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The Reduction of Complexes of Pentaammineruthenium(III) with Pyridine Derivatives

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The rate of reduction of pentaammineisonicotinamideruthenium(III) by Cr^{2+} is found to be more than 2×10^4 times greater than that reported[1] for the reduction of the corresponding Co(III) complex. The great disparity in rate between the reduction of Ru(III) and Co(III), with only a small difference in driving force for the reaction, is to be contrasted to the modest disparity (factor of 10) that exists in the rates of reduction of Co(III) and Cr(III), where the difference in driving force is much greater. A stepwise transfer has been suggested[1] for the reduction of the Co(III) and Cr(III) complexes. By contrast it is proposed that in the reduction of Ru(III), the electron is transferred directly to the final acceptor orbital. The difference in behavior of Co(III) and Cr(III) on the one hand and Ru(III) on the other is ascribed to the fact that only for the latter does the acceptor orbital match the symmetry of the ligand carrier orbital. Intermediates were observed in the reduction of ruthenium complexes with isonicotinamide, nicotinamide, and the ester of isonicotinic acid as ligands. These intermediates have ruthenium bound to the pyridine nitrogen and Cr(III) to the amide or carbonyl group. The aquation reactions in each case involve loss of Cr(III) from the ligand. Rather complete studies of the kinetics of the reactions for the two "iso" ligands were carried out. The half-time for the aquation of the Cr(III)–ester bond at high acid concentration is *ca.* 19 sec at 25°.

Introduction

Reactions of Cr^{2+} with pentaamminecobalt(III) complexes of nicotinamide and isonicotinamide have been shown to proceed by remote attack.[1] When the bridging ligand contains a conjugated bond system, electron transfer may take place through the extended π system. If this is indeed the case, symmetry matching among metal donor–ligand π system–metal acceptor orbitals may be expected[2] to play a role in determining the nature of the electron-transfer process. The symmetry relationship has been examined by studying the reduction by Cr^{2+} of some complexes of Ru(III). This oxidizing agent with electronic structure $t_{2g}{}^5e_g{}^0$ employs a t_{2g} acceptor orbital of π symmetry, and the results are to be compared to those already obtained[1] by studying corresponding complexes of $Co(NH_3)_5{}^{3+}$ ($t_{2g}{}^6e_g{}^0$) and $Cr(H_2O)_5{}^{3+}$ ($t_{2g}{}^3e_g{}^0$), each of which employs an e_g acceptor orbital of σ symmetry. Though it is true that for Cr(III) an incoming electron can, in principle, be accommodated in an orbital of π symmetry, the energy to produce such an electronically excited state ($\sim 10^4$ kcal) much exceeds the energies of activation for the reduction of Cr(III) complexes by Cr(II).

Experimental Section

Reagents.—Water used in all kinetic experiments was redistilled from alkaline potassium permanganate. All chemicals used were of reagent grade. The reaction mixtures were adjusted to the desired ionic strength using lithium perchlorate or lithium bromide. The lithium perchlorate was prereduced with Cr(II) and recrystallized twice again before use. The lithium bromide was recrystallized twice before use. Hydrobromic acid was purified by redistilling 48% hydrobromic acid twice. Hexaaquochromium(III) was prepared either by reduction of chromium trioxide with formic acid in the presence of excess perchloric acid[2] or by reduction of potassium dichromate with hydrogen peroxide in the presence of excess perchloric acid. Vanadyl perchlorate was prepared from vanadyl sulfate by the method of Rossotti and Rossotti;[3] chromium(II) perchlorate and vanadium(II) perchlorate solutions were prepared by reducing the chromium(III) and vanadium(IV) perchlorates, respectively, over zinc amalgam under an atmosphere of nitrogen or argon. Analytical grade Dowex 50W-X2 resin, 200–400 mesh, hydrogen ion form, was purchased from Bio-Rad Laboratories and cleaned by successive washings with water, acid, base, basic peroxide, water, acid, acetone, and water.

Preparation of $[(NH_3)_5RuL](ClO_4)_2$, Where L = Pyridine, Nicotinamide, Isonicotinamide, Methyl Nicotinate, or Methyl Isonicotinate.—Chloropentaammineruthenium(III) dichloride

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[1] F. R. Nordmeyer and H. Taube, *J. Amer. Chem. Soc.*, **88**, 4295 (1966); **90**, 1162 (1968).

[2] J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 120 (1964).

[3] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

was obtained following the method of Vogt, Katz, and Wiberley.[4] A 0.100-g portion of chloropentaammineruthenium(III) dichloride (0.343 mmol) was added to 2 ml of an Ag(I) solution which was made up by dissolving 0.749 g of silver oxide (0.323 mmol) in 2 ml of hot water by dropwise addition of trifluoroacetic acid. The silver chloride formed was digested and removed by filtration. The Ru(III) complex was reduced over zinc amalgam in the presence of a 30-fold excess (*ca.* 1 g) of L. After 30-min reaction time, the zinc amalgam was removed by filtration and a saturated solution of sodium perchlorate was added to the highly colored reaction mixture to precipitate $[(NH_3)_5RuL](ClO_4)_2$. The crude perchlorate salts[5] were recrystallized from hot methanol and washed with cold methanol and ether. Yields from 60 to 70% were obtained.

Preparation of $[(NH_3)_5RuL](ClO_4)_3$.—The Ru(III) complexes were prepared by oxidizing the Ru(II) complexes with Ag(I) or Ce(IV). Using the Ag(I) method, about 0.100 g of $[(NH_3)_5RuL](ClO_4)_2$ was added to 2 ml of a solution containing a 10–20% excess of a solution of silver trifluoroacetate. The silver metal was removed by filtration. The yellow filtrate was cooled and a saturated solution of $NaClO_4$ free of chloride ion was added to induce precipitation. Using the Ce(IV) method, about 0.100 g of $[(NH_3)_5RuL](ClO_4)_2$ was added to 2 ml of water, and a 0.2 *N* ceric perchlorate solution in 3 *N* $HClO_4$ was added in excess. A saturated $NaClO_4$ solution was added dropwise to induce precipitation. The crude yellow product was recrystallized from warm (45–50°) 0.10 *N* $HClO_4$ and washed with ether. Yields of about 50% were obtained.

Preparation of *cis*-$[(NH_3)_4RuL_2](ClO_4)_2$ and *cis*-$[(NH_3)_4RuL_2](ClO_4)_3$, Where L = Isonicotinamide or Methyl Isonicotinate.—*cis*-Dichlorotetraammineruthenium(III) chloride used as the starting material was prepared by the method of Gleu and Breuel.[6] A portion (0.340 mmol) of *cis*-$[(NH_3)_4RuCl_2]Cl\cdot0.75H_2O$ was added to 2 ml of a solution containing 0.32 mmol of silver trifluoroacetate. The silver chloride formed was digested and removed by filtration. The Ru(III) complex was reduced over zinc amalgam in the presence of a 30-fold excess of ligand L. After 1 hr of reaction time the zinc amalgam was removed by filtration and a saturated solution of sodium perchlorate was added to precipitate the highly colored *cis*-$[(NH_3)_4RuL_2](ClO_4)_2$. The crude product was recrystallized from warm (40–45°) 0.10 *N* $HClO_4$ and washed with ether. Yields of 65–75% were obtained.

The Ce(IV) method described above was used to prepare the corresponding Ru(III) complexes.

Analyses.—Microanalyses for the ruthenium complexes are summarized in Table I. The analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Stanford University.

Perchlorate ion concentration was determined by the method of Gould and Taube[7] as modified by Deutsch.[8]

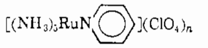
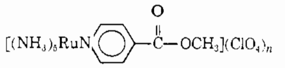
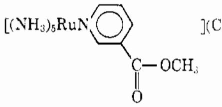
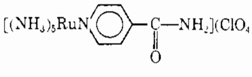
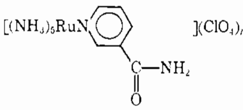
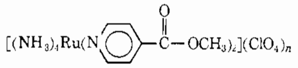
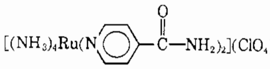
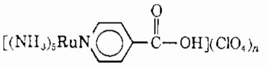
The total chromium concentration of a solution was measured by oxidizing aliquots with hydrogen peroxide in basic solution and determining the chromate produced spectrophotometrically.[9] The concentration of Cr(II) in a solution was assumed to be equal to the total chromium concentration of the solution from which it was made.

The total vanadium concentration of vanadyl perchlorate stock solutions was determined by oxidizing an aliquot with permanganate, destroying the excess permanganate with nitrite followed by urea, and titrating the sample with a standardized ferrous solution using a platinum indicator electrode.[10] The concentration of V(II) was assumed to be equal to the total vanadium concentration of the solution from which it was made.

The concentration of free acid in hexaaquochromium(III) perchlorate solutions was determined by potentiometric titration after converting the Cr(III) to the tris(oxalato)chromium(III) ion.[11] The free acid concentration of the vanadyl perchlorate solution was calculated from the known total perchlorate and total vanadium concentrations.

TABLE I

MICROANALYSES OF RUTHENIUM COMPLEXES[a]

Complex		n = 2		n = 3	
		Calcd	Found	Calcd	Found
	% C	12.9	12.9	10.6	10.5
	% H	4.3	4.5	3.5	3.9
	% N	18.1	18.0	14.9	14.6
	% Cl	15.3	15.2	18.9	18.4
	% C	16.1	15.7	13.5	13.4
	% H	4.2	4.2	3.5	3.6
	% N	16.1	16.2	13.5	13.6
	% Cl	13.6	13.9	17.1	16.9
	% C	16.1	16.3	13.5	13.2
	% H	4.2	4.3	3.5	3.7
	% N	16.1	15.9	13.5	13.3
	% Cl	13.6	13.5	17.1	16.9
	% C	14.2	13.9	11.9	12.3
	% H	4.1	4.0	3.5	3.5
	% N	19.3	18.6	16.2	16.2
	% Cl	14.0	14.0	17.5	17.1
	% C	14.2	14.5	11.9	11.9
	% H	4.1	4.4	3.5	3.5
	% N	19.3	18.8	16.2	16.2
	% Cl	14.0	14.0	17.5	17.3
	% C	26.2	26.5	22.6	21.9
	% H	4.0	4.2	3.5	3.7
	% N	13.1	12.8	11.3	11.1
	% Cl	11.1	9.2	14.4	14.4
	% C	23.5	23.3	20.2	19.7
	% H	3.9	4.2	3.4	3.6
	% N	18.3	16.8	15.7	15.2
	% Cl	11.6	10.3	15.0	14.7
	% C			11.9	11.8
	% H			3.3	3.3
	% N			13.8	
	% Cl			17.5	16.3

[a] Microanalyses were performed by the Microanalytical Laboratory of the Stanford University Department of Chemistry.

