The *cis*-dicyanocobalt(III) complex offers an opportunity for a double-bridged transition state. No $(H_2O)_4Cr(CN)_2^+$ could be isolated by ion exchange from a quenched reaction. This is not necessarily proof of its unimportance, however, since it reacts[19] with Cr^{2+} at a rate not greatly different from that of $Cr^{2+} + Co(en)_2(CN)_2^+$. It is possible that this suspected intermediate never builds up to detectable levels.

Acknowledgment. We thank Dr. T. W. Newton and R. H. Moore for supplying the computer programs[16] and Professor A. F. Voigt for use of the scintillation counter.

Appendix

Derivations will be presented for the equations used for calculations of specific activities in the tracer experiments on the Cr^{2+}-catalyzed isomerization of $CrNC^{2+}$. The expressions will be simplified by the abbreviations A = $CrNC^{2+}$, B = Cr^{2+}, and C = $CrCN^{2+}$ to designate the species, and *A*, *B*, and *C* their concentrations, respectively.

A subscript indicates time and a superscript a tagged Cr atom. The value ΣB stands for $[Cr^{2+}] + [{}^*Cr^{2+}]$. Exchange of B and C is specifically excluded and, as discussed in the text, is treated as a correction to the final equation.

According to model I (eq 12, 13) the differential equations are

$$-\mathrm{d}A/\mathrm{d}t = (k' + k_c'\textstyle\sum B)A \tag{16}$$

$$\mathrm{d}C^*/\mathrm{d}t = -\mathrm{d}B^*/\mathrm{d}t = k_c'AB^* \tag{17}$$

Solutions of (16) gives *A* as a function of time

$$A = A_0 \exp[-(k' + k_c'\textstyle\sum B)t] \tag{18}$$

Substitution of this result into (17) and integration give

$$\ln(B^*/B_0^*) = [k_c'A_0/(k' + k_c'\textstyle\sum B)]\{\exp[-(k' + k_c'\textstyle\sum B)t] - 1\} \tag{19}$$

At the end of a tracer experiment, the concentration of B* is

$$B^*_\infty = B^*_0 \exp[-k_c'A_0/(k' + k_c'\textstyle\sum B)]$$

The final specific activity *a* of B in these experiments, where $B^*_0 = \Sigma B$ is

$$a_B = B^*_\infty a_0/\textstyle\sum B = a_0 \exp[-k_c'A_0/(k' + k_c'\textstyle\sum B)] \tag{20}$$

Conservation of activity provides a relation from which a_c can be calculated

$$a_c = (a_0 - a_B)\textstyle\sum B/A_0 \tag{21}$$

Similar expressions can be derived for the other three models.

Reductions of Pentaamminecobalt(III) Complexes of Substituted Pyridines by Chromium(II)

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Abstract: Reactions of Cr^{2+} with the pentaamminecobalt(III) complexes of pyridine, nicotinamide, and isonicotinamide were studied. All the complexes are reduced at rates described by a rate law of the form $k(Co^{III})\cdot(Cr^{2+})$. The pyridinepentaammine complex produces only $Cr(H_2O)_6^{3+}$ from Cr^{2+}, and *k* for the reaction at 25° is $4.0 \pm 0.1 \times 10^{-3}\ M^{-1}\ sec^{-1}$ ($\Delta H^{\ddagger} = 9 \pm 2$ kcal/mole, $\Delta S^{\ddagger} = -39 \pm 7$ eu). The nicotinamidepentaammine complex yields two products by parallel reaction paths: $Cr(H_2O)_6^{3+}$ with $k = 1.4 \pm 0.1 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25° ($\Delta H^{\ddagger} = 9 \pm 2$ kcal/mole, $\Delta S^{\ddagger} = -36 \pm 7$ eu) and an amide-bound Cr^{III}–nicotinamide complex with $k = 3.3 \pm 0.2 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25° ($\Delta H^{\ddagger} = 10 \pm 1$ kcal/mole, $\Delta S^{\ddagger} = -31 \pm 3$ eu). The isonicotinamidepentaammine complex reacts to produce an amide-bound Cr^{III}–isonicotinamide complex with $k = 17.4 \pm 0.5\ M^{-1}\ sec^{-1}$ at 25° ($\Delta H^{\ddagger} = 3.9 \pm 0.3$ kcal/mole and $\Delta S^{\ddagger} = -40 \pm 1$ eu). The latter Cr^{III} complex reacts further under the influence of Cr^{2+} to produce a pyridinyl nitrogen-bound Cr–isonicotinamide complex according to a (H^+) dependent equilibrium. Aquations of the Cr^{III} products were also studied. The structures of Cr^{III} products were assigned on the basis of their infrared spectra. These structures demonstrate that the Cr^{III} products are formed *via* activated complexes in which the oxidizing and reducing centers are coordinated to remote positions of the bridging ligand. Arguments based on rate comparisons indicate that complexes of isonicotinamide react with Cr^{2+} by a radical intermediate mechanism.

