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Hydrolysis of Coordinated Cyanate Ion. A Comparison of the Isocyanatopentaammine Complexes of Ruthenium(III) and of Rhodium(III)

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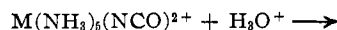
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A kinetic study of the acid-catalyzed hydrolysis of coordinated cyanate ion to coordinated ammonia plus carbon dioxide has been carried out for the complex ions $\text{Ru}(\text{NH}_3)_5(\text{NCO})^{2+}$ and $\text{Rh}(\text{NH}_3)_5(\text{NCO})^{2+}$. In dilute acid, the hydrolysis of each complex displayed a simple second-order rate law: $d[\text{M}(\text{NH}_3)_5(\text{NCO})^{2+}]/dt = k_2[\text{M}(\text{NH}_3)_5(\text{NCO})^{2+}][\text{H}^+]$ with $k_2 = 0.62 \pm 0.02 \text{ M}^{-1} \text{ sec}^{-1}$ for $\text{M} = \text{Rh}(\text{III})$ ($\Delta H^\ddagger = 10.9 \text{ kcal/mol}$, $\Delta S^\ddagger = -23 \text{ eu}$) and with $k_2 = 0.059 \pm 0.001 \text{ M}^{-1} \text{ sec}^{-1}$ for $\text{M} = \text{Ru}(\text{III})$ ($\Delta H^\ddagger = 12.2 \text{ kcal/mol}$, $\Delta S^\ddagger = -23 \text{ eu}$) at 25.0° . At higher acid concentrations ($>0.1 \text{ M}$), hydrolysis of the rhodium(III) complex displays more complicated spectrophotometric kinetics owing to the relative stability of a reaction intermediate $\text{Rh}(\text{NH}_3)_5(\text{NH}_2\text{CO}_2\text{H})^{3+}$ which can be isolated as a solid salt and characterized spectroscopically. This species decomposes in the solid form and in aqueous solution to give CO_2 plus $\text{Rh}(\text{NH}_3)_5^{3+}$. In aqueous solution, the decomposition follows the rate law $d[\text{Rh}(\text{NH}_3)_5(\text{NH}_2\text{CO}_2\text{H})^{3+}]/dt = (k_0 + k_{-1}[\text{H}^+]^{-1})[\text{Rh}(\text{NH}_3)_5(\text{NH}_2\text{CO}_2\text{H})^{3+}]$ with $k_0 = 2.1 \times 10^{-3} \text{ sec}^{-1}$ and $k_{-1} = 0.96 \times 10^{-3} \text{ M sec}^{-1}$ at 25° . These data and reactivity differences between the ruthenium(III) and rhodium(III) complexes are interpreted in terms of the probable hydrolysis mechanism.

Introduction

Reactions of ligands coordinated to transition metals have been a topic of considerable interest in recent years.¹ These studies have taken the form of comparisons of reaction characteristics of coordinated *vs.* uncoordinated (free) ligands and comparisons of different metal ion coordination sites with ligand reactions. Relatively few studies (outside organometallic systems) have compared ligand reactivity between analogous complexes where the only difference is a single nuclear charge or a single d-orbital electron. Comparisons of such compound pairs have been made² for properties and some reactions of organonitrile ligands in the isoelectronic complex ions $\text{Ru}(\text{NH}_3)_5(\text{RCN})^{2+}$ and $\text{Rh}(\text{NH}_3)_5(\text{RCN})^{3+}$ (both low-spin $4d^6$) where the principal difference is a single metal atom nuclear charge and have been made for some ammine complexes of Ru(II) and Ru(III) where the difference is one $4d$ electron and consequently a $+1$ difference in ionic charge.³ In the present study are compared the reactivity of coordinated cyanate ion in the analogous complexes $\text{Ru}(\text{NH}_3)_5(\text{NCO})^{2+}$ (low-spin $4d^6$) and $\text{Rh}(\text{NH}_3)_5(\text{NCO})^{2+}$ (low-spin $4d^6$) having the same electrostatic charge but electronic configurations differing by one d-orbital electron.

The principal reaction with which this study is concerned is the acid-catalyzed hydrolysis of coordinated cyanate ion to carbon dioxide plus coordinated ammonia (eq 1). Balahura and Jordan⁴ have reported a similar



study of the analogous cobalt(III) complex (eq 1, $\text{M} = \text{Co}(\text{III})$) where they demonstrated that the reaction rate is first order in acid concentration. A similar acid-catalyzed pathway has been reported for the hydrolysis of cyanic acid (HNCO) to CO_2 plus NH_4^+ .

Experimental Section

Materials.—Chloropentaammineruthenium(III) chloride, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, was prepared by published methods from ruthenium trichloride (Engelhard Industries).^{5a} Chloropentaammine-rhodium(III) chloride, $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, was prepared by the method of Johnson and Basolo⁵ from rhodium trichloride (Engelhard Industries). Aquopentaamminerhodium(III) perchlorate, $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}][\text{ClO}_4]_2$, was prepared using the method of Foust² by refluxing aqueous $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ 2 hr in the presence of stoichiometric silver(I) perchlorate ($\text{Ag}(\text{I}):\text{Rh}(\text{III}) = 3$). Filtration of the hot reaction solution followed by addition of sodium perchlorate leads to a nearly quantitative yield of solid $[\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}][\text{ClO}_4]_3$. Sodium cyanate (Sargent), urea (Mallinckrodt), and Spectrograde *N,N*-dimethylacetamide (Aldrich) were obtained from commercial sources and used without further purification.

