seems to be negative, though still small) and the rates are limited by the entropy of activation. The facile reduction of $[(NH_3)_5CoO]_2^{5+}$ compared to $[(NH_3)_4Co-OH]_2^{4+}$ is not surprising. When the superoxo ion is oxidant, the electron is absorbed into an orbital centered largely on the oxygen,[3] and the bond rearrangement accompanying electron transfer is small—thus note that the molecular framework remains intact on electron transfer. However, when the dihydroxo-bridged species is the oxidant, the electron absorbed enters an orbital centered largely on Co, which is antibonding with respect to Co and one or more ligands. Rather drastic rearrangement of the molecular structure preceding electron transfer is called for, and the rate of reduction is correspondingly less.

Our kinetic results differ from those of Sykes[1] in that we have observed only a single path for the reductions, whereas he reports three parallel paths for the reduction by Fe^{2+}. These paths differ in the way they depend on (H^+). The rate law reported by him has the form

$$-d\ln([(NH_3)_5CoO]_2^{5+})/dt = (Fe^{2+})[(k_A/(H^+)) + k_B + k_C(H^+)]$$

His value of $k_B = 4.73 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25° ($E_B = 9.6$ kcal/mol) is directly comparable to the specific rates we have recorded. The importance of the term first

order in (H^+) when Fe^{2+} is the reducing agent is not unexpected. We have concluded that the dominant form of the intermediate in acidic solution contains one proton more than the reactants, and the kinetic assistance by the proton in forming the intermediate is not unexpected when a weak reducing agent is used. The term inverse in (H^+) may reflect the fact that OH^- stabilizes $Fe(III)$ over $Fe(II)$, and some kinetic assistance from the stabilization can be expected.

All of the reactions are probably of the outer-sphere type. Direct attack on oxygen may be prevented by the steric requirements of the NH_3 ligands on the cobalt centers. The operation of an outer-sphere mechanism can explain why Cr^{2+} reacts less rapidly than does V^{2+}. The changes in dimension required when Cr^{2+} is oxidized more than compensate for the greater driving force for the Cr^{2+} compared to the V^{2+} reaction.

The Acid-Catalyzed Aquation of Hexaammineruthenium(II) and Pentaamminepyridineruthenium(II) Complex Ions

By PETER C. FORD, JOHN R. KUEMPEL, and HENRY TAUBE

The aquation rates of $Ru(NH_3)_6^{2+}$ and $Ru(NH_3)_5py^{2+}$ have been measured in acidic aqueous solutions. It is found that the rate of loss of coordinated ammonia or pyridine from these increases with increasing hydrogen ion concentration, the differential rate law for the loss of the first NH_3 from $Ru(NH_3)_6^{2+}$ being: $-d[Ru(NH_3)_6^{2+}]/dt = k_1[H^+][Ru(NH_3)_6^{2+}]$, where $k_1 = (1.24 \pm 0.03) \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 25°. The pentaamminepyridine complex ion aquates at a somewhat slower rate. Electron-withdrawing substituents on the pyridine ring stabilize the complex, resulting in even slower aquation rates. The stoichiometries and rate laws are described. To explain the results, a mechanism is proposed in which an interaction of a proton with ruthenium π d electrons labilizes the metal–nitrogen bonds.

Introduction

Recent experiments in this laboratory have been concerned with the preparation and characterization of ruthenium complex ions of the type $Ru(NH_3)_5pyX^{2+}$, where X is a variable group attached to the pyridine ring.[1] In the course of this research it was noticed that these complexes undergo slow aquation reactions in acidic solutions at rates which increase with increasing hydrogen ion concentration. This interesting observation led us to investigate these reactions more carefully and to extend the experiments to include the simpler ion $Ru(NH_3)_6^{2+}$.

Experimental Section

Materials.—Water, which had been passed through an ion-exchange column and then distilled, was redistilled in an all-glass apparatus from basic potassium permanganate before being used to prepare the solutions. $Ru(NH_3)_6Cl_3$, obtained from Johnson Matthey and Co., London, was purified by double recrystallization from 1 M HCl and from water. $Ru(NH_3)_5Cl_3$ was prepared from $Ru(NH_3)_6Cl_3$ as described in the literature.[2] The syntheses of $Ru(NH_3)_5py(ClO_4)_2$ and $Ru(NH_3)_5pyX(ClO_4)_2$, where X = m-CH_3, m-Cl, p-CH_3, and m-CO_2CH_3, are also reported elsewhere.[1]

All kinetic experiments involving $Ru(NH_3)_6^{2+}$ were run in 1.0 M ionic strength mixtures of p-toluenesulfonic acid ($C_7H_7SO_3H$) and lithium p-toluenesulfonate ($C_7H_7SO_3Li$). These mixtures

(1) P. Ford, D. P. Rudd, R. Gaunder, and H. Taube, *J. Am. Chem. Soc.*, **90**, 1187 (1968).

(2) K. Gleu and K. Rehm, *Z. Anorg. Allgem. Chem.*, **227**, 237 (1936).

were prepared by partial neutralization of the reagent acid (Matheson Coleman and Bell) with reagent lithium carbonate. The excess acid concentration was determined by titration with standard sodium hydroxide solution. Reduction of the ruthenium complexes to the +2 state was accomplished in 10^{-3} M $C_7H_7SO_3H$ with amalgamated zinc.[3] Oxidizable impurities were removed from the reaction solutions prior to addition of the reduced ruthenium complexes by treatment with pure lead metal.

In the kinetic measurements and product studies involving the $Ru(NH_3)_5py^{2+}$ and $Ru(NH_3)_5pyX^{2+}$ species, reagent grade hydrochloric acid and ACS reagent grade sodium chloride (Baker and Adamson) were used to maintain constant chloride ion concentration.

During reduction and kinetic studies, oxygen was eliminated by continuously purging the solutions with argon gas, which had been pretreated in chromous scrubbing towers to remove oxygen. Earlier experiments involving the $Ru(NH_3)_5py^{2+}$ complex were performed using nitrogen as the "inert" atmosphere. These studies gave rate constants identical with those measured under argon; however, the product distributions were different owing to the formation of Ru(II) molecular nitrogen complexes[4] from reaction intermediates.

All spectrophotometric measurements were made with a Cary Model 14 or 15 spectrophotometer.