Pentaamminecobalt(III) complexes of a wide variety of organic molecules have been examined in reactions with reducing agents such as Cr^{2+}.[1] In these investigations most interest has been placed on the rates and rate laws of these reactions. In only a few instances were the identity or yields of the Cr^{III} products examined. It appeared to us that, in addition to a rate study, such an examination might be worthwhile for the reactions of Cr^{2+} with pyridine-, nicotinamide-, and isonicotinamidepentaamminecobalt(III). In a pre-

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(1) See, for example, (a) H. Taube, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 107; (b) E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965); (c) *ibid.*, **88**, 2983 (1966).

vious communication[2] regarding the latter two of these complexes, we have reported preliminary results which show that they undergo reduction by remote attack of Cr^{2+}. We now report the results of our continued investigations of the products and rates of these reactions.

Experimental Section

Reagents. Water redistilled from alkaline permanganate was used to prepare solutions for kinetic study. Stock solutions of chromium(II) perchlorate were prepared by treating chromium(III) solutions with amalgamated zinc under an atmosphere of oxygen-free nitrogen. The ionic strength of all reaction mixtures for kinetic study was adjusted to 1.00 *M* using lithium perchlorate.

The complexes of pyridine, nicotinamide, and isonicotinamide[3] were prepared according to a modification of the method described by Gould.[1b] The ligands were treated with aquopentaamminecobalt(III) perchlorate in N,N-dimethylformamide (DMF), and the resulting complexes were recovered as described below.

Pyridinepentaamminecobalt(III) Perchlorate. Aquopentaamminecobalt(III) perchlorate and a 40-fold excess of pyridine were dissolved in a minimum of DMF at 100° (about 4 ml of DMF/g of aquopentaammine) and maintained at this temperature for 30 min. The DMF solution was cooled and combined with an equal volume of water. The iodide salt of the pyridinepentaammine was precipitated from this solution by adding an excess of sodium iodide. The crude iodide salt was recrystallized from a sodium iodide solution. The recrystallized iodide salt was treated in solution with silver perchlorate. The silver iodide was removed by filtration, and the perchlorate salt of pyridinepentaamminecobalt(III) was crystallized by concentrating the filtrate (by rotary evaporation) and adding 60% perchloric acid. The absorption spectrum of this salt shows maxima[4] at 252 mμ (ε 3160), 340 (54.4), and 474 (63.8).

Anal. Calcd for $[(NH_3)_5CoNC_5H_5](ClO_4)_3$: C, 11.5; H, 3.83; Co, 11.3; Cl, 20.4; N, 16.1. Found: C, 10.5; H, 3.74; Co, 11.3; Cl, 20.4; N, 16.2.

