements are more marked when neighboring substituents feature the softer sulfur and nitrogen donor centers. The acidity dependence by the acetato complex leads to a specific rate of 0.25 M^{-1} sec^{-1} for the reduction, probably by an outer-sphere path, of the protonated form of this derivative. A number of the inverse acid paths observed for Cr^{2+} reductions of complexes having a neighboring COOH group disappear with Eu^{2+}. For three of the complexes, each having a CHO group remote from, but conjugated with, $COOCo^{III}$, the rate law for reduction with Eu^{2+} includes a term first order in H^+. Experience with other reductants indicates that these reactions proceed, at least in part, by initial Eu^{2+} attack at CHO. This remote path is much less facile for Eu^{2+} than for Cr^{2+}. The observed patterns support the view that the several variants of the inner-sphere mechanism which have been defined for Cr^{2+} extend also to Eu^{2+} and that mediating paths or chelating functions featuring hard donor centers especially favor reductions by Eu^{2+}.

Aside from reductions by Cr^{2+}, which center may be considered the prototype inner-sphere reductant,[2] strong evidence

---

[1] Sponsorship of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) H. Taube, H. Myers, and R. L. Rich, *J. Amer. Chem. Soc.*, 75, 4118 (1953); (b) H. Taube and H. Myers, *ibid.*, 76, 2103 (1954); (c) H. Taube and E. S. Gould, *Accounts Chem. Res.*, 2, 321 (1969).