Apparatus and Techniques.—Visible and uv spectroscopic measurements were made on a Cary Model 14 or 15 recording spectrophotometer. These instruments were equipped with thermostated cell compartments and were used in some kinetic experiments. Nmr spectra were measured using a Varian T-60 nmr spectrometer thermostated at 35°.

Molar extinction coefficients of the ammineruthenium complexes were determined from solutions of complex prepared by dissolving the perchlorate salt in the desired medium. However, in the case of pyridinepentaammineruthenium(II) complex, the perchlorate salt of which is particularly light sensitive and in general quite sensitive to decomposition, the molar extinction coefficient was determined by generating the complex in solution by reducing a solution of $(NH_3)_5RuCl^{2+}$ containing an excess of pyridine with Cr^{2+}, care being taken to exclude light.

Reaction rates which were too rapid to be studied by conventional methods were measured with a stopped-flow apparatus similar to that described by Dulz and Sutin.[12,13]

Oxidation potentials were determined by measuring the potential of an equimolar mixture of Ru(II) and Ru(III) complexes at a platinum electrode *vs.* a silver wire in a 1.0 *M* KCl–0.001 *N* HCl medium. The standard oxidation potential for the $Ru(NH_3)_6^{2+}$–$Ru(NH_3)_6^{3+}$ couple is known to be -0.095 ± 0.004 V,[14] so that $E°$ for the couple being measured could be determined

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[4] L. Vogt, T. Katz, and S. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

[5] These perchlorate salts have proved to be explosive.

[6] K. Gleu and K. Breull, *Z. Anorg. Allg. Chem.*, **237**, 335 (1938).

[7] E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964).

[8] E. A. Deutsch and H. Taube, *Inorg. Chem.*, **7**, 1532 (1968).

[9] G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

[10] L. Meites, "Handbook of Analytical Chemistry," McGraw-Hill, New York, N. Y., 1963, pp 3–73.

[11] W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

[12] G. Dulz, Ph.D. Thesis, Columbia University, 1962.

[13] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

[14] J. R. Kuempel in T. Meyer and H. Taube, *ibid.*, **7**, 2369 (1968).

from the difference in measured potential between it and the hexaammine couple both measured under identical conditions. An electrolytic cell consisting of three compartments separated by coarse glass frits was used. One compartment was equipped with a glass frit for deoxygenation with argon. The three compartments were filled with supporting electrolyte. Equal volumes of equimolar Ru(II) and Ru(III) solutions were added to one compartment and the potential was measured at a Sargent platinum electrode *vs.* a silver wire using a Beckman Expandomatic pH meter.

Product studies were made to characterize the products of the reaction of the ammineruthenium(III) complexes with Cr(II) and V(II). When a single Ru(II)-containing species was formed, it was characterized and its concentration determined spectrophotometrically. When two Ru(II)-containing species were found, the one of lower charge was separated by an ion-exchange technique and then characterized, and its concentration was determined spectrophotometrically. The amount of the higher charged species was determined by difference. When an intermediate in the reaction was not long-lived enough to be studied by conventional spectrophotometric techniques, it was characterized by scanning its spectrum in the stopped-flow apparatus. For the product studies an all-glass apparatus was used, so designed that reactants could be prepared and mixed and products could be sampled into a spectrophotometric cell, all under an argon atmosphere. The ion-exchange column was designed so that the contents could be deoxygenated with argon. A separatory funnel containing the elutants could be attached to the top of the column and deoxygenated. A sample of the product mixture was added to the column through a serum-capped inlet using the syringe technique. Ru(II)-containing species were separated by elution with 1.5 *M* $LiClO_4$–0.1 *N* $HClO_4$.

Treatment of Data.—All kinetic data could be interpreted on the basis of a second-order reaction or consecutive second-order, first-order reactions. By adjusting concentrations, the consecutive reactions proved to be separable in every instance.

Results

Spectra: Visible, Uv, and Nmr.—The spectral properties of the pentaammineruthenium(II) and pentaammineruthenium(III) complexes are summarized in Table II, and those of the tetraammine complexes are given in Table III. The general characteristics of the spectra of the monopyridine complexes have been discussed elsewhere.[15] Here we only point out in addition that the bis-pyridine complexes of Ru(II) show two charge-transfer bands in the visible region of the spectrum. One of these bands is close in energy to that of the monopyridine complex and the other is shifted to lower wavelengths. An interpretation of this absorption pattern is forthcoming.[16]

TABLE II

SPECTRAL PROPERTIES OF THE PENTAAMMINERUTHENIUM COMPLEXES[a]

	$(NH_3)_5RuL^{2+}$		$(NH_3)_5RuL^{3+}$	
L	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
Pyridine (py)	407	7.78	261	4.67
	245	4.62	255	4.71
			248	4.70
Isonicotinamide[b] (isoamide)	478	10.5	276	6.06
	260	3.72	355 sh	
Isonicotinamide[c] (isoamide)	481	11.1		
	260	4.6		
Nicotinamide (amide)	427	6.05	240 sh	
	254	5.24	212	9.82
	212	6.95		
Methyl isonicotinate (isoester)	495	12.4	280	6.69
	265	3.77	335 sh	
Methyl nicotinate (ester)	417	5.91	242	5.02
	254	6.01	217	10.2
	217	10.3		

[a] All measurements made in 1.0 *M* $HClO_4$ unless otherwise specified. [b] Measurements made in 0.10 *M* $HClO_4$. [c] Measurements made in 0.10 *M* HBr.

TABLE III

SPECTRAL PROPERTIES OF THE TETRAAMMINERUTHENIUM COMPLEXES[a]

	$(NH_3)_4RuL_2{}^{2+}$		$(NH_3)_4RuL_2{}^{3+}$	
L	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, nm	$10^{-3}\epsilon$, M^{-1} cm^{-1}
Isonicotinamide (isoamide)	478	13.9	335 sh	
	413	10.6	272	11.8
	257	7.70	260 sh	
Methyl isonicotinate[b] (isoester)	492	15.7	330 sh	
	421	11.7	278	12.8
	264	8.25		

[a] All measurements made in 0.10 *M* $HClO_4$ unless otherwise specified. [b] Measurements made in 1.0 *M* $HClO_4$.

Proton nmr was used to determine the configuration of the $(NH_3)_4RuL_2{}^{2+}$ complexes. Comparison of the proton spectrum of uncomplexed methyl isonicotinate with that of the corresponding tetraammineruthenium(II) complex (*cf.* Figure 1) shows that two new signals of equal intensity appear for the complex. These are attributed to the proton resonance of the ammonia groups of the complex, and, on this basis, we assign the cis configuration to the tetraammineruthenium complexes.

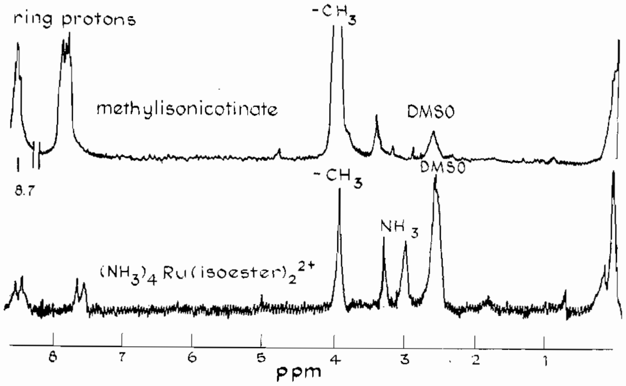

Figure 1.—Nmr spectra of methyl isonicotinate and $(NH_3)_4Ru(isoester)_2{}^{2+}$ in DMSO at 35°.

Oxidation Potentials.—Formal reduction potentials (that is, not extrapolated to zero ionic strength but referring to a medium at unit ionic strength) were measured for a series of Ru(III)–Ru(II) complexes. The reduction potentials are summarized in Table IV; their implications for the main purposes of this paper will be considered in the Discussion.

Kinetic Results.—Second-order rate constants for the reduction of the ammineruthenium(III) complexes by Cr^{2+} are summarized in Table V. Over the range studied the rates are independent of $[H^+]$. Under the conditions of the experiments the reduction of *cis*-$(NH_3)_4Ru(isoamide)_2{}^{3+}$ by Cr^{2+} was about half complete by

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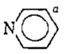
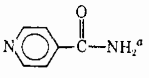
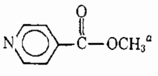
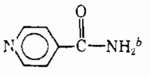
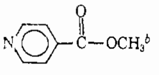
[15] P. Ford, DeF. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

[16] A. M. Zwickel and C. Creutz, to be submitted for publication.

TABLE IV

SUMMARY OF THE FORMAL REDUCTION POTENTIALS

Ligand L	$E°$, V
[a]	0.42
[a]	0.44
[a]	0.46
[b]	0.70
[b]	0.74

[a] $e^- + (NH_3)_5RuL^{3+} = (NH_3)_5RuL^{2+}$. [b] $e^- + (NH_3)_4RuL_2^{3+} = (NH_3)_4RuL^{2+}$.

the time the reaction mixture reached the observation point. The reaction followed fairly good second-order behavior through the second half-life.