Nicotinamidepentaamminecobalt(III) Perchlorate. The aquopentaammine and a 12-fold excess of nicotinamide (Eastman White Label) were dissolved in a minimum of DMF at 100° and maintained at this temperature for 1 hr. The DMF solution was collected and filtered to remove crystals of excess nicotinamide. The crude iodide salt of the nicotinamidepentaammine was obtained by adding an equal volume of water and an excess of sodium iodide to the DMF solution. The crude iodide salt was dissolved and reprecipitated with sodium iodide. The iodide salt was dissolved in a minimum of water at room temperature, and one-half volume of 70% perchloric acid was added. Crystals of nicotinamidepentaamminecobalt(III) perchlorate form slowly from this medium. The perchlorate salt was twice recrystallized from perchloric acid; it was shown to be free from iodide by tests with silver nitrate. The absorption spectrum of this salt shows maxima at 339 mμ (ε 54.2) and 476 mμ (ε 62.3).

Anal. Calcd for $[(NH_3)_5CoNC_5H_4CONH_2](ClO_4)_3$: C, 12.8; H, 3.75; Cl, 18.8; Co, 10.4; N, 17.4. Found: C, 13.1; H, 4.2; Cl, 17.7; Co, 10.1; N, 16.9.

Isonicotinamidepentaamminecobalt(III) Perchlorate. Best results were obtained when a aquopentaammine and a 12-fold excess of isonicotinamide were dissolved in a minimum amount of DMF at 100° and maintained at this temperature over Linde 5A $^1/_{16}$-in. molecular sieve pellets for 90 min. The DMF solution was cooled and filtered. The crude iodide salt of the isonicotinamidepentaammine was obtained by adding three volumes of water and an excess of sodium iodide to the solution. The crude iodide salt was twice recrystallized from sodium iodide solution. A solution of the recrystallized iodide salt was treated with silver perchlorate, and the silver iodide was removed by filtration. The perchlorate salt was obtained by concentrating the filtrate by rotary evaporation and adding concentrated perchloric acid. The extremely soluble perchlorate salt of isonicotinamidepentaammine was recrystallized several times from perchloric acid solution. This purification procedure satisfactorily eliminated a second pentaamminecobalt(III) complex having a more soluble iodide salt and a less soluble perchlorate salt than the desired isonicotinamidepentaammine complex. The absorption spectrum of the isonicotinamidepentaamminecobalt(III) perchlorate shows maxima at 261 mμ (ε 5160), 338 (61), and 475 (64.4).

Anal. Calcd for $[(NH_3)_5CoNC_5H_4CONH_2](ClO_4)_3$: C, 12.8; H, 3.75; Cl, 18.8; Co, 10.44; N, 17.4. Found: C, 12.9; H, 3.71; Cl, 18.9; Co, 10.58; N, 17.5.

Preparation of Reaction Mixtures. All solutions containing Cr^{2+} were mixed and enclosed in an atmosphere of nitrogen to prevent oxidation by oxygen. Reaction mixtures of the pyridine or nicotinamide complexes and Cr^{2+} were prepared in an all-glass apparatus and transferred under nitrogen pressure into a spectrophotometric cell. The solutions were isolated in the cell, and absorbance measurements were obtained as soon as a minute after mixing.

The rapid reaction of the isonicotinamidepentaammine complex with Cr^{2+} made necessary a faster means of mixing and observing spectral changes. An all-glass apparatus of the type described by Endicott and Taube[6] was used for runs under various conditions. The majority of runs were performed using a spectrophotometric cell stoppered with serum caps. In a typical experiment, all reagents except Cr^{2+} solution were added to the cell, purged with nitrogen, and thermostated, and the reaction was begun by adding required amounts of Cr^{2+} solution with a hypodermic syringe and needle. With either of these rapid techniques, absorbance measurements could be obtained about 10 sec after mixing. Results obtained with the two rapid techniques agreed within experimental error.

Apparatus. Absorbance measurements were made on a Cary Model 14 recording spectrophotometer. This instrument was equipped with the thermostatable cell compartment and thermostatable cell holder supplied by Cary Instruments. More accurate temperature control was provided by a water bath positioned in the cell compartment of the spectrophotometer. The opposite ends of the cell bath were fitted with quartz windows so that absorbance measurements could be made while the cell was immersed in the flow of water from a constant-temperature bath. Special precautions were taken to avoid condensation of water vapor on any parts in the optical path of the spectrophotometer.