Syntheses. $[\text{Ru}(\text{NH}_3)_5(\text{NCO})]\text{Br}_2$.— $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (0.27 g, 0.93 mmol) was digested in a 5-ml silver trifluoroacetate solution (prepared by dissolving Ag_2O (0.20 g, 0.86 mmol) in sufficient aqueous trifluoroacetic acid). The resulting solution was filtered to remove silver chloride and deaerated by entraining with argon in a small separatory funnel. The Ru(III) of this solution was then reduced by adding granular zinc amalgam (0.5 g) and agitating the solution with a stream of purified argon. After sufficient time (about 10 min) to effect complete reduction to Ru(II), the solution was neutralized with sodium bicarbonate, solid sodium cyanate (0.5 g, 7.7 mmol) was added to it with agitation, and the resulting mixture was immediately filtered. The filtrate solution was then exposed to air to allow slow oxidation to Ru(III). Subsequent addition of sodium bromide solution gave a dark yellow precipitate which was recrystallized from hot water to give 0.21 g (0.54 mmol, 58% yield) of $[\text{Ru}(\text{NH}_3)_5$ -

(1) For an extensive review see M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York, N. Y., 1968.

(2) R. D. Foust, Jr., and P. C. Ford, presented at the Pacific Conference for Chemistry and Spectroscopy, San Francisco, Calif., Oct 1970; to be submitted for publication.

(3) (a) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 227 (1970); (b) R. E. Clarke and P. C. Ford, *ibid.*, **9**, 495 (1970); (c) P. C. Ford, R. D. Foust, Jr., and R. E. Clarke, *ibid.*, **9**, 1933 (1970).

(4) R. J. Balahura and R. B. Jordan, *ibid.*, **9**, 1567 (1970).

(5) S. A. Johnson and F. Basolo, *ibid.*, **1**, 925 (1962).

(NCO)]Br₂. *Anal.* Calcd for CH₁₅N₆OBr₂Ru: C, 3.1; H, 3.9; N, 21.7. Found: C, 3.2; H, 3.9; N, 21.3.

[Rh(NH₃)₅(NCO)][ClO₄]₂.—The synthesis procedure was a modification of the method of Balahura and Jordan⁴ used to prepare the analogous cobalt(III) compound. [Rh(NH₃)₅H₂O][ClO₄]₃ (0.321 g, 0.64 mmol), urea (0.33 g, 5.5 mmol), "Linde" molecular sieve (0.5 g, Type 3A), and 5 ml of Spectrograde *N,N*-dimethylacetamide were heated together for 3 hr at 125° in a small, round-bottom flask with occasional stirring. After this period, the mixture was filtered while hot, and 2-butanol (about 30 ml) was added to the filtrate solution to give, after cooling, a very pale yellow precipitate. This solid was collected to give, after cooling, a very pale yellow precipitate. This solid was collected by filtration and recrystallized from ethanol-water to give 0.176 g (0.41 mmol, 65% yield) of microcrystalline [Rh(NH₃)₅(NCO)][ClO₄]₂. *Anal.* Calcd for CH₁₅N₆O₂Cl₂Rh: C, 2.8; H, 3.5; N, 19.6. Found: C, 2.8; H, 3.8; N, 19.2.

Spectra.—All uv-vis spectra reported were obtained with a Cary Model 14 recording spectrophotometer at room temperature, of dilute solutions in red distilled water. Solutions for extinction coefficient measurements were prepared gravimetrically, and absorption maxima and extinction coefficient values were determined from reproducible duplicate solutions. These data for the isocyanatopentamminerhodium(III) and -ruthenium(III) ions are listed in Table I.

TABLE I
UV SPECTRA OF CYANATE COMPLEXES

	λ_{\max} , nm	ϵ , M ⁻¹ cm ⁻¹
[Ru(NH ₃) ₅ (NCO)]Br ₂	347	3610 ± 40
	265	292 ± 5
[Rh(NH ₃) ₅ (NCO)][ClO ₄] ₂	323	276 ± 5
	269	160 ± 5

Infrared spectra were obtained for solid samples in KBr disks using a Perkin-Elmer 225 recording infrared spectrophotometer. Absorption maxima (±2 cm⁻¹ for sharp peaks) are reported for the isocyanato complexes in Table II.