Stoichiometric Measurements.—The products of the aquation of $Ru(NH_3)_6^{2+}$ in acidic solution were determined in two ways. First, an aliquot of the reaction mixture was transferred using syringe techniques[5] to an amount of pyridine in excess of the total amount of acid present. Visible and uv spectra of the resulting solution were compared with those of $Ru(NH_3)_5py^{2+}$.[1] As will be shown in the Results section, the initial aquation of $Ru(NH_3)_6^{2+}$ is followed by a slower further reaction. In order to characterize the further reaction, a second method of product analysis was used. The reaction was initiated in 1 M $C_7H_7SO_3H$. At various times during the reaction, 1.0-ml aliquots were taken and the ruthenium complexes were oxidized to the +3 state by bubbling oxygen through them. It has been shown that this procedure quenches the acid decompositions in this system.[3] The oxidized samples were then diluted to twice their volume and placed on small cation resin columns (Bio-Rad AG 50WX2; 200–400 mesh, sodium form; the columns were 5 and 40 mm in cross section and height, respectively). When 15 ml of 0.5 M NaCl was used as an eluent, it was found that all ruthenium species remained on the columns and all of the NH_4^+ produced by the reaction was washed through. The separated NH_4^+ was collected in saturated boric acid solutions and quantitatively determined using the indophenol method.[6]

The product study in the case of the aquation of the $Ru(NH_3)_5py^{2+}$ and related species was more complicated. Solutions for product studies were prepared in a way analogous to that used in the preparations for the rate measurements (see following section). After the reaction had proceeded to the desired point, it was quenched by bubbling oxygen gas through the mixture. The resulting ruthenium(III) complexes and other species were separated by elution from a cation-exchange resin (Bio-Rad AG50WX2) using acidic sodium chloride solutions as eluents. Constant-volume aliquots were taken to provide a quantitative estimate of the species eluted. Ammonium ion was determined quantitatively by adding Nessler's reagent to volumes of early aliquots and comparing the optical densities to those of standards prepared using ammonium chloride solutions of known concentrations and the same Nessler's reagent. Absorbances at 400 and 425 mμ were measured as described by Vogel.[7] Other species were identified by their elution behavior and uv spectra.

Kinetic Measurements.—The acid hydrolysis reactions of $Ru(NH_3)_6^{2+}$ were initiated by adding samples of $Ru(NH_3)_6^{2+}$ (obtained by reducing $Ru(NH_3)_6Cl_3$ in very dilute acid solution) to concentrated $C_7H_7SO_3H$–$C_7H_7SO_3Li$ mixtures of known compositions such that the resulting mixtures had an ionic strength of 1.0 M and the total ruthenium concentration was about 5 × 10^{-4} M. At various times, 1.0-ml aliquots of the reacting solutions were quickly transferred by syringe to 2.0-ml deaerated aliquots of a 2 M pyridine solution in a 1-cm optical cell, taking care to exclude air. The resulting change to more basic conditions stopped the acid hydrolysis reaction, and after 5 min the color of the $Ru(NH_3)_5py^{2+}$ species developed quantitatively. The absorbance of this ion at 408 mμ was used to calculate the concentrations of $Ru(NH_3)_5H_2O^{2+}$ produced by the reaction at various times. Independent measurements showed that $Ru(NH_3)_6^{2+}$ reacts with pyridine much less rapidly than does the aquo ion and that the rate of this slow reaction ($k \simeq 1 \times 10^{-6}$ sec^{-1}) was independent of pyridine concentration over the range 0.1–2 M. The extinction coefficient of the pyridine complex was measured independently by quickly adding a known amount of $Ru(NH_3)_5H_2O^{2+}$, prepared by reducing $Ru(NH_3)_5Cl_3$ under conditions identical with those of the kinetic runs, to the pyridine solution and measuring the absorbance at 408 mμ. The value of 0.77×10^4 M^{-1} cm^{-1} obtained in this manner agrees well with the previously determined value[1] of 0.778×10^4 M^{-1} cm^{-1}.

Because of complicating side reactions, it was not possible to measure during a kinetic run a value of absorbance corresponding to complete replacement of one coordinated NH_3 by an H_2O, so it was necessary to calculate this value using the initial concentration of $Ru(NH_3)_6^{2+}$ and the extinction coefficient of $Ru(NH_3)_5py^{2+}$.

The kinetic experiments were performed at different temperatures. A few experiments were repeated in which HCl replaced $C_7H_7SO_3H$ as the acid.

A qualitative experiment was performed to check the rate of hydrolysis of $Ru(NH_3)_6^{2+}$ in basic solution. A dilute $C_7H_7SO_3H$ solution containing $Ru(NH_3)_6^{2+}$ was added to an argon-purged 1 M NaOH solution, taking care to exclude atmospheric oxygen. Aliquots (1.0 ml) of this mixture were withdrawn at various times and added to 2.0-ml aliquots of a 1 M $C_7H_7SO_3Hpy$ solution in a 1-cm optical cell, and the absorbance was measured at 408 mμ. After 100 min, only a trace of $Ru(NH_3)_5py^{2+}$ was detected. That this procedure does measure the $Ru(NH_3)_5OH^+$ produced by the hydrolysis of $Ru(NH_3)_6^{2+}$ was shown by adding a dilute $C_7H_7SO_3H$ solution containing $Ru(NH_3)_5H_2O^{2+}$ to a solution 1 M in pyridine and 1 M in NaOH and observing a quantitative conversion of the complex to $Ru(NH_3)_5py^{2+}$. These experiments set an upper limit of 3×10^{-6} M^{-1} sec^{-1} on the second-order rate constant for the base hydrolysis of $Ru(NH_3)_6^{2+}$.

The decomposition of $Ru(NH_3)_5py^{2+}$ in different hydrochloric acid solutions was initiated by delivering the desired amount of deoxygenated acid solution into a Zwickel flask[8] containing a sample of solid $Ru(NH_3)_5py(ClO_4)_2$ under an argon atmosphere. Typically, 20 ml of solution was added to 0.8 mg of solid. After about 1 min of agitation to ensure complete dissolution of the solid, the solution was transferred to an argon-filled spectrophotometric cell equipped with stopcocks to prevent contact of the reaction solution with air. The changes in the solution spectrum were followed by periodic scanning of the region 500–200 mμ. Rates were measured as a function of the optical density changes at 400 and 430 mμ.

Results

Products of $Ru(NH_3)_6^{2+}$ Aquation.—When pyridine, which rapidly replaces H_2O but not NH_3 in the coordination sphere of Ru(II), is used to measure the

(3) J. F. Endicott and H. Taube: (a) *J. Am. Chem. Soc.*, **84**, 4984 (1962); (b) *Inorg. Chem.*, **4**, 437 (1965).