In Table VI are summarized the average rate con-

TABLE VI

SPECIFIC RATES AND ACTIVATION PARAMETERS FOR THE REDUCTION OF AMMINERUTHENIUM(III) COMPLEXES BY CHROMIUM(II)[a]

Complex	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
$(NH_3)_5Ru(py)^{3+}$	$(3.37 \pm 0.09) \times 10^3$	3.0 ± 0.5	-32 ± 2
$(NH_3)_5Ru(isoamide)^{3+}$ [b]	$(3.92 \pm 0.15) \times 10^5$	0.0 ± 0.5	-46 ± 2
$(NH_3)_5Ru(amide)^{3+}$	$(2.30 \pm 0.15) \times 10^4$	1.10 ± 0.18	-35 ± 1
$(NH_3)_5Ru(isoester)^{3+}$	$(4.08 \pm 0.10) \times 10^4$	1.54 ± 0.7	-32 ± 2
$(NH_3)_5Ru(ester)^{3+}$	$(6.68 \pm 0.06) \times 10^3$	2.03 ± 0.6	-34 ± 2
$(NH_3)_4Ru(isoamide)_2^{3+}$ [b]	$(7.0 \pm 0.6) \times 10^6$		
$(NH_3)_4Ru(isoester)_2^{3+}$	$(1.10 \pm 0.02) \times 10^6$		

[a] All values are at $\mu = 1.0$ and 25° unless otherwise stated. [b] $\mu = 0.10$.

TABLE V

RATE CONSTANTS FOR THE REDUCTION OF AMMINERUTHENIUM(III) COMPLEXES BY CHROMIUM(II)

Complex	$10^4(Cr^{2+})$, M	$10^5(Ru^{III})$, M	(H^+), M	Temp, °C	$10^{-4}k$, M^{-1} sec^{-1}
py[a]	18.1	4.24	1.00	15.0	0.263
				20.0	0.295
				25.0	0.328
				30.0	0.350
				33.0	0.357
				25.0	0.333
	1.84	4.34	1.00	25.0	0.339
	1.36	4.28	1.00	25.0	0.326
	34.0	4.63	0.97	25.0	0.343
				30.0	0.364
	34.0	4.51	0.50	25.0	0.352
				20.0	0.302
Isoamide[b]	1.36	4.27	0.099	25.0	39.3
	1.36	4.02	0.099	25.0	38.5
	1.36	4.04	0.050	25.0	37.4
	1.36	3.99	0.099	25.0	40.9
				30.0	38.1
	1.36	3.98	0.099	25.0	38.8
				15.0	38.0
				20.0	38.0
	1.36	4.20	0.099	25.0	36.8
				15.0	35.3
	1.36	4.02	0.099	30.0	37.7
	1.36	4.00	0.099	30.0	41.9
	1.36	4.00	0.099	30.0	40.8
	1.36	4.01	0.099	15.0	37.9
	1.36	3.98	0.099	15.0	37.9
				15.0	40.7
Amide[c]	13.8	6.26	1.00	25.0	2.25
	13.8	6.26	1.00	15.0	2.05
				20.0	2.19
				25.0	2.30
				30.0	2.44
	13.8	6.28	1.00	15.0	2.15
				20.0	2.22
				25.0	2.37
				30.0	2.43
	13.6	6.22	0.50	25.0	2.25
	6.80	6.26	1.00	25.0	2.45

Complex	$10^4(Cr^{2+})$, M	$10^3(Ru^{III})$, M	(H^+), M	Temp, °C	$10^{-4}k$, M^{-1} sec^{-1}
Isoester[d]	9.04	4.24	1.00	25.0	3.56
	9.04	4.24	0.500	25.0	4.10
	9.04	4.24	1.00	25.0	3.99
	9.04	4.24	0.0393	25.0	4.04
	9.04	4.24	0.0767	25.0	4.30
	9.04	4.24	0.0767	25.0	4.25
	9.04	4.24	0.0767	25.0	4.22
	9.04	4.24	1.00	15.0	3.53
	9.04	4.24	1.00	33.0	4.22
	9.04	4.24	1.00	25.0	4.20
	9.04	4.24	1.00	15.0	3.38
	9.04	4.24	1.00	30.0	4.05
	9.04	4.24	1.00	20.0	3.66
	9.04	4.24	1.00	15.0	3.61
				20.0	3.66
				25.0	3.85
	9.04	4.24	1.00	25.0	3.97
				30.0	4.15
				33.0	4.22
	0.792	4.0	1.00	25.0	3.61
	8.98	4.12	1.00	25.0	4.16
	8.98	4.10	0.500	25.0	4.35
	8.98	4.09	0.0502	25.0	4.20
	8.98	4.08	0.0392	25.0	4.40
Ester[e]	18.1	6.43	0.0767	25.0	0.660
	18.1	6.45	1.00	15.0	0.574
				20.0	0.612
				25.0	0.675
				30.0	0.693
				33.0	0.738
	18.1	6.45	1.00	15.0	0.539
				20.0	0.613
				25.0	0.663
				30.0	0.714
				33.0	0.738
(Isoamide)$_2$[f]	1.32	3.77	0.099	25.0	[g]
	0.370	1.89	0.099	25.0	600
	0.370	1.90	0.099	25.0	760
(Isoester)$_2$[h]	0.370	1.65	0.999	25.0	108
	0.370	1.64	0.999	25.0	111
	0.449	1.63	0.999	25.0	111

[a] All runs were made at $\mu = 1.0$ and were followed at 407–408 nm unless otherwise stated. [b] All runs were made at $\mu = 0.10$ and were followed at 520 nm. [c] All runs were made at $\mu = 1.0$ and were followed at 427 nm unless otherwise stated. [d] All runs were made at $\mu = 1.0$ and were followed at 515 nm unless otherwise stated. [e] All runs were made at $\mu = 1.0$ and were followed at 417 nm. [f] All runs were made at $\mu = 0.10$ and were followed at 505 nm. [g] Reaction about 96% complete before reaction mixture reached the observation point. [h] All runs were made at $\mu = 1.0$ and were followed at 512 nm.

stants for each complex at 25° and the activation parameters obtained from analysis of the rate data. As will be shown below, the activation parameters for the nicotinamidepentaammine complex are composites of the activation parameters for the parallel paths of the reaction.

Summarized in Table VII are the results of a limited number of experiments to determine the rate of reduction of the pentaammineruthenium(III) complexes by V^{2+}. These experiments were undertaken to assess the rate pattern for a genuine outer-sphere reductant as an aid in interpreting the results for Cr^{2+}. The specific rate for substitution of water on V^{2+} is 90 sec^{-1};[17] the rates of reduction of these Ru^{III} complexes by V^{2+} are much too fast to involve substitution of L into the coordination sphere of vanadium prior to electron transfer.

Table VII

Rate Constants for the Reduction of Pentaammineruthenium(III) Complexes by Vanadium(II)[a]

Complex	$10^5(V^{2+})$, M	$10^5(Ru^{III})$, M	$10^{-5}k$, M^{-1} sec^{-1}	Temp, °C
py	9.88	5.00	1.19	25.0
Ester	9.88	5.00	3.63	25.0
Ester	9.88	5.10	3.53	25.0
Isoester	9.88	5.08	5.99	25.0
Amide	9.88	4.06	9.5	25.0
Isoamide	14.8	4.01	11.3	25.0
Isoamide	7.41	3.96	13.2	25.0
Isoamide	7.41	3.99	12.7	25.0
			12.8	30.0
			13.0	20.0
Isoamide	7.41	3.96	12.5	15.0
			13.0	20.0
			11.7	30.0

[a] All runs were at $\mu = 1.0$ and 1.0 M H^+.

Products of the Reduction of Pyridinepentaammineruthenium(III) by Chromium(II).—The spectrum of a product solution prepared in the absence of light by adding either an excess of Cr^{2+} or a deficiency of Cr^{2+} to a solution of $(NH_3)_5Ru(py)^{3+}$ shows that the major Ru(II) product is $(NH_3)_5Ru(py)^{2+}$. Using ϵ_{407} 7.78 × 10^3 for $(NH_3)_5Ru(py)^{2+}$, 92–96% of the total ruthenium was accounted for as the pyridine complex. Considering the experimental error involved in determining ϵ for $(NH_3)_5Ru(py)^{2+}$, these results are consistent with complete conversion to $(NH_3)_5Ru(py)^{2+}$ as the final Ru(II) product for the reaction. First-order plots of the kinetic data taken at 10-nm intervals from 385 to 435 nm show little variation in the rate with wavelength, and no deviation in linearity over 80% of the reaction. It is unlikely therefore that an intermediate Ru(II) product is formed at significant concentrations. The above evidence and the slow rate of reduction of the pyridine complex compared to systems to be discussed in which Cr(III) complexes are formed supports an outer-sphere path for the reaction.

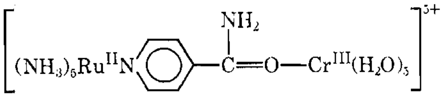
Products of the Reduction of Isonicotinamidepentaammineruthenium(III) by Chromium(II).—The initial product of the reaction of $(NH_3)_5Ru(isoamide)^{3+}$ with Cr^{2+} in 0.100 M $HClO_4$ was found to have an intense visible absorption band centered at 523 nm (ϵ ~13 × 10^3) and a uv band at 268 nm (ϵ ~3.2 × 10^3). The visible absorption band, however, was observed to shift to shorter wavelength with time. The rate of shift of the band was quite slow (~1 nm/hr) when the product solution sample remained in the dark, but the rate of shift increased significantly on exposure of the sample to daylight. In all product studies care was taken to exclude light to minimize complications resulting from the photosensitive reaction.

In perchlorate medium the shift in the band maximum was also accompanied by a significant decrease in absorbance. This is probably caused by oxidation of the Ru(II) species by perchlorate ion. In bromide medium the decrease in absorbance did not occur; therefore, all product studies were done in this medium. The product solution was quite sensitive to air oxidation, and care was taken to exclude oxygen by working under an argon atmosphere.

In bromide medium the initial product of the reaction had an absorption maximum at 505 nm (ϵ 10.7 × 10^3). The shift in band maximum of the initial product to shorter wavelength in bromide solution compared to perchlorate solution is probably a result of ion pairing.[14] After 60–72 hr the absorption maximum shifted to 481 nm, the absorption maximum for $(NH_3)_5Ru(isoamide)^{2+}$ in bromide medium. Using ϵ_{481} 11.1 × 10^3 for $(NH_3)_5Ru(isoamide)^{2+}$, 97–99% of the total ruthenium was accounted for as the isonicotinamide complex.