TABLE II
INFRARED SPECTRA OF CYANATE COMPLEXES (ν , cm⁻¹)^a

[Ru(NH ₃) ₅ (NCO)]Br ₂	[Rh(NH ₃) ₅ (NCO)][ClO ₄] ₂	Assignment
3450 s, b, sh	~3500 s, b, sh	N-H str
3250 vs, b	~3240 vs, b	
2220 vs	2264 vs	C-N str
1615 s, b	1625 s, b	NH ₃ degenerate def
1319 m, sh	1355 m, sh	C-O str
1295 vs	1310 vs	NH ₃ sym def
...	~1100 vs, b	ClO ₄ ⁻
...	938 m	ClO ₄ ⁻
795 s, b	844 s, b	NH ₃ rocking mode
...	636, 629, 626 s	ClO ₄ ⁻
578 s	585 ms	NCO bend
455 m	473 m	M-NH ₃ str
345 m		

^a KBr pellets. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

Rate Studies.—Rates of the acid hydrolyses were determined for most runs by following the disappearance of a uv absorption band characteristic of the respective isocyanato complex, 347 nm for the Ru(III) species and 323 nm for the Rh(III) species. All runs were carried out using a Cary 14 recording spectrophotometer equipped with a thermostated cell compartment. Solutions and cells were thermostated prior to initiating a run. Reaction rates were studied as a function of [H⁺] and temperature in aqueous dilute HCl solution using NaCl to maintain the ionic strength at either 0.1 or 1.0 *M*. Pseudo-first-order rate constants for the Ru(III) complexes were obtained from the typical $\ln(A_t - A_\infty)$ vs. time plots; however, the consecutive reactions observed with the rhodium(III) complex (see Results) necessitated measuring the kinetics of the initial step at low [H⁺], and the kinetics of the second step, at high [H⁺]. All rate runs were initiated by pipetting or syringing an aliquot of thermostated acid solution into a measured volume of thermostated isocyanato complex solution in the reaction cell, agitating, and transferring the cell immediately to the spectrophotometer cell compartment.

Results

Hydrolysis of Ru(NH₃)₅NCO²⁺ (A).—The reaction between dilute aqueous HCl and A leads to immediate evolution of a gas identified as CO₂ from its infrared spectrum. Addition of concentrated perchloric acid or sodium perchlorate solution precipitates an essentially quantitative yield of [Ru(NH₃)₆][ClO₄]₃ identified by its exact duplication of the ir and uv spectral properties of an authentic sample of the hexaammine complex. These products clearly identify the acid hydrolysis as following eq 1 and the cyanate ion complex as the N-coordinated isocyanatopentaammineruthenium(III). (Hydrolysis of the O-coordinated isomer would be expected to give Ru(NH₃)₅H₂O³⁺ under the reaction conditions.) Heterogeneous reaction between cold aqueous 6 *M* HClO₄ and the solid [Ru(NH₃)₅(NCO)]Br₂ gives a white solid whose properties are somewhat different from those of the dilute acid product. For example, the solid effervesces slightly on dissolution in neutral water, although the uv spectrum of the resulting solution is that of Ru(NH₃)₆³⁺. However, no effervescence was observed on dissolution of this product in cold aqueous 6 *M* HCl, and the uv spectrum of the resulting solution, while similar to that of Ru(NH₃)₆³⁺ under identical conditions, displayed an additional absorption at 234 nm. The ir spectrum (KBr pellet) was essentially identical with [Ru(NH₃)₆][ClO₄]₃ but had a single extra band at 2320 cm⁻¹ indicative of some CO₂ trapped in the solid matrix. The solid decomposed slowly at room temperature and after several hours displayed properties identical with those of [Ru(NH₃)₆][ClO₄]₃. These rather insubstantial data support the tentative conclusion that the isolated product of the 6 *M* HClO₄ hydrolysis is a mixture of the hexaammine and an unstable carbamic acid complex [Ru(NH₃)₅(NH₂CO₂H)][ClO₄]₃ analogous to the product isolated under similar conditions of hydrolysis of the isocyanatorhodium(III) complex (see below).

The rates of the dilute HCl hydrolysis of A were determined spectrophotometrically by following the disappearance of the 347-nm band (Table I). The reactions were first order in [A] giving linear $\ln(A_t - A_\infty)$ vs. *t* plots over 3 or more half-lives for all acid concentrations examined (0.003–1.0 *M*), hence the rate law

$$-\frac{d[A]}{dt} = k_A'[A] \quad (2)$$

The rate constant k_A' obeys a simple first-order dependence on acid concentration (Figure 1) to give the rate law

$$-\frac{d[A]}{dt} = k_{2A}[H^+][A] \quad (3)$$

Table III summarizes the values of k_{2A} determined at several temperatures (ionic strength maintained at 0.1

TABLE III
RATE PARAMETERS FOR THE HYDROLYSIS OF
Ru(NH₃)₅(NCO)²⁺ IN DILUTE HCl

Temp, °C	k_{2A} , M ⁻¹ sec ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu
25.1	0.0593 ± 0.0011	12.2 ± 0.5	-23 ± 2
26.1	0.0668 ± 0.0012		
35.0	0.113 ± 0.006		
44.4	0.220 ± 0.010		

^a [Ru(NH₃)₅(NCO)²⁺]_{initial} = ~2.2 × 10⁻⁴ *M* for all runs, μ = 0.10 (Cl⁻).