(4) D. E. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).

(5) G. Svatos and H. Taube, *ibid.*, **83**, 4172 (1961).

(6) W. T. Bolleter, C. J. Bushman, and P. W. Tidwell, *Anal. Chem.*, **33**, 592 (1961).

(7) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 783.

(8) A. M. Zwickel, Ph.D. Thesis, University of Chicago, 1959.

concentration of $Ru(NH_3)_5H_2O^{2+}$ in an acidic solution of $Ru(NH_3)_6^{2+}$, rate data plots of the appearance of $Ru(NH_3)_5H_2O^{2+}$ indicate first-order behavior for the initial 2 half-lives. These results support the view that the initial product of the aquation of $Ru(NH_3)_6^{2+}$ in the noncomplexing, acidic solutions used in these studies is $Ru(NH_3)_5H_2O^{2+}$.

After about 2 half-lives of the initial reaction, the kinetic plots begin to show deviations from first-order behavior, and the absorbance of the pyridine complex at 408 mμ eventually exceeds that calculated for the loss of a single ammonia. Concurrent with the excess absorbance is the appearance of a shoulder on the short-wavelength side of the absorption band at 408 mμ. This complicating behavior is due to a further loss of ammonia forming more highly aquated ruthenium(II) ammines. The ion of formula $Ru(NH_3)_4py_2^{2+}$ (presumed to be in a *cis* configuration) has been synthesized and is found to have absorption maxima at 370 and 405 mμ. Figure 1 is a plot of the number of ammonium ions liberated per ruthenium *vs.* time for a reaction carried out in 1 M $C_7H_7SO_3H$. The ammonium ions were separated from the oxidized ruthenium species using cationic exchange. The data show an initial fast loss of the first ammonia followed by slower loss of the second and still slower loss of the third.
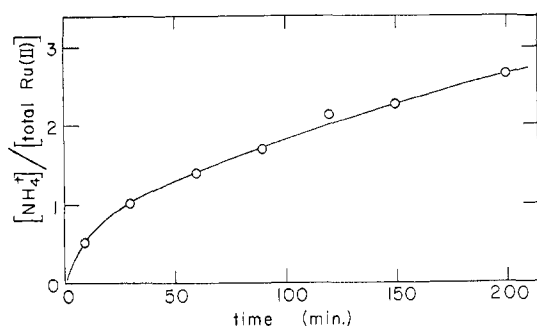

Figure 1.—Ratio of liberated NH_4^+ to total Ru(II) species present *vs.* time for the aquation of $Ru(NH_3)_6^{2+}$ in 1 M *p*-toluenesulfonic acid at 25°.

Products of $Ru(NH_3)_5py^{2+}$ Aquation.—The product distribution in the decomposition of $Ru(NH_3)_5py^{2+}$ is more complicated. Product solutions of this reaction were quenched with molecular oxygen to give the corresponding Ru(III) species which are much less labile under the reaction conditions. It was independently established that the reaction of $Ru(NH_3)_5py^{2+}$ with O_2 in dilute acid gives exclusively $Ru(NH_3)_5py^{3+}$ within the limits of the experimental observation. This reaction is not instantaneous but is rapid with respect to the aquation reaction. In interpreting the observations described below, it must be borne in mind that Ru-(III)–Cl bonds can be established during the reaction with O_2, by virtue of Ru(II) catalysis of the substitution of Cl⁻ for H_2O. In the absence of other anionic ligands, the net charge $[(3 - n)+]$ of a Ru(III) species indicates the number (n) of coordinated chlorides.

After quenching, the reaction products were sepa-

rated by chromatography using a cation-exchange column. The results of several experiments are summarized in Table I. The first species eluted is ammonium ion, the concentration of which was quantitatively determined by careful use of Nessler's reagent. The large amount of NH_4^+ found compared to the amount of $Ru(NH_3)_5py^{2+}$ reacted demonstrates that the initial decomposition step is followed by subsequent aquation of the metal–ammonia bonds in the resulting intermediates. The fact that hexaammine-

TABLE I

SEPARATION OF O_2-OXIDIZED AQUATION PRODUCTS OF $Ru(NH_3)_5py^{2+}$ USING CATION EXCHANGE[a]

Isolated products in order of elution	2.00 M HCl	2.00 M HCl	0.10 M HCl	0.10 M HCl
	Concentration of eluted species × 10⁴, M			
(1) NH_4^+	Pos; concn not detd	10.6	Pos; concn not detd	2.9
(2) pyH⁺	1.0	1.71	1.12	1.05
(3) +1 ion, λ_{max} 330 mμ	...	Trace	Trace	Trace
(4) $Ru(NH_3)_5Cl^{2+}$	...	...	0.12	0.20
(5) +2 ion, λ_{max} 341 and 255 mμ	0.14[b]	0.17[b]	0.23[b]	0.21[b]
(6) $Ru(NH_3)_5py^{3+}$	0.77	0.70	1.31	1.10
Total Ru(III) species[d] present	2.1	2.7	2.8	2.7
Total py species separated, (6) + (5) + (2)	1.91	2.58	2.66	2.36
Fraction of starting material unreacted,[c] (6)/[(6) + (5) + (2)]	0.44 0.40	0.32 0.27	0.48 0.49	0.44 0.47

[a] Temperature 25°; ionic strength 2.00 M (NaCl). [b] Concentration based upon identification as $Ru(NH_3)_4pyCl^{2+}$ and the estimate of ϵ_{255} 4.6 × 10³. [c] Estimated from kinetic rate constants. [d] Based on initial concentration of $Ru(NH_3)_5py^{2+}$ in the reaction solution.

ruthenium(II) in acid solution aquates in the first stage about 10 times as rapidly a pentaamminepyridineruthenium(II) loses pyridine (see below) suggests that $Ru(NH_3)_5(H_2O)^{2+}$, if an intermediate, would not accumulate but would undergo further aquation. For the product study carried out in 2 M hydrochloric acid (column 2, Table I), $Ru(NH_3)_5py^{3+}$ representing a concentration of 0.7 × 10⁻⁴ M in the reaction solution was recovered, compared to 2.7 × 10⁻⁴ M in the starting solution. The total ammonia concentration (in all forms) in the complex which had reacted would then equal 10.0 × 10⁻⁴ M, a figure which is close to the 10.6 × 10⁻⁴ M free ammonia eluted and determined by Nessler's reagent. Though the experimental error in this procedure is rather large, 10% being a not unreasonable estimate, it is clear that most of the ammonia bound to the substrate becomes separated from the metal ion center after the initial decomposition step. For this to be true, the specific rate of aquation of ruthenium–ammonia bonds in the decomposition intermediates must be greater than in the original complexes under these reaction conditions. The product study carried out at more dilute acid resulted in a much lower percentage of free ammonia. However, it should be noted that the free ammonia:ruthenium(II) ratio was always found to be greater than 1.0 and that there is the possibility that Cl⁻, which can with facility displace H_2O

from the coordination sphere of Ru(II), labilizes the complex.