Computer programs were written in ALGOL 60 and were compiled and executed on a Burroughs B5500 located at the Stanford University Computation Center.

Treatment of Data. The data describing the disappearance of reactants by a second-order process according to the rate equation

$$\text{rate} = k(\text{Co}^{\text{III}})(\text{Cr}^{2+})$$

were treated using the relation

$$\ln\left[1 + \frac{\left(\frac{b}{a} - 1\right)(A_0 - A_\infty)}{A_t - A_\infty}\right] = (b - a)kt + \ln\frac{b}{a}$$

Here a and b are the initial concentrations of the reactants, A_0 and A_∞ are the initial and final absorbances, and A_t is the absorbance measured at time t. Since A_0 could not be measured, it was calculated from the concentrations and extinction coefficients of the reactants. The left side of the equation was plotted against time, and the second-order rate constant was calculated from the slope of this line.

The data for first-order and pseudo-first-order reactions (Co^{III} or Cr^{2+} in large excess) were treated with the usual plot of ln $|A_t - A_\infty|$ *vs* t. Second-order rate constants were obtained by dividing the slope by the average concentration of the excess reagent.

Kinetic measurements were made on a system that could be described in terms of the following set of first-order reactions

$$A \xrightarrow{k_1'} B$$

$$A \xrightarrow{k_1''} C$$

$$B \xrightarrow{k_2} C$$

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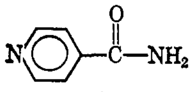
(2) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **88**, 4295 (1966).

(3) Isonicotinamide is



Nicotinamide has the amide group in the 3 position.

(4) Previously reported maxima for pyridinepentaammine are at 475 mμ (ε 64.0) and 338 mμ (ε 52)[1b] and at 480 mμ (ε 46).[5]

(5) R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

(6) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

The rate equations for this system may be integrated to give

$$(\mathrm{A}) = ae^{(k_1'+k_1'')t}$$

$$(\mathrm{B}) = a\frac{k_1'}{k_2 - (k_1' + k_1'')}\left(e^{-(k_1'+k_1'')t} - e^{-k_2t}\right)$$

$$(\mathrm{C}) = a - [(\mathrm{A}) + (\mathrm{B})]$$

where a is the initial concentration of A.

The expression[7] for the absorbance of a reaction mixture at time t

$$A_t = A_\infty + al\left[\epsilon_\mathrm{A}e^{-(k_1'+k_1'')t} + \epsilon_\mathrm{B}\frac{k_1'}{k_2 - (k_1' + k_1'')} \times \left(e^{-(k_1'+k_1'')t} - e^{-k_2t}\right) - \epsilon_\mathrm{C}\frac{1}{k_2 - (k_1' + k_1'')} \times \left((k_2 - k_1'')e^{-(k_1'+k_1'')t} - k_1'e^{-k_2t}\right)\right]$$

may be obtained by assuming that Beer's law holds for each absorbing species and introducing the integrated rate expressions for (A), (B), and (C). ϵ_A, ϵ_B, and ϵ_C are the extinction coefficients of A, B, and C, respectively, and l is the optical path length. The absorbance data arising from these reactions were handled with a computer program[8] that provides least-squares estimation of nonlinear parameters. The values of k_1', k_1'', k_2, and ϵ_A were adjusted by the program to bring the values of A_t calculated from the above expression into agreement with the measured values.

Results

The pyridine-, nicotinamide-, and isonicotinamide-pentaamminecobalt(III) complexes were found to react with Cr^{2+} to produce equimolar amounts of Co^{2+} and Cr^{III}. The identity and behavior of the Cr^{III} complexes will be discussed later in this section.

