$(3,5\text{-}Me_2pz)_2]Mo(CO)_2(\eta^3\text{-}C_7H_7)$.[12] A main argument against this mechanism is that it cannot explain, by itself, equilibration of the Me ligands for isomers A and B because the Me ligand in the cap would remain distinct. Thus, at a minimum, equilibration of the Me ligands by the triangular face rotational mechanism is necessary. Also, this mechanism was not observed for **2**, a molecule structurally very similar to **1**, up to 86 °C. One might also anticipate that the 3-Me substituents on the pyrazolyl rings would impede such a rotation as observed with $[HB(3,5\text{-}Me_2pz)_3]Zr(Cl)_2O\text{-}t\text{-}Bu$, a nonfluxional molecule up to 110 °C.[1b]

(12) Calderon, J. L.; Cotton, F. A.; Shaver, A. *J. Organomet. Chem.* **1972**, *42*, 419.

Acknowledgment. We express our great appreciation for the assistance rendered by Dr. Ron Garber and J. Art Anderson in obtaining NMR spectra and for useful discussions. The use of the facilities at the University of South Carolina Regional NMR Center, funded by the National Science Foundation (CHE82-07445), is acknowledged.

Registry No. I, 86120-30-1; $TaMe_3Cl_2$, 3020-02-8; $K[H_2B(3,5\text{-}Me_2Pz)_2]$, 53241-68-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and listings of structural factor amplitudes for $[H_2B(3,5\text{-}Me_2pz)_2]TaMe_3Cl$ (11 pages). Ordering information is given on any current masthead page.

Synthesis, Linkage Isomerism, and Ligand Reactivity of (Urea)pentaamminerhodium(III) Complexes

Neville J. Curtis, Nicholas E. Dixon, and Alan M. Sargeson*

Contribution from the Research School of Chemistry, Australian National University, Canberra 2601, Australia. *Received November 1, 1982*

Abstract: The synthesis and reactions in aqueous solution of both O- and N-bonded linkage isomers of the [(urea)pentaamminerhodium(III)](3+) complex ion are described. Under neutral and basic conditions, the O-bonded isomer rearranges and hydrolyzes to give mixtures of the deprotonated N-bonded form and the $[(NH_3)_5RhOH]^{2+}$ ion. Under acidic conditions, the two isomers interconvert and ultimately produce mixtures of $[(NH_3)_5RhOH_2]^{3+}$ and $[(NH_3)_6Rh]^{3+}$ ions. The former arises by hydrolysis of the O-bonded isomer while the latter derives from the N-bonded species, at least in part by way of intermediate $[(NH_3)_5RhNCO]^{2+}$ ion. At pH 2.05 and 25 °C, the decomposition of the $[(NH_3)_5RhNH_2CONH_2]^{3+}$ ion by this path occurs ca. 30 000 times faster than the analogous reaction of urea under similar conditions.

The very slow decomposition of urea[1-3] in aqueous solution is ascribed to an elimination reaction producing ammonia and cyanic acid as sole products (eq 1, $k = 6 \times 10^{-10}$ s^{-1} at 25 °C).[4] The

$$NH_2CONH_2 \rightarrow NH_3 + HNCO \rightleftarrows NH_4^+ + NCO^- \quad (1)$$

rate of reaction is insensitive to pH over a wide range but rises above pH 12 and decreases at very low pH. The increase under basic conditions is ascribed to specific-base catalysis, rather than any change in mechanism, while the decrease in rate in acidic solutions is attributed to protonation of the substrate.[5,6]

By contrast, the enzymatic decomposition of urea catalyzed by jack bean urease is a hydrolytic process producing carbamate and ammonium ions as the initial products[7] (eq 2). Since the

$$NH_2CONH_2 + H_2O \rightarrow NH_2COO^- + NH_4^+ \quad (2)$$

spontaneous hydrolysis of urea has never been observed in competition with the slow elimination reaction and since $k_{cat.}$ for the urease-catalyzed reaction[8] is 3.5×10^3 s^{-1} at 25 °C, it is apparent that the urea molecule is activated to hydrolysis by a factor[6] in excess of 10^{14}. Jack bean urease is a nickel(II) metalloenzyme[9] with each of its six identical subunits containing one active site[10,11] and two metal ions,[12] and at least one of these nickel ions is implicated in the hydrolysis.[8-12] On the basis of studies of the substrate specificity and inhibition data, a mechanism involving both nickel ions has been proposed.[8] Coordination of the substrate to one nickel ion through its carbonyl oxygen is argued to activate it toward attack by hydroxide ion coordinated at the other metal center. Such activation, at least for the individual processes, has been proposed for the reactions of zinc metalloenzymes,[13] and there is ample precedence for both roles for the metal ion in the hydrolysis of amino acid esters and amides.[14]

In order to assess the effect of coordination to a metal ion on the susceptibility of urea to hydrolysis, we have examined the reactions of pentaamminecobalt(III) complexes of urea (O-coordinated)[15] and *N,N*-dimethylurea (N-bonded).[16] In neither study was hydrolysis of coordinated urea observed, although for the former a small percentage of $[(NH_3)_5CoOH]$ produced in the base hydrolysis arose via carbonyl rather than cobalt–oxygen cleavage.[15] It was clear from these studies that any reaction at

(1) Werner, A. E. "The Chemistry of Urea"; Longmans, Green and Co.: London, 1923; pp 31–48.
(2) Warner, R. C. *J. Biol. Chem.* **1942**, *142*, 705–23.
(3) Shaw, W. H. R.; Bordeaux, J. J. *J. Am. Chem. Soc.* **1955**, *77*, 4729–33.
(4) Calculated from data in ref 3, extrapolated to 25 °C.
(5) Shaw, W. H. R.; Walker, D. G. *J. Am. Chem. Soc.* **1958**, *80*, 5537–42.
(6) Blakeley, R. L.; Treston, A.; Andrews, R. K.; Zerner, B. *J. Am. Chem. Soc.* **1982**, *104*, 612–4.
(7) Blakeley, R. L.; Hinds, J. A.; Kunze, H. E.; Webb, E. C.; Zerner, B. *Biochemistry*, **1969**, *8*, 1991–2000.
(8) Dixon, N. E.; Riddles, P. W.; Gazzola, C.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 1335–44.
(9) Dixon, N. E.; Gazzola, C.; Blakeley, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975**, *97*, 4131–3. Dixon, N. E.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 469–73. Dixon, N. E.; Gazzola, C.; Asher, C. J.; Lee, D. S. W.; Blakeley, R. L.; Zerner, B. *Ibid.* **1980**, *58*, 474–80.
(10) Dixon, N. E.; Hinds, J. A.; Fihelly, A. K.; Gazzola, C.; Winzor, D. J.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 1323–34.
(11) Dixon, N. E.; Gazzola, C.; Watters, J. J.; Blakeley, R. L.; Zerner, B. *J. Am. Chem. Soc.* **1975**, *97*, 4130–1.
(12) Dixon, N. E.; Blakeley, R. L.; Zerner, B. *Can. J. Biochem.* **1980**, *58*, 481–8.
(13) Brown, R. S.; Huguet, J.; Curtis, N. J. In "Metal Ions in Biological Systems", Sigel, H., Ed.; Marcel Dekker: New York, 1983; Vol. 15, pp 55–99.
(14) Dixon, N. E.; Sargeson, A. M. In "Zinc Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1983; pp 253–352.
(15) Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688–97.
(16) Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M., submitted for publication.