The second species eluted from the column is free pyridinium ion. Its concentration in the product solution (as estimated from its spectrum, ϵ_{253} 5.3 $\times$ 10^3)[1] is less than that corresponding to the total substrate reacted, particularly at lower acid concentrations. Part of the pyridine may remain coordinated to a ruthenium(II) moiety other than the pentaammine (see below).

The third species eluted is observed in trace quantities. The ionic charge is +1, and the only spectral feature is a broad absorption band centered at approximately 330 mμ. This is probably a ruthenium moiety of the type $RuL_4Cl_2{}^+$, where L can be either NH_3 or H_2O. The spectrum of cis-$Ru(NH_3)_4Cl_2Cl$ has two absorption bands of about equal intensity at 310 and 352 mμ (ϵ ~1.5 $\times$ 10^3).[9] At very low concentrations, the appearance of this spectrum is a broad absorption centered at about 330 mμ.

The fourth species has the apparent charge of +2, an absorption band at 328 mμ, and appears only in the experiments done at lowest acid concentration. The charge and spectrum strongly suggest that this species is chloropentaammineruthenium(III); this ion is known to have an absorption maximum at 328 mμ (ϵ ~2 $\times$ 10^3).[10] The chloropentaammine would be expected as the product of the O_2 oxidation of either $Ru(NH_3)_5Cl^+$ or $Ru(NH_3)_5H_2O^{2+}$ in chloride media.[3] The labile $Ru(NH_3)_5H_2O^{2+}$ is the expected intermediate of the direct replacement of pyridine by water.

The fifth ion detected in the elution was again more evident at lower acid concentrations but did appear in all experiments. It has an apparent charge of +2 and two absorption bands in the uv region at 341 and 255 mμ (both quite broad) in the approximate intensity ratio 1:5 (Figure 2). An aliquot containing this species was reduced over amalgamated zinc under an argon atmosphere. The result was a yellow solution (original solution colorless) having absorption maxima at 400 and 243 mμ with the intensity ratio 1.2:1 (Figure 2). The similarity of the spectrum of the reduced species to that of $Ru(NH_3)_5py^{2+}$ (absorption maxima at 408 and 244 mμ)[1] implies similarity in structure. The +2 charge of the oxidized ion is evidence (in the absence of any other anions) for the coordination of one chloride; hence the eluted ion is very likely $Ru(NH_3)_4$-$Clpy^{2+}$. As the chloride ion would be expected to be quite labile to aquation once the metal complex is reduced, the reduced species is probably $Ru(NH_3)_4$-$(H_2O)py^{2+}$.

The only +3 species separated and detected by ion exchange is $Ru(NH_3)_5py^{3+}$ (from unreacted starting material) which is identified by its characteristic uv spectrum.[1]

The estimate based on the rate studies of the amount of starting material which has reacted agrees quite well
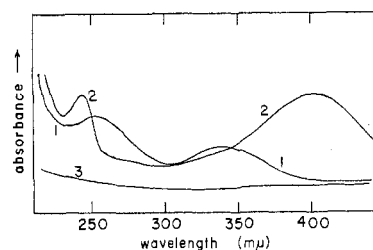

Figure 2.—Ultraviolet spectrum of an ion-exchanged aliquot of an $Ru(NH_3)_5py^{2+}$ reaction mixture. The aliquot contained +2 ion (no. 5); 1 is before and 2 is after reduction with Zn(Hg); 3 is a base line.

with the total pyridine found in the product species (Table I). The ion-exchange technique is apparently successfully separating and identifying nearly all of the pyridine species. The technique, of course, is most successful with the pyridine compounds because of the strong π-π^* absorption bands characteristic of the aromatic ring. However, in each case, the total of the pyridine species isolated was somewhat less than the initial concentration in the reaction solution. This difference may arise from some systematic error in the estimation of the molarities from the spectra of the ion-exchange aliquots or from the failure to isolate or identify pyridine species present in small amounts. An accurate accounting of the ruthenium species in the product solution is very difficult under the reaction conditions because products in great variety are possible (including polymeric forms), and most of these have not been characterized. Ruthenium complexes other than those listed in Table I were not detected in the ion-exchange elutions. It is probable that the ruthenium missing from the material balance was bound into nonelutable polymeric species and/or complexes which were eluted but not detected owing to their low concentrations and relatively small molar extinction coefficients.

An attempt was made to trap ruthenium intermediates not containing the ruthenium(II)–pyridine bond which might be produced in the initial stages of aquation at higher acid concentrations. With this goal in mind, about 5 min after a reaction was started, a slow stream of oxygen gas was passed into the solution. It was shown independently that the oxidation of pentaamminepyridineruthenium(II) is relatively slow with respect to that of other $Ru^{II}(NH_3)_5X$ species (X = H_2O or Cl^-), so that the O_2, when it is first introduced, should not rapidly deplete the starting material but should rapidly oxidize the nonpyridyl complexes, thereby fixing the ligands of these intermediates in the less labile coordination sphere of ruthenium(III). When the experiment was carried out in 2 M hydrochloric acid, with the initial $Ru(NH_3)_5py^{2+}$ concentration 2.7 $\times$ 10^{-4} M, approximately 15 min elapsed after passing O_2 into the solution before the yellow color of $Ru(NH_3)_5py^{2+}$ had completely faded. Consequently, during this time the substrate was decomposing in the presence of a low concentration of molecular

(9) Sample provided by J. A. Stritar; spectrum published by H. Hartmann and C. Buschbeck, *Z. Physik. Chem.* (Frankfurt), **11**, 120 (1957).

(10) H. Hartmann and C. Buschbeck, *ibid.*, **11**, 120 (1957).

oxygen which could act as a trapping agent for non-pyridyl ruthenium(II) intermediates.