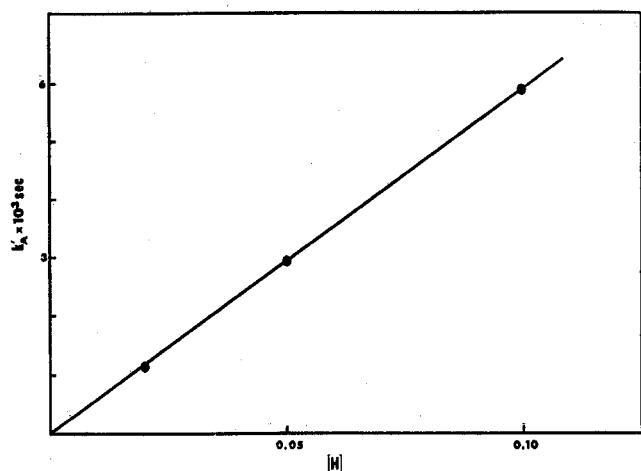


Figure 1.— $[H^+]$ dependence of rate constant k_A' for hydrolysis of $Ru(NH_3)_5(NCO)^{2+}$ (25.1° , $\mu = 0.10$).

M with NaCl) and the activation parameters calculated for 25.1° .

Hydrolysis of $Rh(NH_3)_5NCO^{2+}$ (B).—The reaction between dilute aqueous HCl and the rhodium(III)-cyanato ion complex (B) also leads to immediate gaseous evolution of CO_2 . Perchlorate addition precipitates an essentially quantitative yield of $[Rh(NH_3)_6][ClO_4]_3$ identified by comparison of the product's spectral properties with literature values and by nitrogen analysis (calcd, 16.69%; found, 16.23%). These products identify the hydrolysis of B as eq 1 ($M = Rh(III)$) and the nature of B (prepared by the reaction between $Rh(NH_3)_5H_2O^{3+}$ and urea) as isocyanatopentaammine-rhodium(III).

The hydrolysis of $[Rh(NH_3)_5NCO][ClO_4]_2$ in 6 M aqueous acid (either homogeneous in cold 6 M HCl followed by perchlorate addition or heterogeneous in cold 6 M $HClO_4$) gives a solid which is not the perchlorate salt of $Ru(NH_3)_6^{3+}$. The absence of visible bubbles also suggests that CO_2 is not formed in the reaction. The product (C) of the 6 M acid hydrolysis does effervesce vigorously (releasing CO_2) when dissolved in neutral water, the resulting solution having a uv spectrum consistent with that of the hexaammine. Dissolution in cold 4 M HCl, however, did not result in CO_2 formation and the solution displayed a uv spectrum distinguishably different from that of $Rh(NH_3)_6^{3+}$ under similar conditions: λ_{max} 314 nm (ϵ 154) and 259 nm (ϵ 122) compared to 307 nm (ϵ 135) and 256 nm (ϵ 105) for $Rh(NH_3)_6^{3+}$ in 4 M HCl. The ir spectrum of C (KBr pellet) is dependent on the time the sample has been in the spectrophotometer irradiation beam. When the spectrum was rapidly scanned immediately after placing the sample in the beam, a strong absorption at 1760 cm^{-1} consistent with the presence of a $-CO_2H$ group was observed along with the bands expected for the perchlorate salt of a rhodium(III)-ammine complex cation. After several minutes in the spectrophotometer beam (even at low beam intensity) the sample's spectrum changed, the most prominently changed features being the disappearance of the 1760-cm^{-1} band and development of a new band at 2335 cm^{-1} indicative of CO_2 trapped in the KBr solid matrix. These data strongly suggest that C is the relatively unstable, nitrogen-coordinated carbamic acid complex $[Rh(NH_3)_5(NH_2CO_2H)][ClO_4]_3$

which might be expected as an intermediate in the hydrolysis described by eq 1.

The rates of the acid hydrolysis of B were determined spectrophotometrically by following the disappearance of the 323-nm band (Table I). In contrast to the hydrolysis of the Ru(III) analog, A, the resulting $\ln(A_t - A_\infty)$ vs. time rate plots were not simply linear at all acid concentrations. At low acid concentrations, simple first-order dependence on $[B]$ is observed; at intermediate acid concentrations ($\sim 0.05\text{ M}$), a complicated curve is observed, while at high acid concentrations ($> 0.2\text{ M}$), a simple first-order reaction is again observed. However, this reaction was preceded by another reaction too fast to follow by the conventional techniques employed (see curves 1, 2, and 3 in Figure 2). This behavior sug-

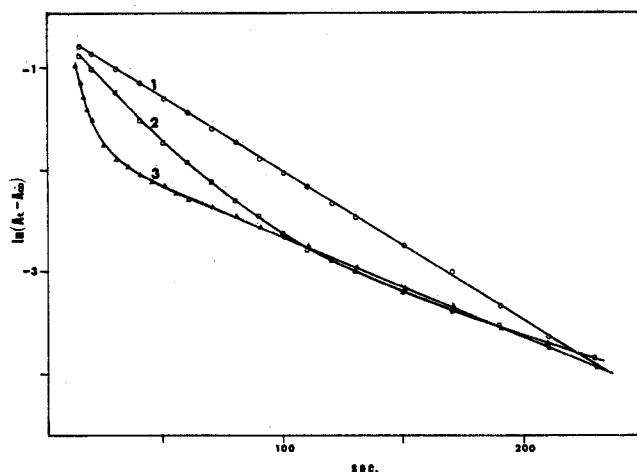


Figure 2.— $\ln(A_t - A_\infty)$ vs. t plots for $Rh(NH_3)_5(NCO)^{2+}$ hydrolysis at different acid concentrations (25°): curve 1, $[H^+] = 0.0234\text{ M}$, $\mu = 0.10$; curve 2, $[H^+] = 0.050\text{ M}$, $\mu = 0.10$; curve 3, $[H^+] = 0.20\text{ M}$, $\mu = 0.2$.

gests consecutive pseudo-first-order reactions having different dependence on $[H^+]$, where in low $[H^+]$ the first reaction is rate determining while in high $[H^+]$ the second reaction is rate determining. Consequently these can be resolved independently by determining the rates at the extremes of $[H^+]$ concentrations.