The stoichiometry for the pyridine complex was demonstrated by an analysis of spectral changes in the 350–750-mμ range attending the reaction with Cr^{2+}. In experiments with (H^+) between 0.07 and 0.70 M, the observed spectral changes throughout the visible region agreed, within experimental error, with those calculated from the extinction coefficients of Co^{III}, Cr^{2+}, and Cr^{III}, assuming 1 mole of $Cr(H_2O)_6{}^{3+}$ was produced per mole of Co^{III} consumed. Cr^{III} products other than $Cr(H_2O)_6{}^{3+}$ would have been detected in these experiments except in the unlikely event that they have spectra similar to that of $Cr(H_2O)_6{}^{3+}$. These experiments serve to establish the stoichiometry to within 5% for the pyridine complex.

The stoichiometry for the nicotinamide and isonicotinamide complexes was determined by allowing a measured amount of Cr^{2+} to react with an excess of the Co^{III} complex. The Co^{2+} produced was determined[9] by a standardized procedure. For both complexes 0.99 ± 0.01 mole of Co^{2+} was produced per mole of Cr^{2+} in experiments with (H^+) in the 0.1–1.0 M range. These observations exclude net reduction of the ligands during the electron-transfer reaction.

Second-order rate constants for the reactions of the Co^{III} complexes with Cr^{2+} appear in Table I. No (H^+) dependence was observed in the range studied.

Table I. Kinetic Data for the Reductions of Pentaamminecobalt(III) Complexes by Chromous Ion[a]

Complex	Temp, °C	$(Co^{III})_0 \times 10^3$, M	$(Cr^{II})_0 \times 10^3$, M	$(H^+)_0$, M	k, M^{-1} sec^{-1}
Pyridine[b]	25.0	9.2	7.0	0.63	4.02×10^{-3}
	25.0	9.4	7.0	0.10	3.84×10^{-3}
	25.0	6.7	6.7	0.076	3.84×10^{-3}
	34.9	9.0	7.0	0.63	6.78×10^{-3}
	34.9	9.3	7.0	0.63	6.50×10^{-3}[c]
	44.8	9.2	7.0	0.63	12.8×10^{-3}
	44.8	9.3	7.0	0.10	13.4×10^{-3}
Nicotinamide	25.0	1.55	1.01	0.865	0.0465
	25.0	1.49	1.00	0.089	0.0475
	25.0	1.50	1.00	0.50	0.0517
	25.0	1.52	1.00	0.25	0.0517
	25.0	1.51	1.00	0.87	0.0477
	25.0	1.49	1.00	0.099	0.0480
	4.6	0.914	7.00	0.63	0.0127
	4.6	0.894	7.00	0.10	0.0126
	15.2	0.907	7.00	0.63	0.0252
	15.2	0.908	7.00	0.10	0.0255
	34.8	0.906	7.00	0.63	0.0778
	34.8	0.902	7.00	0.10	0.0784
	44.9	0.893	7.00	0.63	0.136
	44.9	0.896	7.00	0.10	0.141
Isonicotinamide	24.8	1.37	0.970	0.99	17.3
	24.8	1.41	0.911	0.01	16.7
	24.8	1.39	0.882	0.50	17.5
	24.8	1.53	0.900	0.10	17.6
	15.0	1.39	0.850	0.10	13.3
	15.3	1.015	5.00	0.97	13.6
	15.3	1.027	5.00	0.056	14.0
	15.3	0.995	5.00	0.506	13.5
	5.0	1.37	0.909	0.10	10.4
	5.0	1.34	0.903	0.10	10.1
	5.0	1.41	0.877	1.00	10.5
	4.7	1.038	5.00	0.97	9.87
	4.7	0.989	5.00	0.056	10.24
	4.7	1.015	5.00	0.506	9.78

[a] All runs at 1.0 M ionic strength. [b] Previously reported rates for this complex are 6×10^{-3} M^{-1} sec^{-1} at 25° and 1.5 M ionic strength[1b] and 4×10^{-3} M^{-1} sec^{-1} at 25° and 1 M $HClO_4$.[5] [c] In this run the absorbance at 570 mμ was followed; in all other runs the absorbance at 475 mμ was followed.