0002-7863/83/1505-5347$01.50/0

the ligand carbonyl occurred too slowly to compete with linkage isomerism or rupture of the metal–ligand bond. Analogous N- and O-bonded (urea)pentaamminerhodium(III) complexes have now been prepared in order to reduce further the lability of the systems to metal ion–ligand rupture. In this paper, we report the results of studies of their respective reactivity in aqueous solution.

Experimental Section

Ultraviolet spectra were recorded by using a Cary 14 spectrophotometer. IR spectra were recorded by using KBr disks and a Perkin-Elmer PHM 683 spectrophotometer. NMR spectra were measured with JEOL "Minimar" MHR 100-MHz (^{1}H) and CXP 200 (^{13}C, proton decoupled) spectrometers using D_2O or Me_2SO-d_6 as solvents, at ambient temperature (25–35 °C), using sodium 4,4-dimethyl-4-silapentanesulfonate (DSS) or Me_4Si as internal references for proton spectra and Me_4Si or 1,4-dioxane for ^{13}C spectra, unless otherwise specified. Reported chemical shifts (ppm) are relative to these references: downfield shifts are positive. Measurements of pH were made under nitrogen at 25 °C, using a Radiometer PHM 26 meter, G202B glass, and a K4112 calomel electrode or GK2401B combination electrode, calibrated by using two standard buffers. Concentrations of OH^- were determined from the measured values of pH, assuming K_w' of 1.71×10^{-14} at 25 °C and 1.0 M ionic strength.[17] All evaporations were carried out with a Buchi rotary evaporator under reduced pressure (<20 mm) such that the solution did not exceed 25 °C.

Syntheses. $[(NH_3)_5RhOH_2](ClO_4)_3$ and $[(NH_3)_6Rh](ClO_4)_3$ were prepared from $[(NH_3)_5RhOSO_2CF_3](CF_3SO_3)_2$, as previously reported,[18] and $[(NH_3)_5RhNCO](ClO_4)_3$ by the published method.[19] All C, H, and N analyses agreed with calculated values within ±0.3%.

$[(NH_3)_5RhOC(NH_2)_2](S_2O_6)_{3/2}\cdot{}^3/_2H_2O$ and $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$. To a solution of recrystallized urea (12 g) in 180 mL of dry sulfolane was added $[(NH_3)_5RhOSO_2CF_3](CF_3SO_3)_2$ (20 g) in small portions over 10 min. and the reaction was left to stir for 2.5 h at room temperature. The clear yellow solution was transferred to a larger flask, and 20 mL of ethanol and 1.5 L of ether were added, with vigorous stirring. The ether layer was decanted and filtered through a bed of Hyflo Supercel filter aid. The oily residue was then dissolved in 20 mL of ethanol and the procedure repeated five times. The resultant pale yellow solid was dissolved in 100 mL of water, filtered, and cooled in ice and solid $NaClO_4.H_2O$ added. The resultant crystals were collected, washed with ethanol and ether, and dried in air. IR analysis indicated the presence of both the N- an O-bonded isomers and also some cyanate (2260 cm^{-1}). To a cold, filtered solution of the product in 300 mL of water was added a saturated solution of $Na_2S_2O_6$ (15 g) in water. After 15 min, the pale yellow crystals of the O-bonded isomer were collected, washed with ethanol/water (1:1), ethanol, and then ether and dried in air (9.25 g, 57%): IR 1580, 1640 cm^{-1}. Anal. Calcd for $CH_{22}N_6O_{11.5}RhS_3$: C, 2.33; H, 4.20; N, 19.03; S, 18.67. Found: C, 2.2; H, 4.2; N, 18.9; S, 18.3. The more soluble perchlorate salt, prepared as described for the analogous cobalt complex[15] was used for measurements of the NMR spectra: ^{1}H NMR 3.69 (br s, 3 H), 3.81 (br s, 12 H), 6.57 ppm (br s, 4 H); ^{13}C NMR 127.2 ppm relative to Me_2SO in 4:1 Me_2SO/D_2O. The filtrate from the above step was treated with 20 mL of 1.0 M NaOH and after 30 min acidified to pH 8 with perchloric acid. This solution was passed through a column (14 × 4.5 cm) of Dowex AG1-X4 ion exchange resin, in the nitrate form, and concentrated to 100 mL on a rotary evaporator. The solution was cooled in ice and acidified with 1.0 M HNO_3 to pH 2. After 5 min, the white crystals of the N-bonded isomer were collected, washed with ethanol and ether, and dried. The product was recrystallized by dissolution in cold 0.5 M LiOH in 1 M $LiNO_3$ and reacidification with nitric acid (2.45 g, 18%, after washing with ethanol then ether and drying in vacuo): IR 1740 cm^{-1}; ^{1}H NMR (Me_2SO) 3.7 (br s, 15 H), 6.6 (br s, 2 H), 7.1 (br s, 1 H), 7.6 ppm (br s, 1 H); ^{13}C NMR 102.3 ppm relative to dioxane in NaOD/D_2O. Anal. Calcd for $CH_{19}N_{10}O_{10}Rh$: C, 2.77; H, 4.41; N, 32.26. Found: C, 2.8; H, 4.6; N, 32.2. The N-bonded isomer was also made in ca. 70% yield by treatment of the O-bonded isomer with NaOH and isolated as above.

$[(NH_3)_5RhOCONH_2](S_2O_6)$. To 2 g of $[(NH_3)_5RhOH_2](ClO_4)_3$ dissolved in 15 mL of water at 80 °C was added 0.75 g of recrystallized NaNCO, and the mixture was stirred for 30 min with slow cooling to 50 °C. The solution was diluted to 250 mL with water, adjusted to pH 4.7 with acetic acid, and loaded on a Dowex 50W-X2 (Na^+) cation-exchange column. After being washed with water, the products were eluted with 1.0 M $NaClO_4$. Fractions containing the 2+ product (monitored by A_{320}) were combined, concentrated to 30 mL, and cooled. After being left standing overnight at 4 °C, 0.82 g of white crystals were collected and washed with ethanol and ether. Addition of one volume of ethanol yielded a second crop, 0.52 g, which was washed thoroughly with ethanol to remove traces of $NaClO_4$. The combined products were dissolved in 50 mL of water and treated with saturated aqueous $Na_2S_2O_6$. The crystals were collected, washed with ethanol then ether, and dried in vacuo (1.2 g, 74%). Anal. Calcd for $CH_{17}N_6O_8S_2Rh$: C, 2.94; H, 4.20; N, 20.59; S, 15.71. Found: C, 3.2; H, 4.0; N, 20.5; S, 15.7.