Over the low $[H^+]$ range ($0.005\text{--}0.025\text{ M}$), rates first order in $[B]$ are observed giving pseudo-first-order rate constants k_B' which display a simple dependence on $[H^+]$ (Figure 3) to give the rate law

$$-\frac{d[B]}{dt} = k_{2B}[H^+][B] \quad (4)$$

Table IV summarizes the values of k_{2B} determined at

TABLE IV
RATE PARAMETERS FOR THE INITIAL STEP OF THE ACID-CATALYZED HYDROLYSIS OF $Rh(NH_3)_5(NCO)^{2+}$

Temp, $^\circ\text{C}$	k_2^a , $M^{-1}\text{ sec}^{-1}$	ΔH^\ddagger , kcal mol $^{-1}$	ΔS^\ddagger , eu
25.1	0.62 ± 0.02	10.9 ± 0.6	-23 ± 2
34.5	1.08 ± 0.02		
44.0	1.92 ± 0.05		

^a $[Ru(NH_3)_5NCO^{2+}]_{initial} = \sim 3.3 \times 10^{-3}\text{ M}$ for all runs, $\mu = 0.10$ (Cl^-).

several temperatures (ionic strength maintained at 0.1 M with NaCl) and the activation parameters calculated for 25.1° .

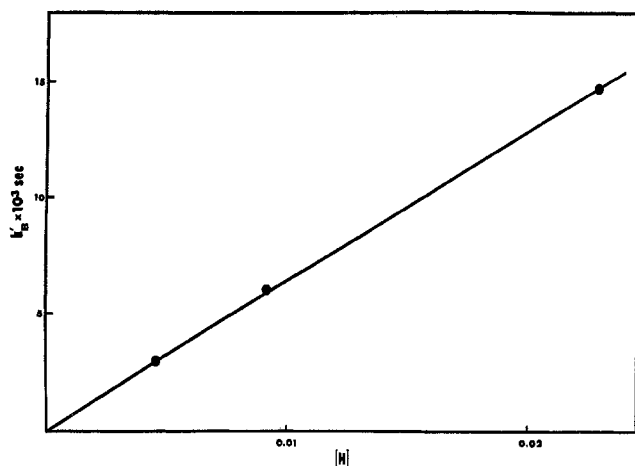


Figure 3.— $[H^+]$ dependence of rate constant k_B' for hydrolysis of $Rh(NH_3)_5(NCO)^{2+}$ (25.1° , $\mu = 0.10$).

Over the high $[H^+]$ range (0.20–1.0 M), the spectrophotometric rate plots are linear for the second reaction stage (Figure 2, curve 3) but the reaction being followed is obviously the disappearance of an intermediate I as extrapolation of these plots to $t = 0$ does not give an absorbance value comparable to that of the starting material. The pseudo-first-order rate constants k_1' include contributions from steps zero order and reciprocal in $[H^+]$ (Figure 4) to give the rate law

$$-\frac{d[I]}{dt} = k_0[I] + k_{-1}[I][H^+]^{-1} \quad (5)$$

where $k_0 = 2.1 \times 10^{-3} \text{ sec}^{-1}$ and $k_{-1} = 0.96 \times 10^{-3} M \text{ sec}^{-1}$ at 25.1° ($\mu = 1.0$ (Cl^-)).

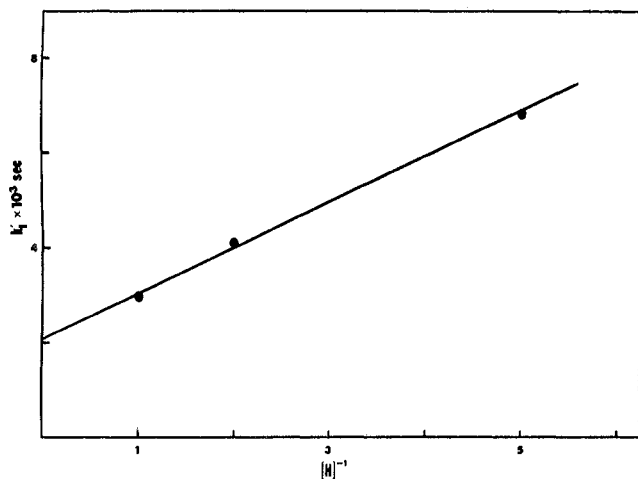


Figure 4.— $[H^+]$ dependence of rate constant k_1' for decomposition of $Rh(NH_3)_5(NH_2CO_2H)^{3+}$ (25.1° , $\mu = 1.00$).