The product mixture was analyzed by the ion-exchange technique, and the following species were isolated: NH_4^+ $(1.0 \times 10^{-4}\ M)$; Hpy^+ $(0.48 \times 10^{-4}\ M)$; +1 ion, no. 3 of Table I (trace); $Ru(NH_3)_5Cl^{2+}$ $(0.19 \times 10^{-4}\ M)$; +2 ion, no. 5 of Table I $(0.18 \times 10^{-4}\ M)$; and $Ru(NH_3)_5py^{3+}$ $(2.11 \times 10^{-4}\ M)$. The total recovered pyridine in all forms was $2.7 \times 10^{-4}\ M$, equivalent within the limits of the technique to the initial concentration which was $2.7 \times 10^{-4}\ M$. Of particular note is the isolation during aquation in 2 M HCl of the chloropentaammine in a yield equaling 40% of the total pyridine released from coordination. This result indicates that $Ru(NH_3)_5H_2O^{2+}$, the probable source of $Ru(NH_3)_5Cl^{2+}$ on quenching, is an intermediate of the aquation at higher as well as at lower acid concentrations. Furthermore, the pyridine-containing +2 ion, no. 5 of Table I, was isolated in a yield equivalent to about 30% of the total substrate reacted. This figure exceeds the yield of this ion in the product studies at 2 M hydrochloric acid reported in Table I, where the amount of ion 5 equaled about 10% of the total reacted substrate.

Direct evidence in support of the presence in the reaction solution of ruthenium(II)–pyridine complexes other than the pentaammine comes from an experiment in which the reaction was quenched with an excess of ammonia. Addition of a large excess of concentrated aqueous ammonia to a 0.1 M hydrochloric acid solution ($[Cl^-] = 2.0\ M$) initially $0.81 \times 10^{-4}\ M$ in $Ru(NH_3)_5^{2+}$ after 42 hr reaction time (about 6 half lives) regenerated the absorption band at 407 mμ characteristic of the starting material (Figure 3). The new peak represented $0.21 \times 10^{-4}\ M$ regenerated $Ru(NH_3)_5py^{2+}$ based upon the molar absorption coefficient of 0.78×10^4. This amount corresponds to 24% of the original substrate concentration. The broad absorption band at 580 mμ (Figure 3) builds up in the later stages of the decomposition reaction after several half-lives have elapsed. There is no significant absorption in this region of the product spectrum when the reaction is run in 2 M HCl. Furthermore, the rate of development of this band is much more rapid when higher concentrations of the substrate are used. These considerations suggest that the species responsible for this band might be a polymeric form of ruthenium(II). Its disappearance on the addition of ammonia, concurrent with the slow buildup of the absorption at 407 mμ implies that the polymeric species contains at least a portion of the remaining coordinated pyridine. In contrast to the result obtained in low acid, addition of excess concentrated aqueous ammonia to a 2 M hydrochloric acid solution initially $2.7 \times 10^{-4}\ M$ in substrate concentration (after about 8 hr reaction time) regenerated only a barely discernible trace of the starting material. This result confirms that nonreactive ruthenium(II)–pyridine species are not present in the product of the aquation in 2 M HCl and that the $Ru(NH_3)_5py^{2+}$ observed on neutralizing the 0.1 M HCl
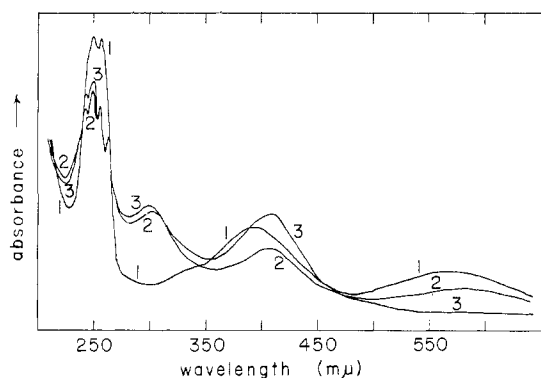

Figure 3.—Ultraviolet spectrum of an $Ru(NH_3)_5py^{2+}$ reaction mixture containing 0.1 M HCl and 1.9 M NaCl; 1 is a scan 42 hr after initiation of the reaction, 2 is a rescan 2 min after neutralization of the acid with large excess NH_3, and 3 is a rescan 140 min after neutralization

product solution was not due to equilibrium recombination of free pyridine and ruthenium(II) in the ammoniacal solution.

Kinetics of Reactions.—The kinetic results of the initial aquation of $Ru(NH_3)_6^{2+}$ are summarized in Figure 4. The reaction rate is first order in complex ion
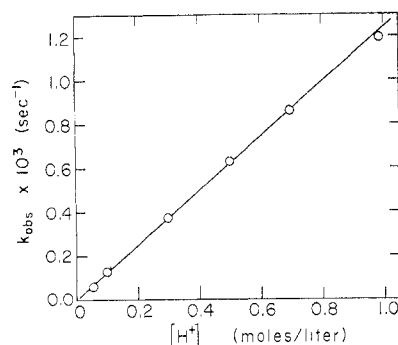

Figure 4.—Hydrogen ion dependence of the observed rate constant for the aquation of $Ru(NH_3)_6^{2+}$; ionic strength = 1.0 M ($C_7H_7SO_3H$); temperature 25.0°.

concentration as measured by the rate of appearance of the product $Ru(NH_3)_5H_2O^{2+}$

$$-d[Ru(NH_3)_6^{2+}]/dt = k_{obsd}[Ru(NH_3)_6^{2+}]\qquad(1)$$

The significant result is the linear dependence of the observed rate constant on the concentration of hydrogen ion as shown in the figure. Under the conditions of these experiments, there is only one important term in the first-order rate constant

$$k_{obsd} = k_1[H^+]\qquad(2)$$

and k_1, the slope of the line, is $(1.24 \pm 0.03) \times 10^{-3}$ M^{-1} sec^{-1}.

An experiment was done using 0.5 M HCl rather than 0.5 M $C_7H_7SO_3H$ (1.0 M Cl$^-$) and the rate in HCl was found to be about 20% more rapid. Since two cations are brought together to form the activated complex, a noticeable effect of changing the identity of the anion at the 1.0 M level is expected, without invoking specific chemical effects.