Kinetic Measurements. Buffers were prepared from reagent grade components and 1.00 M NaOH (Volucon) or standardized $HClO_4$ and CF_3SO_3H solutions and ionic strength made up to 1.0 M with $NaClO_4\cdot H_2O$ or $NaCF_3SO_3\cdot H_2O$.

The kinetics of reactions of $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ in basic media were followed at 25.0 ± 0.1 °C in a thermostated cell by monitoring the absorbance change at 345 nm with either a Cary 118C or 16K spectrophotometer. Equal volumes of solutions of complex (ca. 5 mM) and the buffer at the appropriate ionic strength were mixed in a temperature equilibrated stopped flow reactor fitted to a flow-through cell,[20] and the reaction was followed for at least four half-lives. Control experiments, at a single pH, with varying buffer concentrations of between 0.1 and 0.3 M, indicated the absence of any buffer catalysis. All runs obeyed a strict first-order rate law. Reported values are the average of at least three determinations, and the data were analyzed by best fit to a computed trace using a nonlinear least-squares program. The progress of reactions in acidic media of the O- and N- bonded urea isomers and the cyanato complex at 25.1 ± 0.1 °C were followed at 340 nm by using a Cary 14 or Gilford 2400 spectrophotometer. Weighed samples of complex (finally 2–8 mM) were dissolved in preequilibrated buffer in stoppered cells and immediately transferred to a thermostated cell in the spectrophotometer. Progress curves were monitored for at least 3 half-lives (cyanato complex) or for 1–3 days (urea complexes) and were evaluated by the appropriate least-squares program (see Results). The fit of computed curves was generally good over the course of the reaction ($\sigma < 1\%$).

Product Analyses. Products of the reactions of the urea hydrolyses were separated chromatographically on columns (20 × 2.5 cm) of SP-Sephadex C25 cation-exchange resin. The effluent was monitored spectrophotometrically at 320 nm. $[(NH_3)_5RhOH]^{2+}$/$[(NH_3)_5RhOH_2]^{3+}$ eluted before $[(NH_3)_5RhNHCONH_2]^{2+}$ using 0.07 M Na_2HPO_4/0.07 M KH_2PO_4 solutions, while in 0.1 M solutions of each of these components, $[(NH_3)_6Rh]^{3+}$ was eluted. Complete separation of all components was achieved, and spectrophotometric analyses of the leading and trailing edges showed the bands to be homogeneous. Typically, ca. 50 mg of the complex was dissolved in 15 mL of the buffer at the correct ionic strength at 25 °C and diluted tenfold before loading on the column. Concentrations of products in eluate fractions were determined spectrophotometrically by using spectra of chromatographed authentic samples as references (Table I). Samples at pH 2.05 were left for 5 days, those at pH 6.27 for 16 h, and those at pH 12 for 15 min before analysis was carried out.

The chromatographic behavior of $[(NH_3)_5RhOCONH_2]^{2+}$ was also studied, and it was found to eluate at the same rate as for the deprotonated N-bonded urea complex in the lower concentration phosphate buffer. Separation, however, could be achieved at a lower pH where the urea complex is a trivalent cation, using a medium of 0.2 M glycine/0.1 M HCl/0.2 M NaCl. The fraction containing $[(NH_3)_5RhNHCONH_2]^{2+}$ was rechromatographed in this medium at 5 °C (to avoid decomposition), and no evidence was found for the presence of any divalent ion. The absence of significant amounts of $[(NH_3)_5RhNCO]^{2+}$ at higher pH was indicated in the following experiment. A sample of the O-bonded isomer was incubated at 25 °C at pH 6.27 as before and then acidified to pH 2. After 10 min the sample was neutralized and analyzed as before. The sample did not contain any $[(NH_3)_6Rh]^{3+}$ as would be expected from the known acid-catalyzed decomposition of the cyanato compound.[19]

That treatment of the N-bonded isomer with acid led to the formation of some of the $[(NH_3)_5RhNCO]^{2+}$ ion was indicated by the following experiment. A small volume of water was acidified to pH ca. 3.5 by the addition of HCl, and diluted with four volumes of Me_2SO to ca. 0.3 mL, and $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$ (ca. 40 mg) added. The solution was syringed into a 0.1-mm CaF_2 infrared cell. IR spectra were recorded intermittently over several days at ~20 °C, with solvent as reference. Reference spectra of $[(NH_3)_5RhNCO](ClO_4)_2$, CO_2 and NaNCO were recorded under similar conditions.

Results

Syntheses and Characterization of Complexes. The use of the easily introduced and readily substituted trifluoromethanesulfonate

(17) Dixon, N. E.; Sargeson, A. M. *J. Am. Chem. Soc.* **1982**, *104*, 6716–25.
(18) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 846–7.
(19) Ford, P. C. *Inorg. Chem.* **1971**, *10*, 2153–58.
(20) A device similar to that described by: Inoue, Y.; Perrin, D. D. *J. Phys. Chem.* **1962**, *66*, 1689–93.

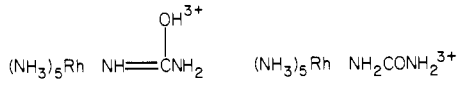
Table I. Electronic Absorption Spectra of Compounds

compound	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})	
$[(NH_3)_5RhOC(NH_2)_2]$-$(S_2O_6)_{3/2}\cdot{}^3/_2H_2O$	330 (163), 266 (114)	*a*
$[(NH_3)_5RhNH_2CONH_2](NO_3)_3$	316 (181)	*a, b*
	315 (152), 259 (112)	*c*
$[(NH_3)_5RhOOCNH_2](S_2O_6)$	324 (145), 260 (100)	*a*
Chromatographed Samples		
$[(NH_3)_5RhOH]^{2+}$/ $[(NH_3)_5RhOH_2]^{3+}$	315 (107), 264 (94)	*a*
$[(NH_3)_5RhNHCONH_2]^{2+}$	318 (158), 259 (153)	*a*
$[(NH_3)_6Rh]^{3+}$	305 (131), 256 (94)	*d*

[a] 0.07 M Na_2HPO_4/0.07 M KH_2PO_4. [b] Divalent ion at this pH. The second ligand field band is obscured by a large charge-transfer band. [c] 0.2 M NaCl, 0.2 M glycine, and 0.1 M HCl. Trivalent ion at this pH. [d] 0.1 M Na_2HPO_4/0.1 M KH_2PO_4.