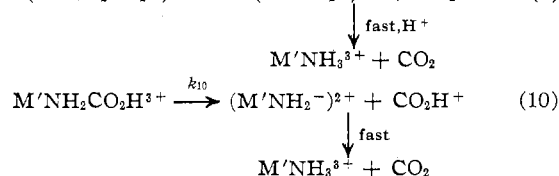
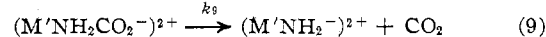
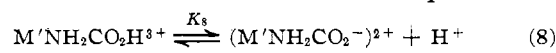
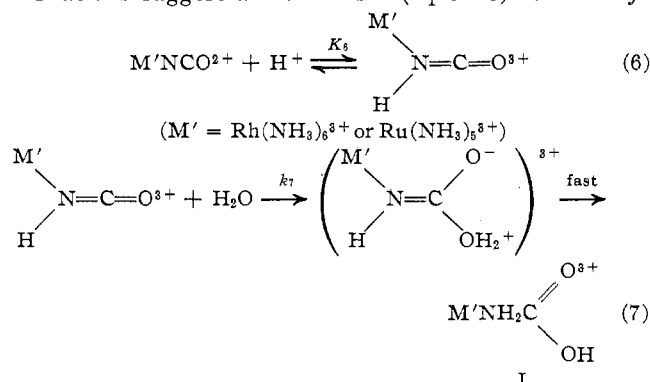
Discussion

The common bonding mode of cyanate ion transition metal complexes is nitrogen coordination⁶ although recently several oxygen-coordinated cyanate complexes have been reported.⁷ Isolation of the respective hexammine products of the acid hydrolysis of $Ru(NH_3)_5(NCO)^{2+}$ (A) and $Rh(NH_3)_5(NCO)^{2+}$ (B) provides con-

vincing evidence that these two complexes display cyanate ion coordination at the nitrogen. A similar observation⁴ was made for the cobalt(III) analog, $Co(NH_3)_5(NCO)^{2+}$. The ir spectra of these species (A and B) are also consistent with those of other known isocyanato (N-coordinated) complexes including $[Co(NH_3)_5(NCO)][ClO_4]_2$ ^{4,8} with the C–O and C–N stretching bands (Table II) for each appearing at higher frequencies than in the spectrum of $KNCO$.⁴

The uv spectra of A and B differ in a manner easily explained in terms of the different electronic configurations. The strong 347-nm absorption band (Table I) of the $4d^6$ Ru(III) species A is undoubtedly a ligand-to-metal charge transfer from a filled ligand π orbital to a partially unfilled metal $d\pi$ (t_{2g} -type) orbital. Similar charge transfers have been recognized⁹ for the halogenopentaammineruthenium(III) ions, $Ru(NH_3)_5X^{2+}$, where $X^- = Cl^-, Br^-,$ and I^- . In contrast, the low-spin $4d^6$ rhodium(III)–isocyanato complex displays two, less intense bands (323 and 269 nm, Table I) which in analogy to other pentaamminerhodium(III) species are recognizable as $d \rightarrow d$ transitions.^{10,11} Osborn, Gillard, and Wilkinson used the energy of the longer wavelength band to assign the position of the ligand X in a spectrochemical series for $Rh(NH_3)_5X^{2+}$. In this manner, the position of $-NCO^-$ (323 nm) in the spectrochemical series is found close to that of OH^- (321 nm)¹⁰ and of $-NH_2CO_2H$ (314 nm, the intermediate in $Rh(NH_3)_5NCO^{2+}$ hydrolysis) is found close to that of H_2O (316 nm).¹⁰ With these additions and with the spectral data reported by Schmidtke¹² for the S- and N-coordinated thiocyanate linkage isomers of $Rh(NH_3)_5(SCN)^{2+}$ (longer wavelength bands at 375 and at 320 nm, respectively), this spectrochemical series reads: $I^- < -SCN^- < Br^- < Cl^- < -NCO^- < OH^- < -NCS^- < H_2O < -NH_2CO_2H < H^- < NH_3 < -NO_2^-$.

Hydrolysis of Coordinated Cyanate.—Certain observations suggest a mechanism (eq 6–10) for the hy-



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hydrolysis to coordinated NH_3 plus CO_2 . (i) In dilute acid, the kinetics of each case studied have displayed a step first order in $[\text{H}^+]$. (ii) A carbamic acid complex ion, $\text{Rh}(\text{NH}_3)_5(\text{NH}_2\text{CO}_2\text{H})^{3+}$, can be isolated under certain hydrolysis conditions for B and a very unstable analog apparently has been isolated for the Ru(III) system. (iii) In more concentrated acid solution, a second step (decomposition of the carbamic acid complex) becomes rate determining for product formation in the Rh(III) system. This second step displays rate terms both independent of $[\text{H}^+]$ and reciprocal in $[\text{H}^+]$. With this scheme, the rate-determining acid hydrolysis step (point (i)), having rate constants k_{2A} for A or k_{2B} for B, reflects the product of a fast proton-dependent equilibrium (eq 6) followed by attack of H_2O to establish the new carbon-oxygen bond (eq 7) giving