A sample of the initial product mixture was placed on an ion-exchange column under an argon atmosphere. The highly colored product mixture remained at the top of the column when elution was attempted with 1.5 M $LiClO_4$–0.10 M $HClO_4$. Blank experiments showed that $(NH_3)_5Ru(isoamide)^{2+}$ would have been eluted rapidly by 1.5 M $LiClO_4$–0.10 M $HClO_4$ solution. In view of the ion-exchange behavior described and the product studies outlined above, we conclude that the reaction of $(NH_3)_5Ru(isoamide)^{3+}$ with Cr^{2+} yields predominantly a *single* highly colored species of charge greater than 2+, which decays slowly to yield $(NH_3)_5Ru(isoamide)^{2+}$ as the only Ru(II) species.

In the reaction of $(NH_3)_5Co(isoamide)^{3+}$ with Cr^{2+} Nordmeyer and Taube[1] have identified the initial product to be an isonicotinamide-bound Cr^{III} species. Shifts in the C=O and C—N stretching frequencies of the species in D_2O showed unambiguously that the Cr^{III} is bound to the amide carbonyl as opposed to the pyridine nitrogen or the amide nitrogen. An intermediate species (I) similar to that characterized by Nordmeyer and Taube, but with Ru(II) still bound to the pyridine nitrogen, is consistent with the results of the product studies outlined above. The difference in the chemistry of the reduction of the Co(III) *vs.* the Ru(III) com-



I

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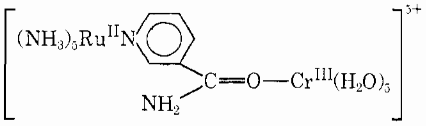
[17] M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

plex is expected because Ru(II) undergoes substitution less readily than Co(II). Species I has a charge of 5+ which is consistent with the ion-exchange experiments. The shift in the charge-transfer band to lower energy is expected on the basis of the electrostatic effect of the positively charged Cr^{III} bound to isonicotinamide.

Ir experiments in D_2O to determine the point of attachment of Cr^{III} were attempted, but because of the sensitivity of species I to oxygen, these experiments were unsuccessful. In analogy to Nordmeyer and Taube's results it is assumed that the Cr^{III} is bound to the carbonyl oxygen of the ligand; this assumption is supported by the fact that the rates of aquation of the Cr(III) products are much the same in the Co(III) and Ru(III) systems.

Products of the Reduction of Nicotinamidepentaammineruthenium(III) by Chromium(II).—With either an excess or a deficiency of Cr^{2+} the spectrum of the product mixture from the reaction of $(NH_3)_5Ru(amide)^{3+}$ with Cr^{2+} within 5 min of mixing has an intense visible absorption band at 421 nm. This band is at a shorter wavelength than expected if $(NH_3)_5Ru(amide)^{2+}$ (λ_{max} 425 nm) were the only Ru(II) product of the reaction.

A sample of the dark orange-yellow product mixture was placed on an ion-exchange column equilibrated at 4° under an argon atmosphere. Elution with a solution of 1.0 *M* $LiClO_4$–0.10 *N* $HClO_4$ moved a yellow band down the column leaving a dark orange-yellow band at the top. The spectrum of a sample of the yellow band eluted from the column has a visible absorption band at 425 nm characteristic of $(NH_3)_5Ru(amide)^{2+}$. By analogy with the product mixture of the reaction of $(NH_3)_5Ru(isoamide)^{3+}$ with Cr^{2+} discussed previously, the dark orange-yellow species on the ion-exchange column is formulated as



II

The fact that *no* blurring or running of the amide 5+ species band occurred on elution is good evidence that the spontaneous or column-catalyzed aquation of this species is slow compared to the time of the experiment (*ca.* 15 min). On this basis the $(NH_3)_5Ru(amide)^{2+}$ separated from the reaction mixture could have been formed only in the primary electron-transfer reaction. We conclude, therefore, that the reaction of $(NH_3)_5Ru(amide)^{3+}$ with Cr^{2+} definitely proceeds by two paths: an inner-sphere path forming the amide 5+ species as the initial product and an outer-sphere path forming $(NH_3)_5Ru(amide)^{2+}$ as the product.[18] In the outer-sphere path hexaaquochromium(III) is assumed to be the final chromium product.

The results of three quantitative ion-exchange experiments at 4° showed that 74 ± 5% of the reaction proceeds by the inner-sphere path and 26 ± 5% by the outer-sphere path. The amount of eluted $(NH_3)_5Ru(amide)^{2+}$ was determined spectrophotometrically. From the amount of $(NH_3)_5Ru(amide)^{3+}$ present initially, the amount of the amide 5+ species produced was determined by difference.

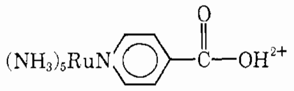
Using the product ratio determined at 4°, the extinction coefficients of $(NH_3)_5Ru(amide)^{2+}$, and the initial concentration of $(NH_3)_5Ru(amide)^{3+}$, it is possible to calculate the spectrum of the amide 5+ species from the initial spectrum of the product mixture. The spectrum thus obtained of the amide 5+ species has an absorption band at 420 nm shifted to shorter wavelength by 5 nm compared to the $(NH_3)_5Ru(amide)^{2+}$ absorption band. This shift is opposite to that observed for the isoamide 5+ species, for which the absorption band is shifted more than 25 mμ to longer wavelength compared to $(NH_3)_5Ru(isoamide)^{2+}$. (Species I will often be called the isoamide 5+ species.)

It is apparent from the product studies that k_{obsd} is the sum of the rate constants for the two parallel paths each of which has its own temperature dependence. Extrapolation of the temperature data from Table V to 4° gives $k_{obsd} = 1.83 \times 10^4\ M^{-1}\ sec^{-1}$. Using the product ratio obtained at 4°, k_{inner} and k_{outer} were calculated to be 1.35×10^4 and $0.48 \times 10^4\ M^{-1}\ sec^{-1}$, respectively, for $\mu = 1.0$.

Since product ratios were not determined at other temperatures, it is impossible to determine the activation parameters for each path directly. From the Eyring plot the composite activation energy for the parallel paths was calculated to be $\Delta H^{\ddagger} = 1.10 \pm 0.18$ kcal mol^{-1} and $\Delta S^{\ddagger} = -35 \pm 2$ eu for $\mu = 1.0$.

Products of the Reduction of (Methyl isonicotinate)-pentaammineruthenium(III) by Chromium(II).—The reaction of $(NH_3)_5Ru(isoester)^{3+}$ with Cr^{2+} is characterized by a series of color changes which are complete in a period of about 5 min after mixing. Several experiments were done to determine the nature of the species present during the reaction sequence. Separate experiments were run adding about a 50% excess of Cr^{2+} and a 30% deficiency of Cr^{2+} to a solution of $(NH_3)_5Ru(isoester)^{3+}$. After the color changes ceased, the spectrum of a sample of the product mixture showed intense absorption bands at 495 and 265 nm as expected for $(NH_3)_5Ru(isoester)^{2+}$. Using ϵ_{495} 12.4×10^3 for $(NH_3)_5Ru(isoester)^{2+}$, 103 ± 2% of the total ruthenium could be accounted for as the isoester complex. The final chromium product is assumed to be hexaaquochromium(III).

The possibility of ester hydrolysis accompanying the reaction of $(NH_3)_5Ru(isoester)^{3+}$ with Cr^{2+} was considered in the analysis of the final products. The product of ester hydrolysis



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[18] Aquation of an N-bound pentaamminecobalt(III) has been shown to be very slow: R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970). There is a close parallelism in the rates of aquation of complexes of $Cr(H_2O)_5{}^{3+}$ and $Co(NH_3)_5{}^{3+}$. On this basis, any N-bonded isomer formed in the present experiments would be counted as part of the inner-sphere component.

was separately synthesized and is found to have an absorption band at 492 nm; however, its molar extinction coefficient is 34% lower than that of $(NH_3)_5Ru(isoester)^{2+}$. The fact that the product studies account for 100% of the Ru(II) as the isoester complex and the fact that the product spectrum was unaffected in the acidity range studied (0.10–1.0 M $HClO_4$) rules out ester hydrolysis in excess of 10% as accompanying the reaction of $(NH_3)_5Ru(isoester)^{3+}$ with Cr^{2+}.

The series of color changes during the reaction suggest that at least one intermediate species is found. With a 20-fold excess of Cr^{2+} and at 1.0 M $HClO_4$, kinetic experiments indicated that the half-life of the intermediate species was about 600 times greater than the half-life of the reaction leading to its formation. The two reactions were therefore completely separable, the formation of the initial product species being complete before it decayed significantly.

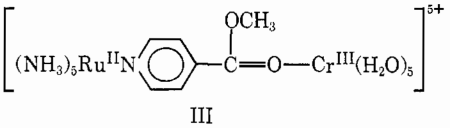
The decay of the initial product species was nonetheless too rapid to permit its characterization by conventional spectrophotometric techniques. However it was possible to obtain its spectrum using the stopped-flow apparatus and observing the change in absorbance between initial and final products at 10-nm intervals. Equation 1 was used to calculate the spectrum of the intial product species, where $\epsilon_{\mathrm{int},\lambda}$ is the molar extinc-

$$\epsilon_{\mathrm{int},\lambda} = \frac{\Delta A_\lambda}{bc} + \epsilon_{\mathrm{prod},\lambda} \qquad (1)$$

tion coefficient for the initial product at wavelength λ, $\Delta A_\lambda = (A_{\mathrm{int}} - A_{\mathrm{prod}})$ at λ, b is the path length, c is the initial concentration of $(NH_3)_5Ru(isoester)^{3+}$, and $\epsilon_{\mathrm{prod},\lambda}$ is the molar extinction coefficient of $(NH_3)_5Ru(isoester)^{2+}$ at λ.

It was assumed for this calculation that the reaction proceeds 100% through the initial product species observed. The initial product decayed too rapidly to permit this assumption to be proven by an ion-exchange experiment. The kinetic data do not rule out a *small* outer-sphere component of the reaction producing $(NH_3)_5Ru(isoester)^{2+}$ initially.