Table II. Specific Rates and Activation Parameters for the Reduction of Pentaamminecobalt(III) Complexes by Chromous Ion[a]

Complex	k, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Pyridine	$4.0 \pm 0.1 \times 10^{-3}$	9 ± 2	−39 ± 7
Nicotinamide	$4.9 \pm 0.2 \times 10^{-2}$	(9.9 ± 0.2)	(−31.6 ± 0.8)
Isonicotinamide	17.4 ± 0.5	3.9 ± 0.3	−40 ± 1

[a] All values reported at 25°.

An analysis of these rate data gives the activation parameters reported in Table II. The average rate constant for each complex at 25° is also given. The large uncertainty in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the pyridinepentaammine is due to nonlinearity in the ln k/T *vs.* $1/T$ plot. Further study will be required to determine whether this nonlinearity is an intrinsic property of the system or the result of experimental errors. The activation parameters for the nicotinamidepentaammine are enclosed in parentheses because they require further interpretation; as will be shown below, the nicotin-

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(7) The system of chemical equations used here was adopted at the suggestion of one of the referees and differs from that originally used. The two methods are equivalent and lead to essentially the same results. We agree that the present treatment is preferable because the relation to the chemical processes can more readily be seen.

(8) Library Program No. 114, Stanford University Computation Center, Nov 29, 1965; based on a paper by D. W. Marquardt, *Siam J.*, 11, 431 (1963).

(9) R. K. Kitson, *Anal. Chem.*, 22, 664 (1950).

amidepentaammine reacts with Cr^{2+} by two parallel kinetic paths and each path will have its own temperature dependence.

Cr^{III} Product from Pyridinepentaammine Reduction. The visible spectra of reaction mixtures indicate that $Cr(H_2O)_6^{3+}$ is the product of the pyridinepentaammine–Cr^{2+} reaction. An additional experiment was done to demonstrate that no intermediate Cr^{III} complex accumulates during early parts of the reaction. Duplicate reaction mixtures of Cr^{2+} and pyridinepentaammine were observed under identical conditions. In one of these mixtures the absorbance at 475 mμ was followed as a function of time; in the other the absorbance at 570 mμ was observed. The absorbance at the former wavelength is dominated by Co^{III}, whereas absorbance at the second wavelength is mainly due to Cr^{III}. These two experiments (the fourth and fifth of Table I) yielded similar first-order plots and rate constants that agree to within 4%. This establishes that a Cr^{III} complex having a spectrum different from that of $Cr(H_2O)_6^{3+}$ does not accumulate as an intermediate in the reaction. If an intermediate had formed with a spectrum similar to that of the pyridine-bound form of the isonicotinamidepentaaquochromium(III) ion (described below), an accumulation of about 5% would have been detected.

Cr^{III} Products from Nicotinamidepentaammine Reduction. Spectral changes accompanying the reaction of nicotinamidepentaammine and Cr^{2+} pointed to the existence of an intermediate Cr^{III} product which aquates to form $Cr(H_2O)_6^{3+}$. The existence of such a Cr^{III} complex was confirmed by its isolation and by a kinetic investigation, both described below.