(triflate) anion[21] allows a straightforward access to pentaamminerhodium(III) complexes.[18] Thus addition of the appropriate ligand to $[(NH_3)_5RhOSO_2CF_3](CF_3SO_3)_2$ gave rise to the urea and aqua pentaammine and hexaammine complexes. While for the analogous cobalt precursor, reaction with urea only appears to give the O-bonded isomer,[15] reaction with the rhodium analogue under similar conditions gives a mixture of both the O- and N-coordinated forms. These two linkage isomers were readily separated by fractional crystallization with appropriate anions. For purposes of product analysis, the carbamato complex $[(NH_3)_5RhOOCNH_2](S_2O_6)$ was prepared by a method similar to that used for the corresponding Co(III) complex.[22] These complexes were characterized by ^1H and ^{13}C NMR and IR spectra and elemental analyses. The structures of the urea isomers were established on the basis of their infrared, near-ultraviolet, and ^1H NMR spectra. The infrared spectrum, in the carbonyl region, of $[(NH_3)_5RhOC(NH_2)_2](S_2O_6)_{3/2}\cdot{}^3/_2H_2O$ was virtually indistinguishable from that for the analogous Co(III) compound.[15] The observed bands at 1580 and 1640 cm^{-1} are similar to those found for other O-bonded urea complexes.[23] Similarly, the sharp band seen for the N-bonded isomer, at 1740 cm^{-1}, is in accord with other complexes of this type.[23] The first ligand field band for the O-bonded isomer appears at 330 nm while that for the other isomer occurs as expected at a lower wavelength (Table I).

The ^1H NMR spectrum of the $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ ion in Me_2SO showed a single resonance at 6.6 ppm (Figure 1), with an intensity consistent with four protons, which is similar to that for the Co(III) analogue[15] and is assigned to the exo-NH_2 protons. Analysis of the NMR spectrum of the N-bonded isomer (Figure 1), also in Me_2SO, implies that the urea exists predominantly as the imidol rather than the amide tautomer. The signal at 6.6 ppm (2 protons) is ascribed to the exo-NH_2 protons by comparison to the O-bonded isomer, while the two lower field protons, which coalesce on addition of HCl, correspond to the alcohol and imine protons. This mode of bonding[24] has been found before for similar metal-coordinated amide complexes.



imidol amide

Reaction of the $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ Ion in Base. In the pH range 6–12, the sole products of reaction of the O-bonded isomer were the deprotonated N-bonded urea complex $[(NH_3)_5RhNHCONH_2]^{2+}$ and $[(NH_3)_5RhOH]^{2+}$ (Table II), separated by ion-exchange chromatography. Both compounds cochromatographed with authentic samples and gave the expected UV/visible absorption maxima (Table I). $[(NH_3)_5RhOOCNH_2]^{2+}$ was not detected (see Experimental Section).

Values of the observed rate constant (k_{obsd}) for the O-bonded isomer (Table III[25]) are plotted as a function of pH in Figure 2. They are independent of pH at values of less than 9; log k_{obsd} rises linearly with pH in the range 10–12, after which curvature of the plot becomes apparent. This curvature is due to ionization of the coordinated urea to give the less reactive conjugate base. All data fit an empirical two-term rate law (eq 3) with $k_s = 1.07 \times 10^{-4}$

$$k_{obsd} = k_s + K_w k_{OH}/(K_a + [H^+]) \quad (3)$$

s^{-1}, $k_{OH} = 0.172$ M^{-1} s^{-1}, and $pK_a = 13.67$, for $K_w' = 1.71 \times 10^{-14}$ (25 °C, ionic strength 1.0 M). The value of 13.67 for the pK_a for the coordinated urea was derived via eq 4, which is the inverse

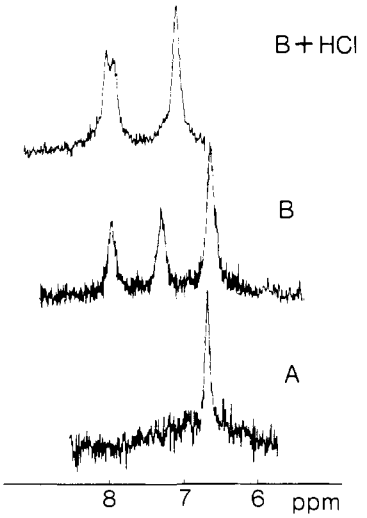


Figure 1. 100-MHz NMR spectra, recorded in Me_2SO, for $[(NH_3)_5RhOC(NH_2)_2](ClO_4)_3$ (A) and $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$ (B), without and with added HCl.

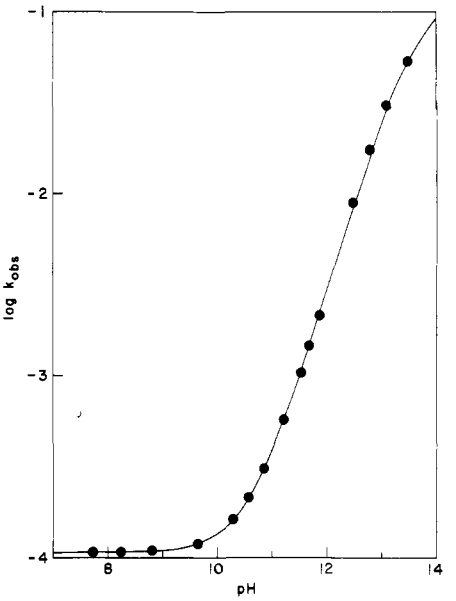


Figure 2. Plot of $-\log k_{obsd}$ vs. pH for the base hydrolysis of $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ at 25 °C and 1.0 M ionic strength. The solid line represents the calculated curve as defined by eq 3.

(21) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470–6.
(22) Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1094–100.
(23) Penland, R. B.; Mizushima, S.; Curran, C.; Quagliano, J. V. *J. Am. Chem. Soc.* **1957**, *79*, 1575–8.
(24) Buckingham, D. A.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3451–6. Brain, D. B.; Burbank, R. D.; Robin, M. B. *Ibid.* **1969**, *91*, 2895–902. Buckingham, D. A.; Keene, F. R.; Sargeson, A. M. *Ibid.* **1973**, *95*, 5649–52.
(25) Supplementary material.

Table II. Product Distributions of the Reactions of $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ and $[(NH_3)_5RhNH_2CONH_2]^{3+}$ Ions at 25 °C and $\mu = 1.0$ M

substrate	reaction pH	reaction time, h	% $[(NH_3)_5RhX]$, X = OH	$NHCONH_2$	NH_3	total
$MOC(NH_2)_2$	12.0[a]	0.25	36.0 ± 1.4	66.8 ± 2.3		102.8 ± 3.7
	6.27[b]	16	37.7 ± 0.9	62.2 ± 2.1		100.0 ± 2.7
	2.05[c]	120	69.0 ± 0.8		31.4 ± 1.8	100.7 ± 1.0
MNH_2CONH_2	2.05[c]	120	56.0 ± 1.8		43.3 ± 1.0	99.3 ± 2.7

[a] 0.1 M triethylamine buffer. Four determinations. [b] 0.1 M 2-(*N*-morpholino)ethanesulfonic acid buffer. Seven determinations. [c] 0.1 M glycine buffer. Three determinations.