The calculated spectrum of the initial product has $\lambda_{\max}$ at 540 nm and is shifted 50 nm to longer wavelength compared to $(NH_3)_5Ru(isoester)^{2+}$. The spectrum is consistent with the presence of a single initial product species, which in analogy to the isoamide system is taken to be



III

The rate constant observed for this electron-transfer reaction is only a factor of 6–10 greater than the outer-sphere specific rate constant for the reduction of $(NH_3)_5Ru(py)^{3+}$ or $(NH_3)_5Ru(amide)^{3+}$ by Cr^{2+}; therefore, a contribution to the reduction of $(NH_3)_5Ru(isoester)^{3+}$ by Cr^{2+} from an outer-sphere path must be considered. Compared to the spectrum of the isoamide 5+ species, the calculated spectrum of the isoester 5+ species is both qualitatively and quantitatively consistent with predominantly an inner-sphere path, but it is impossible to exclude a small (5–10%) outer-sphere component to the reaction.

Products of the Reduction of (Methyl nicotinate)-pentaammineruthenium(III) by Chromium(II).—Addition of either an excess or a deficiency of Cr^{2+} to a solution of $(NH_3)_5Ru(ester)^{3+}$ yields a product mixture whose spectrum taken within 5–10 min of mixing has an intense visible absorption band at 417 nm characteristic of $(NH_3)_5Ru(ester)^{2+}$. Using the experimentally determined molar extinction coefficient for $(NH_3)_5Ru(ester)^{2+}$ at 417 nm 96–98% of the total ruthenium present could be accounted for as the ester complex. The final chromium product was assumed to be hexaaquochromium(III).

The change in absorbance (390, 400, 437, 450, 480, and 500 nm) accompanying the reaction was observed on the stopped-flow apparatus. The final absorbance did not change with time at any wavelength nor were the rate constants wavelength dependent.

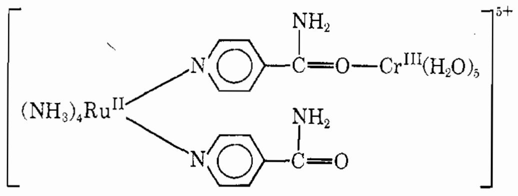
A contribution by an inner-sphere path is *not* ruled out by the above observations. As suggested by the aquation rate of the isoester 5+ species, an ester 5+ species formed by an inner-sphere path would be short-lived and would not be detectable by conventional ion-exchange product studies. Also the spectral data on the amide 5+ species suggest that the spectrum of an ester 5+ species would differ little from the spectrum of $(NH_3)_5Ru(ester)^{2+}$ and therefore a small concentration of an ester 5+ species would have been undetected.

The observed second-order specific rate for this reaction, $(6.68 \pm 0.06) \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$, at 25° lies between the values of $k_{\mathrm{outer}} = 3.37 \times 10^3 M^{-1}\ \mathrm{cm}^{-1}$ (py) and $k_{\mathrm{inner}} \approx 2 \times 10^4\ M^{-1}\ \mathrm{cm}^{-1}$ (isoester). Therefore, a combination of inner-sphere and outer-sphere paths is also not ruled out by the observed rate constant.

Products of the Reduction of *cis*-Bis(isonicotinamide)tetraammineruthenium(III) by Chromium(II).—The reaction of *cis*-$(NH_3)_4Ru(isoamide)_2^{3+}$ with Cr^{2+} produces an initial rapid color change followed by a very slow additional color change. The spectrum of the product mixture in 0.10 M $HClO_4$ taken within 5–10 min of mixing has absorption bands at 503, 424 (sh), and 258 nm. These bands were observed over a period of hours to shift to shorter wavelength.

A sample of the initial product mixture was placed on an ion-exchange column under an argon atmosphere. On elution with 1.5 M $LiClO_4$–0.10 M $HClO_4$, a continuous stream of an orange-yellow species, *cis*-$(NH_3)_4Ru(isoamide)_2^{2+}$, moved down the column from the dark red band at the top. The leading front of the orange-yellow stream was no more intense in color than any other part of the stream, suggesting that column aquation of the $(isoamide)_2$ 5+ species produces all the *cis*-$(NH_3)_4Ru(isoamide)_2^{2+}$. Therefore, we conclude that the reaction of *cis*-$(NH_3)_4Ru(isoamide)_2^{3+}$ with Cr^{2+} yields predominantly a single highly colored species of charge greater than 2+, which decays slowly. Arguments based on absorption spectra as made previously in characterizing the initial product of the reaction of

$(NH_3)_5Ru(isoamide)^{3+}$ with Cr^{2+} are consistent with a formulation of the initial product in this system as



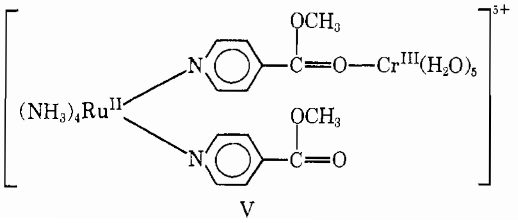
IV

with Cr^{III} bound to the amide carbonyl of one of the isonicotinamide ligands. The formation of the (isoamide)$_2$ 5+ species shows that the reduction reaction is going by an inner-sphere path.

The slow shift in the absorption bands of the initial product to shorter wavelength suggests aquation of the (isoamide)$_2$ 5+ species to give *cis*-$(NH_3)_4Ru(isoamide)_2^{2+}$ and hexaaquochromium(III). The aquation reaction was not studied in detail.

Products of the Reduction of *cis*-Bis(methyl isonicotinate)tetraammineruthenium(III) by Chromium(II).—The reaction of *cis*-$(NH_3)_4Ru(isoester)_2^{3+}$ with Cr^{2+} proceeds through a series of color changes over a period of 1–3 min. The nature of the final highly colored product species was determined spectrophotometrically. A small excess of Cr^{2+} was added to a solution of *cis*-$(NH_3)_4Ru(isoester)_2^{3+}$ using a syringe technique. After no further color changes were observed, the spectrum of a sample of a product mixture was taken. The product species has intense absorption at 492, 421, and 264 nm, characteristic of *cis*-$(NH_3)_4Ru(isoamide)_2^{2+}$. Using the experimentally determined molar extinction coefficients, 100 ± 1% of the total ruthenium can be accounted for as the *cis*-$(NH_3)_4Ru(isoamide)_2^{2+}$ complex. The final chromium product is assumed to be hexaaquochromium(III).

The intermediate species whose presence is indicated by the series of color changes observed, was characterized by scanning its spectrum on the stopped-flow apparatus. The stopped-flow technique was applicable since, as demonstrated by the kinetics of the reaction sequence to be discussed in more detail below, the formation of the intermediate is complete before it decays significantly. The spectrum of the intermediate was calculated from the stopped-flow absorbance data using eq 1. It was assumed for the calculations that the reaction goes 100% through the intermediate observed. The intermediate species has visible absorption bands at 516 and 427 nm (sh). Both bands are shifted to longer wavelength compared to the *cis*-$(NH_3)_4Ru(isoester)_2^{2+}$ bands. On the basis of spectral arguments made previously, the intermediate in this reaction is formulated as



V

The results of a limited number of experiments on the aquation of species V will be presented later.

Aquation of the Isoamide 5+ Species.—The kinetics of the aquation of the isoamide 5+ species was studied using conventional spectrophotometric techniques. All-glass apparatus as outlined in the Experimental Section was used, and the reaction mixtures and cell compartment of the spectrophotometer were thermostated at the desired temperature, care being taken to exclude daylight from the reaction mixtures. The formation of the isoamide 5+ species was complete in the time scale of mixing $(NH_3)_5Ru(isoamide)^{3+}$ and Cr^{2+}. The reaction rate was followed at 550 nm where $\Delta\epsilon$ between the isoamide 5+ species and $(NH_3)_5Ru(isoamide)^{2+}$ is greatest. Kinetic data taken by continuous monitoring of ΔA_{550} or by observing ΔA_{550} at intervals of from 10 min to 1 hr for a short period of time gave the same rate constant, indicating that the light beam in the spectrophotometer did not promote aquation.

From the product studies it is apparent that the isoamide 5+ species decays to $(NH_3)_5Ru(isoamide)^{2+}$ and Cr^{3+} without significant loss of isonicotinamide from the coordination sphere of Ru(II). On this basis the reaction was followed for only 2 half-lives and a calculated value of A_∞ was used to determine values of $A_t - A_\infty$ for kinetic plots. In experiments with excess $(NH_3)_5Ru(isoamide)^{3+}$, A_∞ was calculated from the initial concentration of the isoamide 5+ species as determined by A_{550}, using ϵ 10.7×10^3. In experiments with excess Cr^{2+}, A_∞ was calculated from the initial concentration of $(NH_3)_5Ru(isoamide)^{3+}$ as determined by weight. A plot of log $(A_t - A_\infty)_{550}$ *vs.* time gives a good straight line for 75% of the reaction.

Experiments were run to determine the effect of (H^+) and (Cr^{2+}) on the reaction rate. Data summarized in Table VIII and plotted in Figure 2 show that the observed reaction rate varies linearly with $1/(H^+)$ when $(Cr^{2+}) = 0.0$. As indicated in Table VIII, 4–14% excess $(NH_3)_5Ru(isoamide)^{3+}$ was present in these experiments, but Ru(III) does not appear to affect the reaction rate. The line in Figure 2 conforms to the equation

TABLE VIII

RATE CONSTANTS FOR THE AQUATION OF THE ISOAMIDE 5+ SPECIES IN THE PRESENCE OF EXCESS RUTHENIUM(III)[a]

$10^5(5+)$, *M*	$10^5(Ru^{III})$,[b] *M*	(H^+), *M*	10^5k_{obsd}, sec^{-1}	Temp, °C
7.57	1.04	0.100	1.12	25.0
8.06	0.73	0.0100	1.86	25.0
8.73	0.89	0.0500	1.19	25.0
8.81	0.41	0.0177	1.49	25.0
8.55	0.69	0.100	4.98	35.0
8.57	1.67	0.100	23.3	44.5
8.66	5.31	0.0100	13.4	34.5
8.62	2.59	0.0100	48.7	43.3

[a] All runs were at $\mu = 0.10$. [b] In excess.

$$k_{obsd} = k_2 + \frac{k_3}{(H^+)}$$

where $k_2 = (1.02 \pm 0.01) \times 10^{-5}$ sec^{-1}, $k_3 = (8.4 \pm 0.2) \times 10^{-8}$ *M* sec^{-1} at 25.0°, and $\mu = 0.10$.