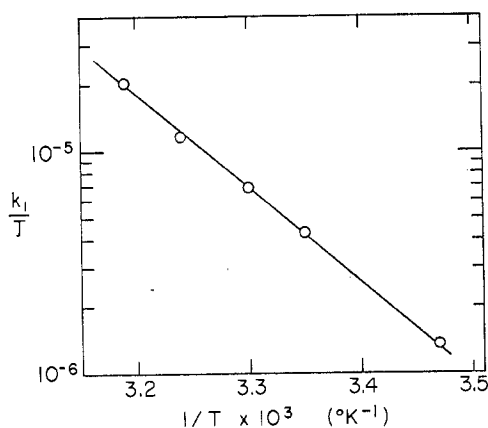Figure 5 shows a plot of the logarithm of k_1/T vs.

Figure 5.—Temperature dependence of the second-order rate constant for the aquation of $Ru(NH_3)_6{}^{2+}$; ionic strength = 1.0 M ($C_7H_7SO_3H$).

Figure 6.—Hydrogen ion dependence of the first-order rate constant for the aquation of $Ru(NH_3)_5py^{2+}$; ionic strength = 2.0 M (NaCl); temperature 25.0°.

$1/T$. The slope of this line yields a value of $\Delta H^{\ddagger}$ of 19.3 ± 0.4 kcal/mol. When this value of $\Delta H^{\ddagger}$ is combined with the rate data at 25°, a value of $\Delta S^{\ddagger}$ of −7.2 ± 0.4 eu is obtained.

The results of the kinetic study of the acid-catalyzed aquation of $Ru(NH_3)_5py^{2+}$ are shown in Table II.

TABLE II

EFFECT OF ACID CONCENTRATION ON THE FIRST-ORDER RATE
CONSTANT FOR THE AQUATION OF $Ru(NH_3)_5py^{2+}$ AT 25°

[H⁺], M	[Cl⁻], M	$10^4 k_{obsd}$, sec⁻¹	[H⁺], M	[Cl⁻], M	$10^4 k_{obsd}$, sec⁻¹
$10^{-3.2}$	2.00^a	0.0163 ± 0.0003	2.00	2.00	2.88 ± 0.10
0.10	2.00^a	0.278	0.20	1.00^b	0.292 ± 0.015
0.20	2.00^a	0.480 ± 0.013	0.50	1.00^b	0.630 ± 0.038
0.50	2.00^a	0.980 ± 0.010	1.00	1.00^b	1.063 ± 0.020
1.00	2.00^a	1.61 ± 0.02	0.98	0.0 (0.98 M $C_7H_7SO_3H$)	0.74 ± 0.02

^{a} Ionic strength = 2.0. ^{b} Ionic strength = 1.0.

The reaction rate is first order in substrate concentration

$$-d[Ru(NH_3)_5py^{2+}]/dt = k_{obsd}[Ru(NH_3)_5py^{2+}] \qquad (3)$$

and is measured by the disappearance of the characteristic charge-transfer absorption band of the complex at 408 mμ. The plot of observed first-order rate constant, k_{obsd}, vs. acid concentration (Figure 6) shows that the reaction becomes first order in [H⁺] at acid concentrations in excess of approximately 0.4 M (μ = 2.0). Under these conditions, the rate constant has the appearance

$$k_{obsd} = k_2[H^+] + k_0$$

where k_0 (the extrapolated intercept) is 0.34 × 10⁻⁴ sec⁻¹ and k_2 (the slope of the dashed line) is 1.27 × 10⁻⁴ M^{-1} sec⁻¹ at 25°. The curvature of the plot in the low-acid range suggests that the k_0 term is also [H⁺] dependent but has a form leading to rate saturation at higher [H⁺]. This term is further dealt with in the Discussion.

The effect of changing the chloride ion concentration is demonstrated by comparing the rates listed in Table II for 2.0 M Cl⁻ and those listed for 1.0 M Cl⁻, where the ionic strenght equals the chloride concentration.
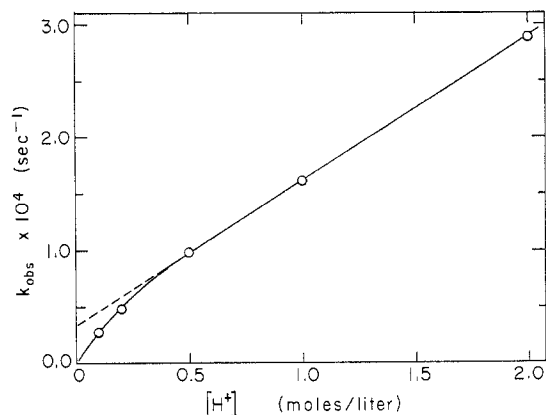
Clearly, ionic strength in general or chloride ion specifically has an effect on the decomposition rate. At 1.00 M H⁺ the reaction in 2 M chloride is 1.5 times more rapid than in 1 M chloride. That chloride itself is not required for the reaction to proceed readily is shown by the similarity of the first-order rate constant of the aquation in 0.98 M $C_7H_7SO_3H$ to that in 1.00 M hydrochloric acid, with no added salt in either case.

The decomposition reaction rate is quite sensitive to the nature of substituents on the pyridine ring (Table III). The greater the ability of substituents to act as

TABLE III

EFFECT OF PYRIDINE SUBSTITUENTS ON THE AQUATION RATE OF
$Ru(NH_3)_5pyX^{2+}$ in 2.00 M HYDROCHLORIC ACID, 25°^{a}

| X	σ constant[11]	$10^4 k_{obsd}$, sec⁻¹
p-CH₃	−0.17	5.90 ± 0.13
m-CH₃	−0.069	3.12 ± 0.02
H	0.000	2.88 ± 0.10
m-CO₂CH₃	0.32	0.34
m-Cl	0.37	0.38 ± 0.02

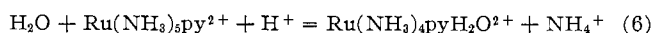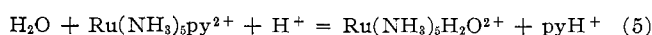^{a} Kinetics of substituted pyridine complexes carried out in an N₂ atmosphere.

electron donors (as estimated by the Hammett σ constant[11]), the faster the reaction proceeds. This tendency is opposite to what might be expected as a consequence of the greater basicity of picolines over py.