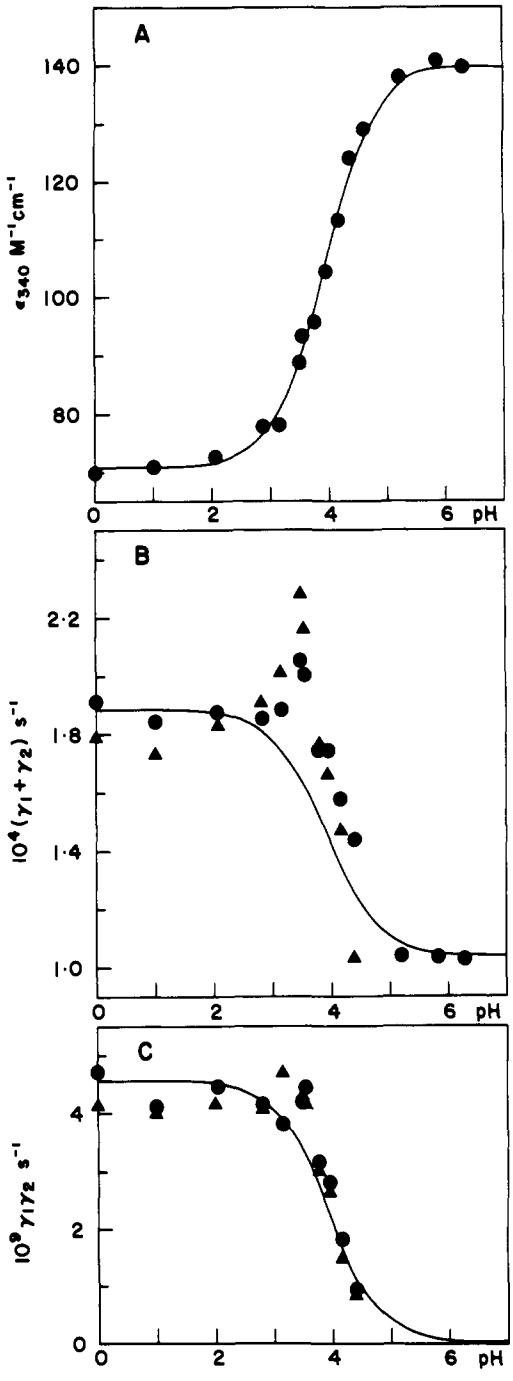


Figure 3. Plots of the variation of ϵ_{340} for $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$ as a function of pH (A) and the variation of the values of $\gamma_1 + \gamma_2$ (B) and $\gamma_1\gamma_2$ (C) as a function of pH, for the N-bonded (▲) and O-bonded isomers (●). For A, the solid line shows the calculated titration curve while for B and C, the lines represent the theoretical curve assuming no contribution to the kinetic parameters from the presence of $[(NH_3)_5RhNCO]^{2+}$ (see text).

of eq 3, using data obtained in high pH solution (0.05–0.5 M NaOH).

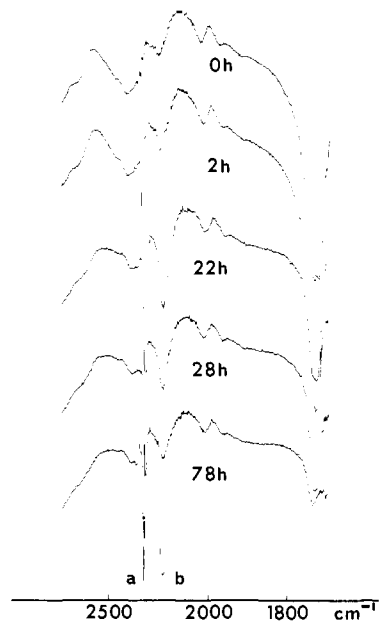


Figure 4. Intermittant scans of the IR spectrum of an acidic solution of $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$ showing reference peaks for CO_2 (a) and $[(NH_3)_5RhNCO](ClO_4)_2$ (b).

to $[H^+]$ (low pH) and of the spontaneous to the base-catalyzed rate at higher pH.

$$\frac{1}{k_{obsd} - k_s} = \frac{K_a}{K_w k_{OH}} + \frac{[H^+]}{K_w k_{OH}} \quad (4)$$

Strictly, the spontaneous term needs to modified to account for the effect of the ionization of the ligand and a more complete equation would be as in eq 5. However, this correction will be

$$k_{obsd} = \frac{k_s[H^+] + K_w k_{OH}}{K_a + [H^+]} \quad (5)$$

insignificant at all pH's because of the relative magnitudes of K_a

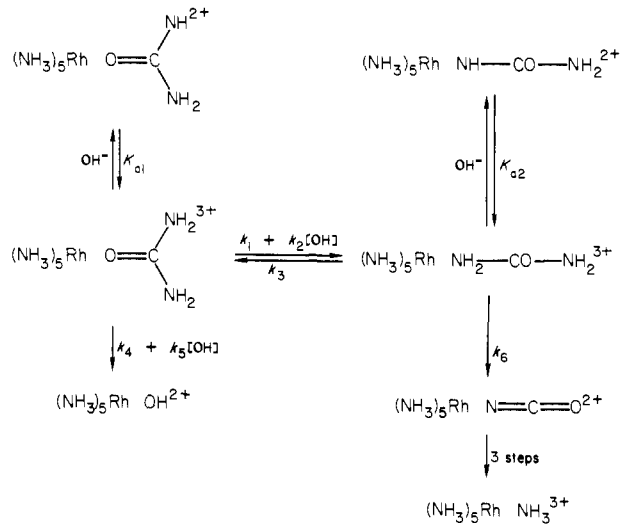
In contrast, the N-bonded isomer is completely stable to reaction at neutral and basic pH even in the presence of buffers. No general-base path is evident therefore with this isomer.

Reactions of the $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ and $[(NH_3)_5RhNH_2CONH_2]^{3+}$ Ions in Acid Solutions. The ultimate products of reactions of both isomers of (urea)pentaammine-rhodium(III) at pH 2.05 were $[(NH_3)_6Rh]^{3+}$ and $[(NH_3)_5RhOH_2]^{3+}$. The proportions of these products, separated chromatographically and identified by their elution characteristics and electronic spectra, depended on the substrate.

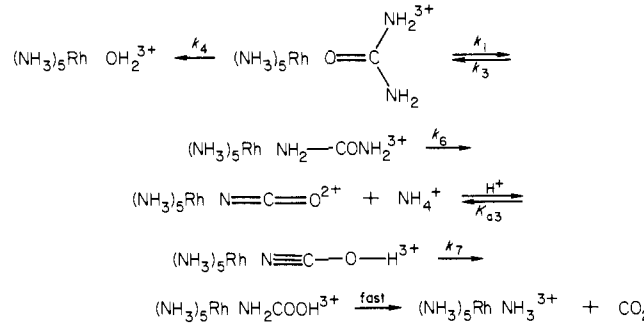
The kinetics of reactions of both isomers were followed in buffered solutions or in CF_3SO_3H solution in the pH range 0–6. For the N-bonded species, A_{320} at first increased to a maximum and then decreased to a stable value[26] while for the O-bonded isomer, A_{320} underwent a rapid followed by a slower decrease. Absorbance vs. time curves exhibited a good fit to an equation involving the summation of two exponentials,[27] eq 6, for which

(26) Similar biphasic behavior has been noted before, e.g., see: Buckingham, D. A.; Francis, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630–9.