$$k_{2A} \text{ (or } k_{2B}) = K_6 k_7 \quad (11)$$

where K_6 and k_7 are functions of the specific system undergoing hydrolysis. There is no evidence which distinguishes whether initial protonation is of the isocyanate nitrogen (eq 6) or of the oxygen to activate the carbon toward nucleophilic water. Protonation of nitrogen serves the purpose and requires fewer proton transfers to convert the species initially formed by H_2O attack into the carbamic acid complex (I). These steps (eq 6 and 7) are the only ones observed kinetically for the ruthenium(III) and cobalt(III) isocyanatopentaammines either because the carbamic acid intermediate is indistinguishable from the product by the kinetic techniques employed or because the subsequent steps are much faster (see below). For the hydrolysis of the Rh(III) complex, B, however, subsequent steps are observable in solution sufficiently acidic that formation of the carbamic acid species (I) is rapid. The rate law for decomposition of I would be explained by the proposed mechanism (eq 8-10) giving $k_0 = k_{10}$ and $k_{-1} = K_9 k_9$. The mechanisms for the $[\text{H}^+]^{-1}$ -dependent decomposition (eq 8 and 9) appears quite reasonable as it involves separation of $(\text{MNH}_2^-)^{2+}$ from a good leaving group (CO_2) for the rate-determining cleavage of the C-N bond. In contrast, eq 10 which employs CO_2H^+ as the leaving group is not as attractive. Nonetheless, the decomposition of I in strongly acidic solutions occurs at rates not explainable simply by $k_{-1}[\text{H}^+]^{-1}$. Another mechanism which would be the kinetic equivalent of eq 10 is a concerted transfer of H^+ to the developing amide group simultaneous with CO_2 departure. Such a transfer could be strictly intramolecular or could involve intervening water molecules.

Comparison of Different Complexes.—Second-order rate constants (25°) and activation parameters for the acid-dependent hydrolysis of coordinated isocyanate and of cyanic acid are summarized in Table V. Perhaps surprisingly, the k_2 's not only of the complexes but also for cyanic acid are quite similar varying only by a factor of about 10. These similarities are somewhat fortuitous, as they result in part from cancellation of ΔH^\ddagger variations by ΔS^\ddagger differences in the opposite direction. Nonetheless, the general patterns of k_2 , ΔH^\ddagger , and ΔS^\ddagger for these reactions suggest that, as Balahura and Jordan⁴ concluded in comparing the HNCO and $\text{Co}(\text{NH}_3)_5\text{NCO}^{2+}$ systems, the hydrolysis mechanisms are similar. More detailed discussion will be restricted to the Ru(III) and Rh(III) systems since the hydrolysis rate studies on $\text{Co}(\text{NH}_3)_5(\text{NCO})^{2+}$ and

TABLE V
HYDROLYSIS RATE DATA FOR COORDINATED CYANATE ION

M'	k_2 , $M^{-1} \text{ sec}^{-1}$	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu	Ref
$\text{Ru}^{\text{III}}(\text{NH}_3)_5$	0.0593 ^a	12.2	-23	f
$\text{Rh}^{\text{III}}(\text{NH}_3)_5$	0.617 ^a	10.9	-23	f
$\text{Co}^{\text{III}}(\text{NH}_3)_5$	0.162 ^b	13.1	-18	g
H^+	0.115 ^{c,d}	15.1 ^e	-13 ^e	h
	0.121 ^{b,d}	14.6 ^e	-14 ^e	i

^a $\mu = 0.10 \text{ M}$. ^b $\mu = 1.0 \text{ M}$. ^c $\mu \cong 0.2 \text{ M}$. ^d Extrapolated to 25° . ^e Calculated from published rate data. ^f This work. ^g Reference 4. ^h M. B. Jensen, *Acta Chem. Scand.*, **12**, 1657 (1958). ⁱ M. W. Lister, *Can. J. Chem.*, **33**, 426 (1955).

HNCO were performed in different laboratories and under nonidentical conditions.

According to the proposed mechanism, the experimental rate constant k_2 is a product of two terms, K_6 and k_7 . The respective activation parameters represent the sum of the appropriate thermodynamic function for eq 6 plus the activation parameter for eq 7. For this reason, the net results may represent a canceling or a reinforcing of reactivity differences for the individual steps. The rate data for the k_2 step show the Rh(III) species to be about tenfold more reactive at 25° than the Ru(III) complex. Since the low-spin d^5 $\text{Ru}(\text{NH}_3)_5^{3+}$ and d^6 $\text{Rh}(\text{NH}_3)_5^{3+}$ fragments have the same net electrostatic charge and very similar masses, differences in their influence on coordinated ligand reactivity would be expected to derive principally from differences in the $d\pi-\pi_L$ (or π^*_L) interactions. This conclusion is substantiated by comparing the acidities of the relevant aquopentaammine complexes (eq 12).