Discussion

The product studies done for the $Ru(NH_3)_6{}^{2+}$ ion show that the net change in the initial stages of the aquation in acid is

$$H_2O + Ru(NH_3)_6{}^{2+} + H^+ = Ru(NH_3)_5H_2O^{2+} + NH_4{}^+ \quad (4)$$
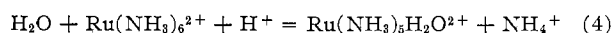
so that the kinetic data recorded in Figure 4 can with confidence be taken to refer to reaction 4. The aquation of the pyridine derivatives is somewhat more complicated. The results of the product studies for $Ru(NH_3)_5py^{2+}$ show that two parallel processes occur in the initial stages

$$H_2O + Ru(NH_3)_5py^{2+} + H^+ = Ru(NH_3)_5H_2O^{2+} + pyH^+ \quad (5)$$

$$H_2O + Ru(NH_3)_5py^{2+} + H^+ = Ru(NH_3)_4pyH_2O^{2+} + NH_4{}^+ \quad (6)$$

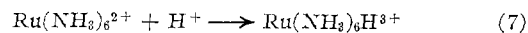(11) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

Reaction 5 leads to a disappearance of the intense charge-transfer absorption which was used to determine the extent of reaction. When reaction 6 takes place, the change in this absorption is only minor, but the fact that $Ru(NH_3)_4pyCl^{2+}$ is a product after the reaction mixture is quenched with oxygen shows that reaction 6 accompanies reaction 5.

The meaning of the specific rates recorded for the aquation of the pyridine complexes is less clear than it is for $Ru(NH_3)_6{}^{2+}$. Since the charge-transfer absorption was used as the basis for calculating specific rates, the results are not complicated by subsequent loss of NH_3, once pyridine has been lost from the coordination sphere, but they are complicated by the fact that reactions 5 and 6 are parallel processes.
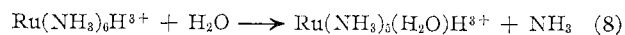
Approximate measurements of the extinction coefficients of the product $Ru(NH_3)_4pyH_2O^{2+}$ have been obtained, and at the two wavelengths used for following the progress of the reaction, namely, at 400 and 430 mμ, they are only slightly less than those of the starting material. Thus the rates measured in our work are those of the loss of py from the Ru(II) center, rather than the sum of the rates for reactions 5 and 6. The trapping experiment using O_2 showed that $Ru(NH_3)_4pyH_2O^{2+}$ accounts for *ca.* 30% of the $Ru(NH_3)_5py^{2+}$ which has reacted, and on this basis we estimate reaction 6 to take place at about half the rate of reaction 5.

The most significant observation made in the course of the kinetic studies is that the release of NH_3 (or of py) from Ru(II) increases markedly with the concentration of acid. Taken out of context with the results of other studies on the aquation of ammonia complexes, this result does not seem remarkable, but in context with them it is quite striking. Wilkins[12] reports that the rate of aquation of $NiNH_3{}^{2+}$ does not increase as the acidity increases, and a similar conclusion follows from the study by Bjerrum and Samm[13] of the aquation of $Cr(NH_3)_6{}^{3+}$. The observations just cited can be rationalized on the grounds that, when NH_3 is coordinated to a metal ion, the molecule has no free electron pairs exposed to electrophilic attack. In the absence of the experimental evidence this result could not have been predicted with any degree of certainty because electrophilic attack by protons has been recorded in the aquation of ions of the type R_2Hg^{2+}.[14] The similarity in terms of electronic structure of an alkyl group to NH_3 is close, but, because C is less electronegative than N, electrophilic attack at a coordinated alkyl group would be expected to take place more readily than on coordinated NH_3.
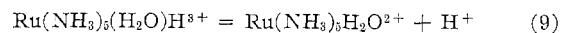
The fact that protons do not assist in the release of NH_3 from Ni^{2+} but do assist in the corresponding process for $Ru(NH_3)_6{}^{2+}$ suggests that attack by protons is not on NH_3 but on the metal ion. The faces of the octahedron for a low-spin d^6 ion are electron rich and it is presumed that a proton engages one of the three electron pairs in a reaction of the type

(12) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).
(13) J. Bjerrum and C. G. Samm, *Acta Chem. Scand.*, **9**, 216 (1955).
(14) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **77**, 3747 (1955).

$$Ru(NH_3)_6{}^{2+} + H^+ \longrightarrow Ru(NH_3)_6H^{3+} \qquad (7)$$

This reaction may be rate determining for the substitution, or it may be a preequilibrium followed by the rate-determining process

$$Ru(NH_3)_6H^{3+} + H_2O \longrightarrow Ru(NH_3)_5(H_2O)H^{3+} + NH_3 \quad (8)$$

and the equilibrium

$$Ru(NH_3)_5(H_2O)H^{3+} = Ru(NH_3)_5H_2O^{2+} + H^+ \qquad (9)$$

Other things being equal, a reaction such as (7) is much more likely for a second- or third-row transition metal ion than it is for one of the first row, because the d electrons can be presumed to extend relatively further into and beyond the first coordination sphere for them (thus note the greater splitting of the d levels for second- and third-row transition elements compared to first-row elements). The basicity of the d electrons for $NiNH_3{}^{2+}$ compared to $Ru(NH_3)_6{}^{2+}$ is further decreased because the presence of the two antibonding σ d electrons for Ni^{2+} increases the Ni–N distance without causing a similar increase in the average distance of the π d electrons. For Cr^{3+} compared to Ru(II) there are the obvious differences that the d orbitals are singly occupied and that the ion has a higher positive charge; both factors will have a profound effect in reducing the basicity of the d electrons.

The seven-coordinated species $Ru(NH_3)_6H^{3+}$ can be regarded as a hydride of Ru(IV). If Ru(II) were a stronger reducing agent, the hydride could conceivably be an intermediate in the reduction of H^+. For our particular case this reaction is slow, but, since in the seven-coordinated species not all of the NH_3 molecules can be equivalent, it is not unreasonable to expect that the lability of at least one of them is greater than it is in the ion $Ru(NH_3)_6{}^{2+}$.

Efforts were made to detect an intermediate in the reaction of $Ru(NH_3)_6{}^{2+}$ with acid. A solution containing $Ru(NH_3)_6{}^{2+}$ was mixed with an excess of 0.5 *M* H_2SO_4 and the uv spectrum (200–500 mμ) of the solution was recorded during the reaction. Independent measurements showed that $Ru(NH_3)_6{}^{2+}$ in dilute sulfuric acid has a broad absorption at 277 mμ ($\epsilon \simeq 620$) and $Ru(NH_3)_5H_2O^{2+}$ has a very similar absorption at 267 mμ ($\epsilon \simeq 530$) as well as a weaker absorption at 410 mμ ($\epsilon \simeq 44$). During the reaction the spectrum of $Ru(NH_3)_6{}^{2+}$ gradually changed to that of $Ru(NH_3)_5H_2O^{2+}$ with no evidence for an intermediate species. The failure to observe an intermediate does, of course, not disprove the mechanism we advance, and merely shows that the intermediate (if there is one) remains at low concentration. It should also be mentioned that there were no anomalies in the kinetic data for the initial phases of the reaction, which could be ascribed to the accumulation of an intermediate.