Scheme I



Scheme II



γ_1 and γ_2 are the time constants for the two exponentials. In each

$$\epsilon_t = \alpha \exp(-\gamma_1 t) + \beta \exp(-\gamma_2 t) + \delta \qquad (6)$$

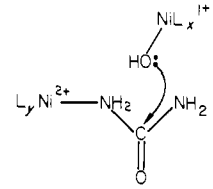
buffer, the values for the corresponding time constants for both isomers were found to be approximately equal and were constant over the pH range 0–3 (Table IV[25]). The rapid decrease in both parameters at higher pH (Figure 3) was attributed to the dissociation of the N-bonded isomer to its inactive conjugate base. The value of the pK_a for this process was found to be 3.93 ± 0.05 from the dependence of the extinction coefficient[28] at 340 nm as a function of pH (Figure 3).

The reaction of the N-bonded isomer was also followed by infrared spectroscopy in a mildly acidic 4:1 mixture of Me_2SO–water. Selected scans and reference spectra are shown in Figure 4. It is apparent that the N-bonded carbonyl vibration at 1740 cm^{-1} steadily decreases in intensity on a time scale consistent with the more detailed kinetic results, while a sharp peak at 2350 cm^{-1}, due to CO_2, appears. Also observed is a transient resonance at 2260 cm^{-1}, which is ascribed to $[(NH_3)_5RhNCO]^{2+}$ by comparison with an authentic sample. This resonance is quite different to that for free cyanate ion (2160 cm^{-1}), and no NCO^- was detected in the reaction.

Discussion

The kinetic and product analyses of the reactions of the isomers of (urea)pentaamminerhodium(III) at pH values in the range 0–14 are consistent with the details in Scheme I. In neutral and basic solutions, linkage isomerization of the O-bonded urea complex to the N-bonded isomer competes favorably with hydrolysis to $[(NH_3)_5RhOH]^{2+}$ and urea. The rate law (eq 3) and product distributions at pH 6.27 and 12.0 (Table II) demonstrate that both the isomerization and the hydrolysis reactions occur by spontaneous ($k_s = k_1 + k_4$) and base-catalyzed ($k_{OH} = k_2 + k_5$) paths and allow separation of the individual rate constants $k_1 = 6.7 \times 10^{-5}$ s^{-1}, $k_2 = 0.11$ M^{-1} s^{-1}, $k_4 = 4.0 \times 10^{-5}$ s^{-1}, and $k_5 = 0.060$ M^{-1} s^{-1}, at 25 °C and 1.0 M ionic strength. The pH profile (Figure 2) is similar to that for the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion[15] and curves at high pH as the complex dissociates with $pK_{a1} = 13.67$ to produce increasing proportions of the conjugate base. Values of the rate constants for the aquation reactions k_4 and k_5 may be compared with the corresponding values of 5.1×10^{-5} s^{-1} and 15.3 M^{-1} s^{-1} for the Co(III) complex.[15] For the Co(III) compound isomerization was not competitive with hydrolysis.

In common with hydrolysis of the Co(III) complex, there was no evidence for the substantial production of $[(NH_3)_5RhOOCNH_2]^{2+}$, as would be demanded were the reaction to model the chemistry of urease. This is less surprising when it is realized that this mode of coordination of urea to Co(III) and Rh(III) appears to result in little polarization of the carbonyl bond.[14] The lowering of pK_a of urea from ca. 14 for the free ligand[29] to 13.19 and 13.67, respectively, for the two complexes, is minimal. In contrast, chelation of glycinamide to Co(III) through its amine nitrogen and carbonyl oxygen atoms lowers the pK_a of the amide proton to 11.2 and renders it 10^4-fold more susceptible to hydrolysis by hydroxide.[30] Urea itself is not hydrolyzed readily in base. Its lack of reactivity in comparison with simple amides probably arises from its greater resonance stabilization; similar considerations may be relevant to the minimal effects of coordination.[14] Were urease to activate urea toward hydrolysis by carbonyl coordination to Ni(II), then an additional means of activation of the carbonyl bond would appear to be necessary. Other evidence has suggested that an active site carboxylic acid may induce greater polarization of the carbonyl bond and presumably increase the reactivity.[8] Roles for the Ni^{2+} ions may involve assistance for the leaving group and supply of a coordinated nucleophile as



The prsent study implies that there is little to be gained by way of activation of urea in just coordinating the carbonyl group unless there are additional influences.

The mechanism of base catalysis of the linkage isomerization has not been studied in detail. However, base catalysis of isomerization of nitrito pentaammine complexes of Co(III), Rh(III), and Ir(III), to the nitro complex, has been argued to proceed via a conjugate base path involving deprotonation of one of the coordinating ammonias, leading to weakening of the metal–oxygen bond and thence to intramolecular rearrangement.[31] Such a mechanism is likely to obtain here although the probing experiments have not, as yet, been done. The deprotonation of an ammonia is known to labilize other groups coordinated to the metal ion, and the bulk of the evidence indicates that the group does not leave the coordination sphere in such processes.

In acidic solutions, the two isomers slowly interconvert and react by distinct pathways; the N-bonded isomer ultimately yields the $[(NH_3)_6Rh]^{3+}$ ion by way of $[(NH_3)_5RhNCO]^{2+}$ while the O-bonded form hydrolyzes to $[(NH_3)RhOH_2]^{3+}$ ion and free urea. Under these conditions the competing pathways are as summarized as in Scheme II. For the case where $k_6 \gg k_7[H^+]/K_{a3}$, or vice versa, the kinetics for such a reaction can be shown to be dependent on two exponentials,[32] as observed. At pH <3, the condition that $k_7[H^+]/K_{a3} \gg k_6$ is satisfied (vide infra) and the time constants

(27) Jackson, W. G.; Harrowfield, J. MacB.; Vowles, P. D. *Int. J. Chem. Kinet.* **1977**, *9*, 535–48.
(28) Balahura, R. J.; Jordan, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 1553–9.
(29) Woolley, E. M.; Hepler, L. G. *Anal. Chem.* **1974**, *44*, 1520–23.
(30) Buckingham, D. A.; Davis, C. E.; Foster, D. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1970**, *92*, 5571–9.

γ_1 and γ_2 (eq 6, Table IV) are related to the individual rate constants as[32]

$$\gamma_1 + \gamma_2 = k_1 + k_3 + k_4 + k_6 \quad (7)$$

$$\gamma_1\gamma_2 = k_3k_4 + k_1k_6 + k_4k_6$$

While the values of the preexponential parameters of eq 6 are predicted to vary depending on whether the O- or N-bonded isomer is the substrate (as observed), the values of the time constants at a particular pH will be equivalent. The observation of near equivalence of the two sets of data argues for a mechanism giving rise to two exponential processes, as in scheme II, rather than unrelated consecutive first-order reactions of the separate isomers.[27]

At pH >6, the N-bonded complex is completely deprotonated and unreactive, hence contributions to the observed rate from those processes whose rate constants are k_3 and k_6 are negligible. Thus in the limit at pH >6, $\gamma_1 + \gamma_2$ becomes 1.07×10^{-4} s^{-1} and $\gamma_1\gamma_2 = 0$, in agreement with the observed values. The values of $\gamma_1 + \gamma_2$ and $\gamma_1\gamma_2$ are independent of pH at pH <3 and reflect the pK_a of the N-bonded isomer at higher pH (Figure 3). Moreover, the rate constant for aquation of the $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion shows no such dependence on pH in this range.[15] These data indicate that the values of k_3 and k_6 ought also to be independent of pH in this range and that the variation in the values for the sum and product of the two time constants with pH is solely ascribable to the effect of deprotonation of the N-bonded isomer.