The Ru(III) complex ($pK_a = 4.2$, 25°)¹³ is more acidic than the Rh(III) analog ($pK_a = 5.9$, 15°)¹⁴ despite the potentially larger effective rhodium nuclear charge. An explanation of this phenomenon may lie in stabilization of the conjugate base $\text{M}(\text{NH}_3)_5\text{OH}^{2+}$ by ligand-to-metal π bonding in the Ru(III) complex, since the d^5 Ru(III) having a π -symmetry d-orbital vacancy would be a better π acceptor than would the d^6 Rh(III).

The π bonding argument applies directly to the proposed hydrolysis mechanism (eq 6-10). Since protonation would reduce the isocyanates' π -donor ability (regardless of protonation site), the basicity of A should be less than that of B (*i.e.*, $K_{6B} > K_{6A}$). In contrast, nucleophilic H_2O attack on the protonated isocyanate (eq 7) would lead to enhanced ligand electron density suggesting that in this step the Ru(III) complex might be the more reactive (*i.e.*, $k_{7A} > k_{7B}$). Since $k_2 = k_7 K_6$, these trends are counter, and the observation $k_{2B} \cong 10k_{2A}(25^\circ)$ implies that (given the proposed mechanism) the effect of metal ion electronic configuration on the protonation equilibrium is the more important rate influence. This conclusion is reasonable in the context that the thermodynamic parameters for K_6 reflect the effect of a fully developed positive charge on the protonated isocyanate while the activation parameters for k_7 reflect only the partial perturbation of the ligand

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electronic properties owing to the developing carbon-oxygen bond in the transition state.

The apparent stability differences between the carbamic acid complex intermediates (I) can also be rationalized by the π -bonding considerations. The amide species ($M'-\ddot{N}H_2$)²⁺ generated by loss of CO₂H⁺ or CO₂ from I or its conjugate base (eq 9 and 10) may very likely be more stable for $M' = Ru(NH_3)_6^{3+}$ than for $M' = Rh(NH_3)_6^{3+}$. In support, the rate¹⁵ of base-

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catalyzed H-D exchange in D₂O of the Ru(NH₃)₆³⁺ ammonia proton is about 3000 times greater than for those of Rh(NH₃)₆³⁺. These reactions, no doubt, also go through intermediates similar to the amide complex ($M'-\ddot{N}H_2$), and the rate differences suggest special stability for the ruthenium(III)-amide species.

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Rhodium(I) and Iridium(I) Complexes with 1,1,1-Tris(diphenylphosphinomethyl)ethane

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Rhodium(I) and iridium(I) complexes of the tripodal ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, TDPME, of the type MCl(CO)(TDPME) were synthesized. The iridium(I) complex appears to be five-coordinate in the solid state but to be capable of dissociating a phosphine ligand in solution. The rhodium(I) complex is apparently a mixture of four- and five-coordinate isomers (with TDPME as either a bidentate or a tridentate ligand) both in the solid state and in solution. The existence of a facile equilibrium between four- and five-coordinate configurations of the rhodium(I) and iridium(I) complexes in solution is suggested by their rapid reaction with carbon monoxide to form dicarbonyl species. Reactions with oxygen, sulfur dioxide-oxygen, and *p*-nitrobenzoyl azide which yield (bidentate) carbonato, sulfato, and isocyanato complexes have been examined. The TDPME complexes differ significantly in reactivity from the rhodium(I) and iridium(I) complexes, *trans*-MCl(CO)L₂, from which they are derived. A five-coordinate d⁸ iridium(I) complex with azido and carbonyl ligands in adjacent coordination sites was synthesized and found to be stable.

Introduction

Recently attention was called to a broad class of atom-transfer redox reactions which could be promoted by a metal which held both oxidant and reductant in cis positions of the coordination sphere.^{2,3} Thermodynamically favorable processes between kinetically inert reactants might be facilitated with the incorporation of the potential reactants in adjacent coordination sites. Significant reactions in this group include those in which the reductant is a gas (carbon monoxide, sulfur dioxide, nitrogen oxides) and the oxidant is molecular oxygen. Stoichiometric reactions of this type have been reported from this and other laboratories.²⁻⁶

Although numerous examples of atom-transfer redox reactions have been reported, our knowledge of the scope and limitation of the various reactions is almost totally empirical. Yet to be established is whether or not coordination at adjacent sites is in itself sufficient to provoke a reaction. Incorporating a tridentate ligand in a d⁶ or d⁸ metal complex would require the other lig-

ands in the coordination sphere to be cis to each other and thus might facilitate reactions of this type.

The ligand 1,1,1-tris(diphenylphosphinomethyl)ethane, 1, TDPME, has been employed in several metal complex systems since it was first reported in 1962.⁷⁻¹⁷ The geometry of the ligand is such that it can occupy three facial sites on a tetrahedron, trigonal bipyramid, square pyramid, pentagonal pyramid, or octahedron but cannot coordinate to three positions of a square plane or three meridial sites of a polyhedron. By occupying three sites of the coordination sphere, the steric relationship of the remaining ligands is often fixed. The situation is complicated if one of the phosphine groups of TDPME is not coordinated^{7,9,14,15,17} or if two metals are bridged by a single TDPME ligand.^{13,16} Davis and Fergusson have recently isolated and characterized two Re^VTDPME complexes of the same stoichiometry, one in which TDPME serves as a tridentate ligand and the other in which it serves as a bidentate ligand.^{17a} As a

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