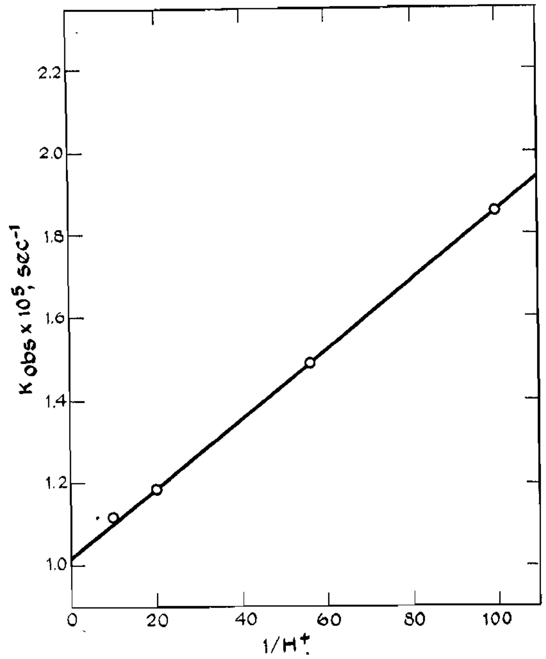
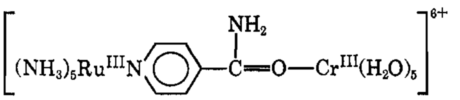


Figure 2.—Plot of k_{obsd} for the aquation of the isoamide 5+ species vs. $1/(H^+)$ at 25° and μ 0.10.

A limited number of experiments were performed to determine the effect of (Cr^{2+}) on the reaction rate. The data indicate that the rate increases with (Cr^{2+}), but the effect was not studied in detail. The dependence of rate on (Cr^{2+}) is weak enough so that this added reaction path does not affect the results of Table VIII which were obtained with Ru(III) in excess.

The rate of aquation of the isoamide 5+ species was determined under conditions of $(Cr^{2+}) = 0.0$ and at two different acid concentrations at different temperatures. Calculated values of $\Delta H^{\ddagger}_{0.100}$ and $\Delta H^{\ddagger}_{0.0100}$ are 28 ± 2 and 33 ± 5 kcal mol^{-1}, respectively. The percentage of the reaction proceeding by each path at $(H^+) = 0.100$ M and $(H^+) = 0.0100$ M, obtained from the rate law at 25°, was used to determine the activation parameters for each path. The values found are $\Delta H^{\ddagger}_{k_2} = 27 \pm 2$ and $\Delta H^{\ddagger}_{k_3} = 39 \pm 5$ kcal mol^{-1}. From the $\Delta H^{\ddagger}$ data $\Delta S^{\ddagger}_{k_2} = 11 \pm 9$ eu and $\Delta S^{\ddagger}_{k_3} = 40 \pm 17$ eu.

Aquation of the Isoamide 6+ Species.—Addition of an equivalent amount of $Cr_2O_7^{2-}$ to a solution containing the highly colored isoamide 5+ species results in a rapid reaction yielding a colorless solution. Addition of an equivalent amount of V^{2+}, an outer-sphere reducing agent,[19] regenerates the isoamide 5+ species quantitatively. Oxidation by $Cr_2O_7^{2-}$ therefore produces



$$\left[(NH_3)_5Ru^{III}N\langle\bigcirc\rangle-\overset{NH_2}{\overset{|}{C}}=O-Cr^{III}(H_2O)_5\right]^{6+}$$

VI

A series of experiments was run to determine the rate of aquation of the isoamide 6+ species. In these experiments a small excess of Cr^{2+} was added to a solution of $(NH_3)_5Ru(isoamide)^{3+}$ to generate the isoamide 5+ species. Immediately thereafter a 30% excess of $Cr_2O_7^{2-}$ was added to the solution to generate the isoamide 6+ species. Aquation of Cr^{III} was allowed to proceed for a given time (0.5–5.5 hr). The reaction mixture was then reduced by addition of a small excess of V^{2+}. The ratio of $(NH_3)_5Ru(isoamide)^{2+}$ to isoamide 5+ species was determined from the absorbance of the reduced solution at 460 and 550 nm. A syringe technique was used for all additions and the volumes were assumed to be additive. Care was taken to exclude daylight and oxygen from the reaction mixtures.

The data obtained for these experiments are summarized in Table IX. First-order plots of the data give good straight lines which pass through the origin. The plots indicate an inverse acid path for the reaction. The observed rate constants at various acid concentrations are summarized in Table X. A plot of k_{obsd} vs. $1/(H^+)$ shows that under the conditions studied the rate law for the reaction is

$$\text{rate} = \left[k_2 + \frac{k_3}{(H^+)}\right](6+)$$

where $k_2 = (2.78 \pm 0.14) \times 10^{-5}$ sec^{-1}, $k_3 = (48.9 \pm 2.4) \times 10^{-8}$ M sec^{-1} at 24°, and $\mu = 0.10$

TABLE IX

KINETIC DATA FOR THE AQUATION OF THE ISOAMIDE 6+ SPECIES[a]

$10^5(6+)_{initial}$, M	t, hr	$10^5(6+)_t$, M	(H^+), M
11.1	2.50	8.23	0.100
10.8	0.75	9.91	0.100
10.8	1.50	8.85	0.100
10.6	2.00	6.87	0.0177
10.8	0.50	9.99	0.0177
10.9	4.00	4.68	0.0177
10.8	0.75	9.57	0.0177
11.0	1.00	8.49	0.0100
10.6	2.00	6.29	0.0100
10.9	1.50	7.13	0.0100
10.7	3.00	4.65	0.0100
10.8	3.00	7.48	0.100
10.8	5.00	5.85	0.100
10.8	4.00	7.03	0.100
10.8	3.00	5.99	0.0177
10.7	4.00	3.53	0.0100
10.8	6.50	4.99	0.100

[a] All runs were at $\mu = 0.10$ and at 24 ± 1°.

TABLE X

OBSERVED RATE CONSTANTS FOR THE AQUATION OF THE ISOAMIDE 6+ SPECIES AS A FUNCTION OF ACID CONCENTRATION[a]

(H^+), M	10^5k_{obsd}, sec^{-1}
0.100	3.28 ± 0.16
0.0177	5.49 ± 0.27
0.0100	7.67 ± 0.38

[a] Rate constants calculated from data given in Table IX.

Aquation of the Isoester 5+ Species.—The rate of aquation of the isoester 5+ species is rapid enough to study on the stopped-flow apparatus but not too rapid to be complicated by the initial electron-transfer reaction. The reaction was followed at 570 nm, a region of maximum absorbance change for the reaction. The kinetic experiments are summarized in Table XI.

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[19] When substitution on $V(H_2O)_6^{2+}$ is rate determining for electron transfer, specific rates in the range of 10–50 are encountered.

TABLE XI

OBSERVED RATE CONSTANTS FOR THE AQUATION OF THE ISOESTER 5+ SPECIES[a]

Run	(H^+), *M*	Temp, °C	10^2k_{obsd}, sec^{-1}
24	1.00	25.0	3.96
25	0.500	25.0	4.39
26	1.00	25.0	3.93
27	0.0393	25.0	9.36
28	0.0767	25.0	6.39
29	0.0767	25.0	6.58
29a	0.0767	25.0	6.37
30	1.00	15.0	1.57
31	1.00	34.0	8.28
		33.0	7.61
32	1.00	25.0	3.82
33	1.00	15.0	1.72
34	1.00	30.0	5.98
35	1.00	20.0	2.41
38	1.00	15.0	1.58
		20.0	2.44
		30.0	6.97
		34.0	9.38
39	1.00	20.0	2.35
		30.0	6.07
		34.0	8.55
40	1.00	30.0	6.03
		34.0	8.79
		33.0	7.89
41	0.0767	15.0	2.17
		20.0	3.68
		25.0	6.23
		30.0	10.5
		33.0	14.3
92	1.00	25.0	7.67
93	0.152	25.0	5.38 (μ = 1.1)
94	1.00	25.0	7.01
95	1.00	25.0	6.26
96	1.00	25.0	3.65
97	1.00	25.0	3.66
98	1.00	25.0	3.77
99	0.500	25.0	3.97
100	0.0502	25.0	7.73

[a] All runs were at $\mu = 1.0$ and were followed at 570 nm. In runs 92, 94, and 95 an excess of Ru^{III} was present. In all other runs Cr^{II} was in excess. The initial concentrations of Ru^{III} and Cr^{II} for all runs except 38–42 and 92–95 have been previously described in Table V. The initial concentrations for 38–42 are the same as for 29. Run, (Cr^{2+}) (*M*), and (Ru^{II}) (*M*): 92, 4.08×10^{-3}, 6.10×10^{-3}; 93, 1.36×10^{-4}, 1.15×10^{-4}; 94, 4.08×10^{-3}, 6.11×10^{-3}; 95, 4.08×10^{-3}, 4.34×10^{-3}.

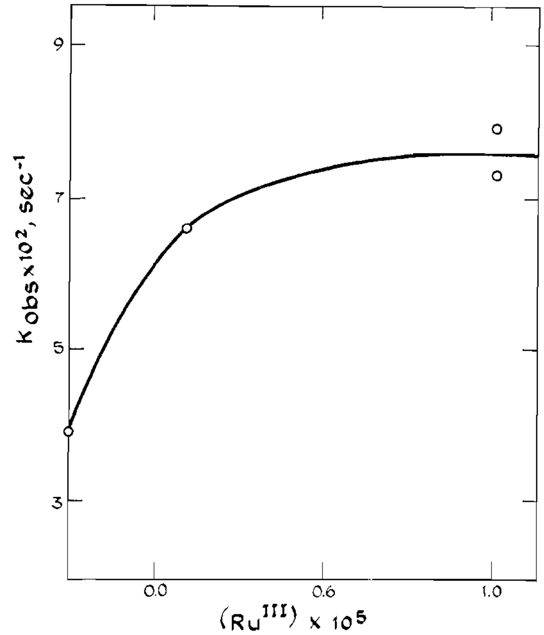

Figure 3.—Plot of k_{obsd} for the aquation of the isoester 5+ species *vs.* concentration of excess Ru^{III} at 25° and $\mu = 1.0$.