The assumption in Scheme II that all the $[(NH_3)_5RhOH_2]^{3+}$ produced derives from $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ is also supported by studies with the Co(III) complex. Competitive solvolysis in the isomerization of the $[(NH_3)_5CoNH_2CONMe_2]^{3+}$ ion to the O-bonded form in acid was barely detectable.[16]

These assumptions, together with the results of the kinetic and product distribution studies (Table II), allow calculation of the rate constants k_1 and k_6 at pH 2.05. Values of the sum and product of the time constants for the two exponentials observed were found to be $(1.85 \pm 0.04) \times 10^{-4}$ s^{-1} and $(4.32 \pm 0.19) \times 10^{-9}$ s^{-2}. For reaction of the O-bonded isomer, at infinite time, it may be shown that[32]

$$1 + \frac{[RhOH_2]}{[RhNH_3]} = \frac{\gamma_1\gamma_2}{k_1k_6}$$

whence $k_6 = 2.0 \times 10^{-5}$ s^{-1}. Similarly for the N-bonded isomer

$$1 + \frac{[RhNH_3]}{[RhOH_2]} = \frac{\gamma_1\gamma_2}{k_3k_4}$$

whence $k_3 = 6.1 \times 10^{-5}$ s^{-1}. The solid lines in Figure 3 represent the calculated lines on the basis of the values determined for k_1, k_3, k_4, and k_6 coupled to the effect of deprotonation of the N-bonded isomer.

The intermediacy of $[(NH_3)_5RhNCO]^{2+}$ in reactions of the two isomers in aqueous solutions is implied by the infrared experiment and also by the following two pieces of evidence. When a sample of the O-bonded isomer was dissolved in water and then precipitated by the addition of 70% $HClO_4$, the crystalline product was shown by infrared to contain both $[(NH_3)_5RhNH_2CONH_2]^{3+}$ and $[(NH_3)_5RhNCO]^{2+}$, as well as starting material. Also, examination of the pH dependence of the plot (Figure 3) of $\gamma_1 + \gamma_2$ shows a marked deviation from the calculated curve at pH ca. 3. It has been shown that the isocyanato complex undergoes an acid-dependent decomposition to give the hexaammine species via the N-bonded carbamato complex,[19] as shown in Scheme II. At pH >1.6, decarboxylation of this species is not rate limiting[33] and the rate law for the overall process is given as in eq 8, where K_{a3}

$$k_{obsd} = k_7[H^+]/K_{a3} \quad (8)$$

is the acid dissociation constant of the coordinated cyanic acid. A value of 0.62 M^{-1} s^{-1} has been determined for k_7 at low pH in the absence of buffers.[19] In order to relate these results to the present work, the kinetics of decomposition of this species were reexamined as a function of pH, using the same conditions as for the urea studies. The observed rate constants were linearly dependent on $[H^+]$ in the pH range 2.2–4.2, giving $k_7/K_{a3} = (0.96 \pm 0.04)$ M^{-1} s^{-1} at 25 °C and 1.0 M ionic strength. Clearly, at pH >3, this rate becomes comparable in magnitude to that for k_6 and the assumption that $k_7[H^+]/K_{a3} \gg k_6$ no longer holds. Such a situation can be described in terms of three exponentials though we have not attempted to factorize the data in this way. This results in the poor agreement which was found between the observed and calculated values for $\gamma_1 + \gamma_2$ seen in the pH range 3–4. Thus the pH behavior for the observed time constants also supports the presence of this intermediate. It is worthy of note that the greater deviation from the calculated values (derived by assuming no contribution from rate-determining $(NH_3)_5RhNCO^{2+}$ decomposition) occurs (Figure 3) for the kinetics of the N-bonded isomer. At lower pH, the influence of the cyanato complex is greater than that for the O-bonded form while at higher pH the ionization of the ligand to the inert 2+ ion is inhibitory.

Table V. Rate and Equilibrium Constants for the Reactions of Urea Pentaammine Complexes of Rh(III) and Co(III)[a]

parameter[b]	Rh(III)[c]	Co(III)
k_1, s^{-1}	6.7×10^{-5}	[d]
k_2, M^{-1} s^{-1}	0.112	[d]
k_3, s^{-1}	6.1×10^{-5}	1.6×10^{-2} [e]
k_4, s^{-1}	4.0×10^{-5}	5.1×10^{-5} [f]
k_5, M^{-1} s^{-1}	0.060	14.8[f]
k_6, s^{-1}	2.0×10^{-5}	[d]
k_7, M^{-1} s^{-1}	0.96, 0.62[g]	0.17[h]
pK_{a1}	13.67	13.19[f]
pK_{a2}	3.93	2.92[e]

[a] μ = 0.1 M, 25.0 °C. [b] Scheme I. [c] This work. [d] Not seen. [e] $[(NH_3)_5CoNH_2CONMe_2]^{3+}$.[16] [f] $[(NH_3)_5CoOC(NH_2)_2]^{3+}$.[15] [g] Reference 19. [h] See ref 26.

The values of the rate and equilibrium constants determined in this study are collected in Table V and compared with analogous figures for the Co(III) complexes.

The formation of $[(NH_3)_6Rh]^{3+}$ from $[(NH_3)_5RhNH_2CONH_2]^{3+}$ represents the first observation of nonenzymatic enhancement of the rate of decomposition or urea at low pH. Comparison of the rate constant k_6 (2.0×10^{-5} s^{-1}) with the estimated value for decomposition of free urea to ammonium cyanate at pH 2–3 (6×10^{-10} s^{-1}) indicates that coordination to the metal centre increases the reactivity some 30 000-fold.

The overall reaction could conceivably occur by one or more of four distinct paths. Nucleophilic attack of water or hydroxide at the carbonyl could produce a tetrahedral intermediate which could collapse with elimination either of NH_3 to give $[(NH_3)_5RhNH_2COOH]^{3+}$ or of $[(NH_3)_6Rh]^{3+}$ to produce free carbamate. The N-bonded carbamato complex is known to decarboxylate[33] on a time scale which would preclude its observation in the present study. Either process would mimic the overall chemistry of urease, and the rate enhancement could reflect the capacity of the metal complex to act as a Lewis acid catalyst of such reactions.[14]

The other two paths involve direct elimination of $[(NH_3)_6Rh]^{3+}$ to produce cyanate ion as the other product or of NH_3 leaving the $[(NH_3)_5NCO]^{2+}$ ion. Either process would parallel the slow decomposition of urea in aqueous solution.