The data in Figure 6 suggest that the rate law for the release of py from $Ru(NH_3)_5py^{2+}$ has the form

$$d[pyH^+]/dt = k_2[H^+] + \frac{k_3[H^+]}{1 + a[H^+]} \qquad (10)$$

where the first term is analogous to the term discussed for $Ru(NH_3)_6{}^{2+}$. The second term "saturates" at

high H^+, and thus the slope at high $[H^+]$ in a plot of k_{obsd} vs. $[H^+]$ can be taken as the value of k_2.

It should be noted that k_2 as measured for release of py ($1.27 \times 10^{-4} \, M^{-1} \, sec^{-1}$ at 25°) is much less than is k_1 as measured for release of NH_3 from $Ru(NH_3)_6$ ($k_1 = 1.24 \times 10^{-3} \, M^{-1} \, sec^{-1}$ at 25°). Since the bases released from the complex are different in the two cases, the implications of the rate comparison are too complex and obscure to be understood. Of more obvious significance is the fact that acid-catalyzed release of NH_3 from $Ru(NH_3)_5py^{2+}$ is about 20 times slower than from $Ru(NH_3)_6^{2+}$, in spite of a possible labilizing effect of py on the position *trans* to it in the complex. Interpreted in terms of the mechanism we propose, this difference can be ascribed at least in part to the circumstance that the d electrons in $Ru(NH_3)_5py^{2+}$ are less basic than in $Ru(NH_3)_6^{2+}$. Evidence has been adduced elsewhere[1] in support of the conclusion that there is significant back-bonding in the $Ru^{II}py$ complexes. This should have the effect of decreasing the electron density on Ru and of decreasing the basicity of the π d electrons.

The explanation offered for the difference in the acid-assisted rate of NH_3 loss from $Ru(NH_3)_2py^{2+}$ and from $Ru(NH_3)_6^{2+}$ serves also to rationalize the data in Table III. The rate of loss from Ru(II) of bases of the type
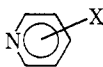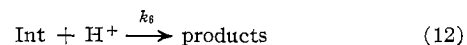

decreases as X becomes more electron withdrawing, as would be expected if protonation of d electrons were the mechanism of reaction. (Implicit in this explanation is the assumption that the k_2 term in the rate law accounts for the differences in rate observed. Since for the pyridine complex this term is by far the more important of the two under the reaction conditions, 2 M HCl, employed to obtain the data in Table III, this assumption seems to be a safe one.) It is seen that the more basic aromatic ligands are released more rapidly, and we must conclude that in this series the effects of back-bonding more than compensate for those arising from σ interactions between the bases and the metal ion.

Interactions between electron-deficient centers and nonbonding d orbitals have been proposed in other systems. To explain the unusually slow rate of exchange of hydrogen between $Ir(NH_3)_6^{3+}$ and $H_2O(l)$, Palmer and Basolo[15] proposed an intramolecular interaction between the hydrogens of the coordinated ammonia and the filled nonbonding d orbitals on iridium. Effects of this kind have also been proposed by Chatt, et al.,[16] in interpreting their measurement of the N–H stretching frequencies in platinum– and palladium–ammine systems. Krause and Goldby[17] considered the possibility of a hydrogen-bond interaction between the HO group of coordinated 2-hydroxyethylaminodi-

acetate and the nonbonding d electrons of the central ion. The effect of acids such as HOAc and H_3BO_3 in accelerating exchange between *trans*-$Pt(py)_2Cl_2$ and Cl^- has been ascribed to the interaction of electrons in nonbonding orbitals on Pt(II) with empty π orbitals in the acids.[18] In view of our results, it seems possible that there is a contribution to the effect which these acids exert by proton interaction with the nonbonding electrons on Pt(II).

Though protonation of the π d electrons seems to us to be the most plausible interpretation of the fact that H^+ promotes aquation of $Ru(NH_3)_6^{2+}$ but not of $Ni-NH_3^{2+}$, on the basis of present evidence we cannot discount the possibility that attack actually occurs on the N center, attack there being promoted by intramolecular hydrogen-bonding effects of the kind described in the previous paragraph. We favor the former mechanism because there is precedent for it, for example in the reaction of hydrogen chloride with Vaska's compound,[19] and it has also been suggested[20] for the acid-catalyzed replacement of CH_3 from Pt(II). Though these are d^8 systems, the extension of this kind of mechanism to the d^6 case is reasonable.

A rate law of the form of the second term on the right-hand side of eq 10 was observed by Baxendale and George[21] for the acid-assisted aquation of $Fe(bipy)_3^{2+}$. An altogether reasonable explanation for this kind of kinetic behavior was offered by Basolo, Hayes, and Neumann,[22] who suggested that the chelate ring opens at a rate independent of acid, to form an intermediate in which only one of the nitrogens of bipy is coordinated to the metal ion. This intermediate (Int) then may revert to the initial reactants or react with H^+ and proceed to products. A scheme of the same general type can explain the second term in the rate law we observed for $Ru(NH_3)_5py^{2+}$

$$Ru(NH_3)_5py^{2+} \underset{}{\overset{k_5}{\rightleftharpoons}} Int \qquad (11)$$

$$Int + H^+ \overset{k_6}{\longrightarrow} products \qquad (12)$$

but in our system the intermediate must be of a different character from that proposed for the $Fe(bipy)_3^{2+}$ system. The activation implied by reaction 11 in the forward direction may be a change in the conformation of the complex. The resulting unstable form then is assumed to be stabilized against the reverse of reaction 11 by interaction with a proton and to yield the product as shown in eq 12.

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(16) J. Chatt, L. Duncanson, and L. Venanzi, *J. Inorg. Nucl. Chem.*, **8**, 67 (1958).

(17) R. A. Krause and S. D. Goldby, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 143.

(18) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

(19) L. Vaska and J. W. DiLuzio, *ibid.*, **84**, 679 (1962).

(20) V. Belluco, M. Giustiniani, and M. Graziani, *ibid.*, **89**, 6494 (1967).

(21) J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 736 (1950).

(22) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Am. Chem. Soc.*, **75**, 5102 (1953).