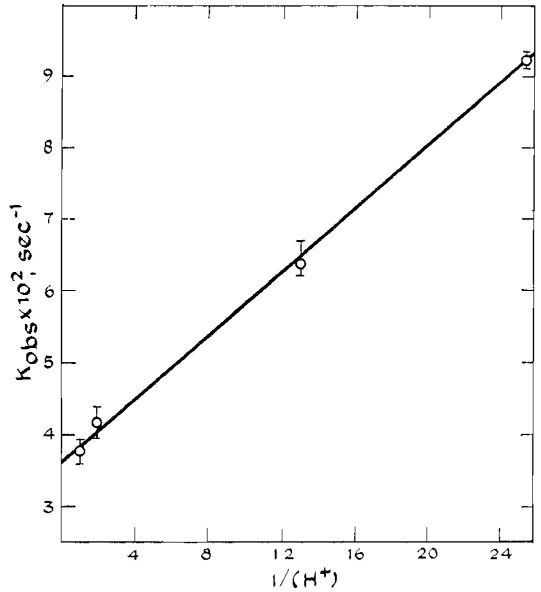

Figure 4.—Plot of k_{obsd} for the aquation of the isoester 5+ species *vs.* $1/(H^+)$ at 25° and $\mu = 1.0$.

The aquation reaction was found to be independent of Cr^{2+} concentration over the range of $(2.4–86) \times 10^{-5}$ *M* Cr^{2+}. Experiments run at $(Cr^{2+}) = 0$ (92, 94, and 95) showed a marked increase in k_{obsd} dependent on the amount of excess Ru^{III}. As shown in Figure 3, k_{obsd} does not vary linearly with (Ru^{III}). It was also noted that the expected change in absorbance associated with the aquation was less in the presence of excess Ru^{III}.

To avoid catalysis, the kinetics of the aquation were studied in the presence of excess Cr^{2+} and the results so obtained are dealt with below.

The rate of aquation was found to be dependent on acid concentration. The plot of k_{obsd} *vs.* $1/(H^+)$ shown in Figure 4 is linear and has a nonzero intercept. The line in Figure 4 is described by the equation $k_{obsd} = k_2 + (k_3/(H^+))$, where $k_2 = (36.5 \pm 1.2) \times 10^{-3}$ sec^{-1}, $k_3 = (2.24 \pm 0.08) \times 10^{-3}$ *M* sec^{-1} at 25°, and $\mu = 1.0$.

The temperature dependence of the aquation of the isoester 5+ species was determined at two acid concentrations, and the data lead to approximate values of the activation parameters for each path. $\Delta H^{\ddagger}_{0.0767}$ and $\Delta H^{\ddagger}_{1.00}$ were calculated to be 17.7 ± 1.0 and 15.0 ± 0.6 kcal mol^{-1}, respectively. The rate law gives the percentage of the reaction proceeding by each path at 1.00 and 0.0767 *M* $HClO_4$. These percentages were used to determine $\Delta H^{\ddagger}$ for each path. The values found were $\Delta H^{\ddagger}_{k_2} = 14.6 \pm 1.0$ kcal mol^{-1} $\Delta H^{\ddagger}_{k_3} = 21.5 \pm 1.0$ kcal mol^{-1}. $\Delta S^{\ddagger}_{k_2}$ and $\Delta S^{\ddagger}_{k_3}$ were then calculated to be -16 ± 3 and 1.5 ± 3 eu, respectively.

Aquation of the Amide 5+ Species.—The rate of aquation of the amide 5+ species was not studied in detail since the relative absorbance change involved in the reaction is quite small. However, from the ion-exchange experiments discussed previously the reaction was shown to be quite slow.

Aquation of the (Isoester)$_2$ 5+ and (Isoamide)$_2$ 5+ Species.—A slow reaction corresponding to the aquation of the (isoamide)$_2$ 5+ species was observed, but it was not studied in detail. Two experiments summarized in Table XII suggest that the rate of aquation of the (isoester)$_2$ 5+ species is somewhat faster than that of the corresponding isoester 5+ species.

TABLE XII

RATE CONSTANTS FOR THE AQUATION OF (ISOESTER)$_2$ 5+ SPECIES IN THE PRESENCE OF EXCESS CHROMIUM(II)[a]

$10^3(\mathrm{Cr^{II}})_{\mathrm{excess}}$, M	$10^3(\mathrm{Ru^{III}})_{\mathrm{initial}}$, M	$(\mathrm{H^+})$, M	k_{obsd}, sec^{-1}	Temp, °C
2.06	1.64	0.999	0.0662	25.0
2.86	1.63	0.999	0.0718	25.0

[a] All runs were at $\mu = 1.0$ and were followed at 560 nm.

Discussion

Electron-Transfer Processes.—The configurations of the activated complexes for the reduction by chromous ion of the ruthenium–ammine complexes studied here parallel those of the corresponding cobalt–ammine complexes, and thus some direct comparison between the rates for the two sets of systems can be made. The reactions with isonicotinamide[1] as ligand have been studied especially carefully and extensively, and the comparisons involving this ligand are of particular interest. The comparison embraces also the pentaaquochromium(III) complex and is restricted to the inner-sphere reaction path which is the only one observed with isonicotinamide as ligand.

The rates of reduction of the pentaaquochromium(III) and pentaamminecobalt(III) complexes have been found[1] to differ by only a factor of 10 at 25°, despite the enormous difference in the driving force for the two reactions. This small rate ratio has been taken to imply that electron transfer in the reduction of these complexes takes place by a stepwise mechanism, the electron being transferred first from the reducing agent to the ligand and then from the ligand to the oxidizing agent. In the limiting case, when each time the ligand accepts an electron, the charge is then passed on to the acceptor center, the rate would be virtually independent of the nature of the acceptor ion. However, in the general case, since the radical ion can also decay to restore chromous ion, the overall rate of reduction will remain somewhat sensitive to the nature of the acceptor ion. The case for stepwise transfer is strengthened by the observation that the rates of reduction of $(\mathrm{bipy})_2\mathrm{Co(isoamide)_2}^{3+}$ by chromous ion[20] differ only slightly from that of $(\mathrm{NH_3})_5\mathrm{Co(isoamide)}^{3+}$ (the specific rate is 14 M^{-1} sec^{-1} for the former complex compared to 17 M^{-1} sec^{-1} for the latter). The insensitivity of rates to the substitution of $(\mathrm{H_2O})_5\mathrm{Cr}^{3+}$ for $(\mathrm{NH_3})_5\mathrm{Co}^{3+}$ has been observed also for other complex reducible ligands. Thus the specific rates for the reduction of acid fumaratopentaaquochromium(III) and of acid fumaratopentaamminecobalt(III) are ~3 and 61 M^{-1} sec^{-1}, respectively,[21] and for the reduction of corresponding monodentate acid oxalato complexes (to form the chelated Cr(III) complex in each case) are 4 and 160 M^{-1} sec^{-1}, respectively.[22] Though the rate ratios are now substantial, they are much lower than those observed for simple bridging groups such as $\mathrm{OH^-}$, $\mathrm{F^-}$, and $\mathrm{Cl^-}$, where they are in excess of 10^5.

If the conclusion about the stepwise mechanism of electron transfer in these systems having Cr(III) or Co(III) as acceptor center and Cr(II) as electron donor is accepted, it finds a ready rationalization based on considering [23,24] symmetries of the metal ion centered and carrier ligand orbitals. In the case of Co(III) and Cr(III) which have electronic structure $t_{2g}{}^6e_g{}^0$ and $t_{2g}{}^3e_g{}^0$, respectively, the added electron enters an e_g orbital having σ symmetry with respect to the metal–ligand bond and therefore overlapping ineffectively with the π ligand orbitals. Upon electron transfer from Cr^{2+} to a low-lying π orbital of the ligand, a distortion in the coordination sphere of the metal oxidant must occur to lower its energy and provide some overlap with the ligand carrier π system before the electron can pass to the metal acceptor. In the context of the results described in the previous paragraph and the rationalization just referred to, the fact that the isonicotinamide complex of Ru(III) is reduced very much more rapidly than that of Co(III) takes on special significance. We suggest that the reason for the large rate increase observed when Ru(III) is the oxidant is that this ion with electronic structure $t_{2g}{}^5\,e_g{}^0$ has a t_{2g} acceptor orbital of π symmetry matching the carrier orbital of the ligand. Once the mismatch between the donor orbital (σ symmetry for Cr^{2+}) has

TABLE XIII

SPECIFIC RATES AND ACTIVATION PARAMETERS FOR THE AQUATION OF Ru–L–Cr 5+ AND 6+ SPECIES[a] $[k_{\mathrm{obsd}} = k_2 + (k_3/(\mathrm{H^+}))]$

Species	k_2, sec^{-1}	k_3, M sec^{-1}	ΔH_{k_2}, kcal/mol	ΔH_{k_3}, kcal/mol	ΔS_{k_2}, eu	ΔS_{k_3}, eu
Isoamide 5+	$(1.02 \pm 0.01) \times 10^{-5}$	$(8.4 \pm 0.2) \times 10^{-8}$	27 ± 2	39 ± 5	11 ± 9	40 ± 17
Isoamide 6+[b]	$(2.78 \pm 0.14) \times 10^{-5}$	$(48.9 \pm 2.4) \times 10^{-8}$				
Isoester 5+	$(36.5 \pm 1.2) \times 10^{-3}$	$(2.24 \pm 0.08) \times 10^{-3}$	14.6 ± 1.0	21.5 ± 1.0	-16 ± 3	1.5 ± 3

[a] All values are at $\mu = 0.10$ and 25° unless otherwise stated. [b] At 24°.

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[20] F. Maspero, experiments done in 1968 at Stanford.

[21] H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970).

[22] M. V. Olson, Ph.D. Thesis, Stanford University, Stanford, Calif., 1969.

[23] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

[24] H. Taube and E. S. Gould, *Accounts Chem. Res.*, **3**, 321 (1969).

been overcome by an appropriate distortion, the electron is accepted into an orbital largely centered on the metal ion but spreading to the ligand. The reaction is no longer stepwise and the rate-determining act, which can be called resonance transfer, involves electron transfer, from the chromous ion directly to the final acceptor orbital.