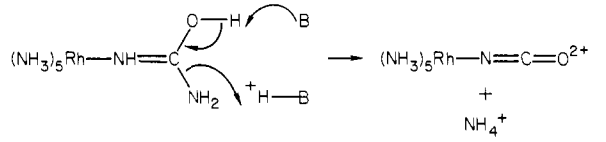
The observation of the intermediate $[(NH_3)_5RhNCO]^{2+}$ ion

(31) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 904–10.

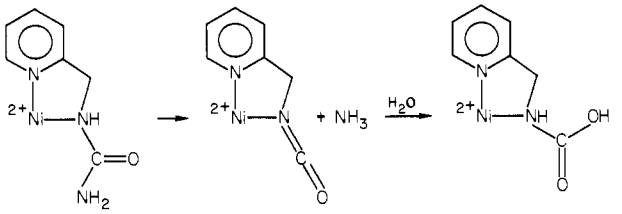
(32) The system studied in the present work is of the form A $\rightleftarrows$ B/A $\rightarrow$ C/B $\rightarrow$ D, which is similar to system 24 (A $\rightleftarrows$ B/A $\rightarrow$ C) discussed in: Capellas, C.; Bielski, B. H. J. "Kinetic Systems"; Wiley-Interscience: New York, 1972. Analysis of this system can be readily extended to include the extra reaction, and again a rate law consisting of two exponentials is seen. Derivation of this equation and those for the product distribution are discussed in an appendix in the supplementary material.

(33) Although the acid form $[(NH_3)_5RhNH_2COOH]^{3+}$ is present at lower pH and is more stable,[19] its decarboxylation ($k > 10^{-3}$ s^{-1}) still occurs much more rapidly than any of the reactions of the isomers of the urea complexes.

Scheme III



Scheme IV



and lack of free NCO^- ion implies that a major path for the reaction is elimination of the exo-NH_2 group. However, we cannot exclude the other paths as smaller contributors but a multiplicity of routes is improbable. Given this understanding, it seems reasonable only to discuss mechanisms for the observed route.

NMR evidence and the low pK_a, characteristic of a coordinated imine, both point to a significant contribution of the imidol tautomer to the structure of the N-bonded urea in solution. There is little literature support for significant amounts of tautomers of amides[34] in solution, though for urea it has been reported[35] that some of the imidol is present, and studies of the substrate specificity of urease can be rationalized in terms of imidol tautomers in its mechanism.[36] The function of the metal ion could then be to provide stability for and to increase the concentration of the imidol tautomer. This would effectively provide a more accessible pathway for decomposition of urea in solution, e.g., as in Scheme III.

With the assumption that the exo-nitrogen atom leaves as NH_3, which is reasonable since this would be far more likely to be the attacking group in the reverse reaction than amide or ammonium[37] ions, then the preferred cleavage of the exo-N–C bond arises from the difference in basicity of the two possible leaving groups. The complex ion $[(NH_3)_5RhNH_2]^{2+}$ is at least 5–6 orders of magnitude more basic than NH_3. The metal ion could also donate $d\pi$ electron density to the π^* orbitals of the imidol and the resulting coordinated cyanate ion. Thereby, it could assist the NH_3 to leave and stabilize the intermediate product.

We have thus far been unable to mimic effectively the chemistry of urease, and this may reflect our inability to model the more subtle effects of the enzyme.[8] The model chemistry indicates that urease could employ a mechanism akin to that in Scheme I if the products were to dissociate from the enzyme following hydration of an (isocyanato)nickel(II) intermediate. The consequence is that NCO^- should be a substrate for urease. Moreover it should be a very effective substrate since only carbamate is detected. This prospect has been tested recently, and there is no evidence whatsoever of enzymatic hydrolysis.[38] In addition such a mechanism could not explain urease-catalyzed hydrolysis of aliphatic amides and is inconsistent with the present evidence that their hydrolysis at the active site of the enzyme occurs by a mechanism analogous to that used for hydrolysis of urea and N-substituted ureas.

Blakeley et al.[6] have recently observed the Ni^{2+}-promoted solvolysis of *N*-(2-pyridylmethyl)urea at elevated temperatures in ethanol–water mixtures. The reaction produced mixtures of 2-pyridylmethylamine and ethyl *N*-(2-pyridylmethyl)carbamate at a rate $>7 \times 10^4$ fold faster than in the absence of metal ion. It is believed to occur by way of solvent addition to the O-coordinated urea carbonyl, as proposed for the enzyme-catalyzed reaction. Although such a mechanism is attractive, it should be noted that the same products would arise from an N-coordinated urea by a mechanism analogous to that of Scheme I, via an intermediate N-coordinated isocyanato species as in Scheme IV.

Acknowledgment. We gratefully acknowledge the ANU microanalytical service for the determination of elemental analyses.

Registry No. $[(NH_3)_5RhOC(NH_2)_2]y(S_2O_6)_{3/2}$, 86064-64-4; $[(NH_3)_5RhOC(NH_2)_2](ClO_4)_3$, 86064-70-2; $[(NH_3)_5RhNH_2CONH_2](NO_3)_3$, 86064-66-6; $[(NH_3)_5RhOSO_2CF_3](CF_3SO_3)_2$, 84254-57-9; $[(NH_3)_5RhOCONH_2](S_2O_6)$, 86064-68-8; $[(NH_3)_5RhOH_2](ClO_4)_3$, 15611-81-1; $[(NH_3)_5RhOH]^{2+}$, 26214-91-5; $[(NH_3)_5RhOH_2]^{3+}$, 15337-79-8; $[(NH_3)_5RhNHCONH_2]^{2+}$, 86064-69-9; $[(NH_3)_6Rh]^{3+}$, 16786-63-3; $[(NH_3)_5RhNCO]^{2+}$, 34420-30-9; NaNCO, 917-61-3; urea, 57-13-6.

Supplementary Material Available: Table III, rate constants for the reaction of the $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ ion at pH >6, Table IV, time constants for the reactions of $[(NH_3)_5RhNH_2CONH_2]^{3+}$ and $[(NH_3)_5RhOC(NH_2)_2]^{3+}$ at acid pH, and the derivation of kinetic and product distribution equations for acid hydrolysis (5 pages). Ordering information is given on any current masthead page.

(34) Skulski, L.; Palmer, G. C.; Calvin, M. *Tetrahedron Lett.* **1963**, 1773–6.

(35) Paisek, Z.; Urbanski, T. *Tetrahedron Lett.* **1962**, 723–7.

(36) Dixon, N. E.; Gazzola, C.; Blakeley, R. L.; Zerner, B. *Science (Washington, D.C.)* **1976**, *191*, 1144–50.

(37) For a discussion of the mechanism of decomposition of urea see: Frost, A. A.; Pearson, R. G. In "Kinetics and Mechanism"; Wiley: New York, 1961; pp 307–316. Shorter, J. *Chem. Soc. Rev.* **1978**, *7*, 1–14.

(38) Blakeley, R. L.; Zerner, B., private communication.