As would be expected if reduction of Ru(III) through the conjugated bond system takes place by resonance transfer, the rate is observed to be quite sensitive to modifications made in the acceptor ion. Changing from the isoamide to the bis-isoamide complex increases the oxidizing power of Ru(III) by *ca.* 0.26 V. Accompanying this increase in driving force, there is an increase in rate by a factor of 9 (the statistical factor of 2 has been allowed for in making the comparison). The effect of the increase in driving force on the reaction rate is considerably less than would be predicted by applying the Marcus correlation.[25] Quite apart from the consideration that this correlation which was developed for outer-sphere reactions may not be strictly applicable to inner-sphere reactions, there is the point that the rates observed for the bis-(bridging ligand) complexes are approaching $10^7\ M^{-1}\ \mathrm{sec}^{-1}$, which seems to be a limiting rate for inner-sphere reductions by chromous ion.[21] The significant observation, though, appears to be that a change in driving force which is modest compared to that differentiating Cr(III) and Co(III) complexes changes the rate as much as does substituting $Cr(H_2O)_5$ for $Co(NH_3)_5$.

It needs to be pointed out that the increase in rate of reduction of Ru(III) compared to Co(III) cannot be attributed solely to an increased driving force for the reduction of the former. The value of the formal reduction potential for $(NH_3)_5Ru(isoamide)^{3+}$–$(NH_3)_5Ru(isoamide)^{2+}$ is 0.44 V. That for the Co(III) couple is more difficult to fix because a value is needed appropriate to the production of the Co(II) species formed directly on electron transfer rather than for $Co^{2+}(aq)$ which is the species eventually formed. A kinetic reduction potential of 0.3 V has been estimated[26] for the reduction of $(NH_3)_5CoOH_2{}^{3+}$, and a value close to this, but possibly somewhat more positive, is likely to be applicable to the present system. In any event, the difference in oxidation potential for the Co(III) and Ru(III) systems will be very much less than for Cr(III) and Co(III).

The reduction of $(NH_3)_5Ru(py)^{3+}$ by chromous ion takes place without transfer of ligand from oxidant to reductant, just as is the case when $(NH_3)_5Co(py)^{3+}$ reacts. The reduction of the former complex is much more rapid, however, a result which is not unexpected. Cobalt(III) accepts an antibonding electron, and a greater distortion of the coordination sphere is needed to lead to trapping of the incoming electron than is the case for Ru(III), which accepts a nonbonding electron. However, it is unexpected that despite the enormous increase in reactivity when the reduction of $(NH_3)_5Ru(amide)^{3+}$ is compared to that of $(NH_3)_5Co(amide)^{3+}$, the partition between the rate leading to ligand attachment and that which does not are very nearly the same. A simple interpretation of this fact is that the rate ratio for the two paths is determined solely by the ligand, and this suggests that the so-called outer-sphere path also involves the ligand intimately as an electron-transfer path. This suggestion is consistent with the fact that the py complexes react more readily than the hexaammine, though it is, of course, not proven by any of the observations referred to.

The relative rates for the reduction by $V(H_2O)_6{}^{2+}$ (a genuine outer-sphere reductant for the pentaammineruthenium complexes) of py, ester, amide, isoester, and isoamide are 1.00, 3.0, 8.0, 5.0, and 10, respectively. It is clear that significant differences in rate are introduced even for outer-sphere reactions by changing the substituents on the heteroligand. The differences are larger than can be accounted for by the changes in driving force, and in terms of the Marcus correlation, differences in self-exchange rates for the Ru complexes must be allowed for. For chromous ion, the relative rates for the same complexes are 1.00, 2.0, 7.0, 12, and 1.1×10^2. These ratios now include both outer-sphere and inner-sphere paths, and the higher values for the iso species in the case of Cr^{2+} compared to V^{2+} can be ascribed to the intervention of the inner-sphere paths for the former reducing agent. The rate ratio for the outer-sphere reduction by Cr^{2+} of the amide compared to the pyridine complex is 1.8, compared to 8.0 for V^{2+} as reducing agent. Thus, without a deeper understanding of the reactivities, the rate data for V^{2+} cannot be used to assess the inner-sphere contribution to the reactions for Cr^{2+} where both mechanisms contribute.

Aquation of Intermediates.—The most novel results in the aquation studies are those obtained for the isoester complex, species III, these representing the first quantitative kinetic data for the aquation of a metal ion complex of an ester.[27] As expected on the basis of earlier observations, the ester function is a good leaving group, and $t_{1/2}$ for the aquation by the acid-independent path at 25° is 19 sec. The path inverse in (H^+) contributes significantly even at 1 M H^+; this path presumably corresponds to aquation of the conjugate base derived from Cr(III) by dissociation of coordinated water.

Catalysis of aquation by Ru(III) was unexpected. It may arise from the combination of reactions

$$(NH_3)_5RuLCr^{5+} + (NH_3)_5RuL^{3+} \rightleftharpoons (NH_3)_5RuLCr^{6+} + (NH_3)_5RuL^{2+}\text{(equil)}$$

$$(NH_3)_5RuLCr^{6+} \longrightarrow (NH_3)_5RuL^{3+} + Cr^{3+}$$

In $(NH_3)_5RuLCr^{6+}$, Ru is tripositive, and the increased inductive effect can account for an increase in the rate of aquation compared to the complex with Ru(II). The operation of the equilibrium would tend to deplete the concentration of the 5+ species, and this could explain the smaller total absorbance change noted when Ru(III) is present.

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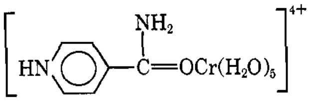
(25) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1969).

(26) A. Haim and H. Taube, *J. Amer. Chem. Soc.*, **85**, 495 (1963).

(27) Some qualitative observations are described by J. R. Hurst and H. Taube, *ibid.*, **90**, 1174 (1968).

As already noted, the rate of aquation of the isoamide 5+ species is similar to that observed for



VII

For the latter complex at 1 *M* H$^+$ the dominant path appears to be independent of (H$^+$), and the specific rate by this path[1] at 25° is 6.5 × 10^{-5} sec^{-1}, compared to 1.02 × 10^{-5} sec^{-1} for the isoamide 5+ species under the same conditions. The values of $\Delta H^{\ddagger}$ do, however, differ significantly; they are 21.9 ± 0.5 kcal/mol for the former complex and 27 ± 2 kcal/mol for the latter, and some influence on the rate of aquation of the group on the pyridine nitrogen has to be admitted.[28] This is borne out by the present studies on the rate of aquation of the isoamide 6+ species. Again at 1 *M* H$^+$, but at 24° rather than 25°, the specific rate is 2.8 × 10^{-5} sec^{-1}. The effects are in the direction of the expected diminishing inductive effects for H$^+$, Ru(III), and Ru(II) but, in view of the differences in $\Delta H^{\ddagger}$ registered, are not entirely to be disposed of quite this simply.

Acknowledgment.—Financial support for this research by the National Science Foundation, both for Grant No. GP 5322 and for the purchase of the spectrophotometer, Grant No. G22611, is gratefully acknowledged.

[28] The ionic strengths do differ in the studies done on VII, and those described in this paper. They are 1.00 and 0.100, respectively, but since the activated complexes have the same charges as do the reactants, it is unlikely that the differences can be ascribed to ionic medium effects.

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A Nuclear Magnetic Resonance Line-Broadening Study of the Azidopentaaquochromium(III) Ion in Aqueous Perchloric Acid

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The solvent proton nmr line broadening caused by $(H_2O)_5CrN_3{}^{2+}$ has been studied in aqueous perchloric acid at 3.0 *m* ionic strength. Studies were carried out at 0, 20, and 36° with varying $HClO_4$ concentrations and between 0 and 70° at 0.082 *m* $HClO_4$. No evidence was found for proton exchange from coordinated N_3H. The exchange of coordinated water protons by acid-catalyzed and uncatalyzed paths has been observed. The general behavior is thus similar to that observed previously for $Cr(OH_2)_6{}^{3+}$. However the $(H_2O)_5CrN_3{}^{2+}$ ion has a short electron spin relaxation time. As a result, when chemical exchange is fast, the line broadening is controlled by the inner-sphere relaxation time.

The rate laws for hydrolysis of azide complexes of chromium(III),[1] cobalt(III),[2] and iron(III)[3] have been found to contain a term first order in hydrogen ion. This term has been associated with the reaction

$$MN_3H + H_2O \longrightarrow MOH_2 + HN_3 \qquad (1)$$

The original intention of this work was to measure the rate and possibly the equilibrium constant for the reaction

$$(H_2O)_5CrN_3{}^{2+} + H_3O^+ \rightleftarrows (H_2O)_5CrN_3H + H_2O \qquad (2)$$

In principle the results could be used to assess the basicity of the coordinated azide ion and to obtain a specific rate constant for reaction 1.

Consideration of the previous work of Swift, *et al.*,[4,5] on $Cr(OH_2)_6{}^{3+}$ indicated that proton exchange from the more basic azide ligand might be measurable. Initial results were qualitatively consistent with proton exchange by reaction 2 with partial saturation of the equilibrium in 3 *M* $HClO_4$. However more detailed analysis and temperature studies have shown that only coordinated water proton exchange causes the observed nmr line broadening. The kinetic parameters for water proton exchange have been determined and are compared to similar results for other hydrated metal ions.

A rather unexpected feature of the $(H_2O)_5CrN_3{}^{2+}$ system is that the electron spin relaxation time is too short to permit observation of an epr signal for the complex ion in solution. As a consequence the transverse relaxation time of the coordinated water protons is unexpectedly long and inner-sphere relaxation becomes a controlling factor for the observed line broadening under certain conditions.

Experimental Section

Solutions of azidopentaaquochromium(III) perchlorate were prepared by the reaction of chromium(III) perchlorate and sodium azide in aqueous solution. Solutions of $((H_2O)_5CrN_3)(ClO_4)_2$ were obtained by ion-exchange separation of the reaction mixture as described by Swaddle and King.[1] The product was identified by comparison of the visible spectrum to that

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[1] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **3**, 234 (1964).

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