Nicotinamidepentaaammine and a sevenfold excess of Cr^{2+} were mixed in a solution of 0.6 M (H^+). The solution, quenched after reaction using 0.1 M $FeCl_3$ in 0.1 M HCl, was immediately mixed with an ice-cold chloroacetate–chloroacetic acid buffer solution in order to raise the pH to *ca.* 2.7. EDTA was included to complex Co^{2+}, Fe^{2+}, and Fe^{3+}. An ion-exchange column was prepared from Chelex-100 (Bio Rad Laboratories, 100–200 mesh, sodium form), which is a weakly acidic cation-exchange resin. The ion-exchange column was preequilibrated with solution at pH 2.7 and was maintained near 0° by circulating ice water. The column was charged with the buffered reaction mixture. Ions complexed with EDTA and a portion of the $CrCl^{2+}$ are eluted during charging; more highly charged Cr^{III} ions are retained by the resin. The column was next eluted with a $H_2PO_4^-$–H_3PO_4 buffer solution of pH 2.44 and ionic strength 0.2 M. This treatment removed the remaining $CrCl^{2+}$ and 99% of the $Cr(H_2O)_6^{3+}$ originally present in the reaction mixture. The Cr^{III} complex was slowly moved by the phosphate eluent, but very little was eluted by the above treatment. The Cr^{III} complex was removed from the column by eluting with 0.5 M $HClO_4$. The strong acid neutralizes the weakly acidic resin causing the retained ion to be released. The solution of the Cr^{III} complex was collected from the column for immediate absorbance measurements. After aquation of the complex was complete, the uv and visible spectrum of the mixture was equal to the superimposed spectra of $Cr(H_2O)_6^{3+}$ and nicotinamide (after allowing for acid-catalyzed amide hydrolysis). The concentrations of $Cr(H_2O)_6^{3+}$ and nicotinamide could be calculated from their absorbance at selected wavelengths.

A blank experiment was performed in which a mixture of aquopentaammine and free nicotinamide was substituted for nicotinamidepentaammine and subjected to identical reaction and separation procedures. In the blank experiment no band of Cr^{III} complex was visible on the column, and a trace of $Cr(H_2O)_6^{3+}$ was the only uv and visible absorbing material eluted by 0.5 M $HClO_4$. This demonstrates that the Cr^{III} complex collected in the aforementioned experiment resulted from the nicotinamidepentaammine–Cr^{2+} reaction.

Analysis of the results of four experiments in which the Cr^{III} complex was collected from the ion-exchange column showed that the collected solutions contained varying amounts of $Cr(H_2O)_6^{3+}$ but no detectable amounts of uncomplexed nicotinamide. Thus it could be concluded that the initial concentrations of complex in each case equalled the concentration of nicotinamide present after complete aquation. The extinction coefficient of the Cr^{III} complex could be accurately determined at any given wavelength using the equation

$$\epsilon_{\text{nic}} = \epsilon_{\text{aq}} + \frac{\Delta A}{(\text{nicotinamide})l}$$

where ϵ_{nic} and ϵ_{aq} are the extinction coefficients of complexed and uncomplexed Cr^{III}, respectively, and ΔA is the absorbance change attending the aquation reaction. The $Cr(H_2O)_6^{3+}$ initially present ranges from 5 to 20% of the total Cr^{III} in the four experiments and almost certainly arises from aquation of the complex on the column. Thus we conclude that we are dealing with a 1:1 complex of nicotinamide and Cr^{III}. Visible absorbance maxima are found at 412 mμ (ϵ 22.9) and 585 mμ (ϵ 22.6).[10]

Infrared spectra of the Cr–nicotinamide complex were obtained in the 1800–1300-cm^{-1} region using D_2O as a solvent. The sample was prepared by an ion-exchange separation identical with that described above except that the column was treated with D_2O, and 0.5 M DCl in D_2O was used instead of 0.5 M $HClO_4$ to elute the complex. The resulting Cr–nicotinamide solution was concentrated by taking off a portion of the solvent under vacuum. The solution was placed in a cold demountable infrared cell (with Irtran-2 windows and 0.1-mm path length), and repeated scans of the ir spectrum were made. The results of this experiment are shown in Figure 1. Peaks at 1618 and 1452 cm^{-1} for a fresh solution are gradually replaced by peaks at 1665 and 1427 cm^{-1}. The final spectrum is identical with that of nicotinamide in acidic D_2O (Figure 1).

Infrared studies of urea complexes[11] have shown that coordination of the nitrogen by Pt^{II} or Pd^{II} causes the stretching frequency of C=O to increase and that of C—N to decrease, whereas coordination of the oxygen, as with the Cr^{III} and Fe^{III} complexes, produces the opposite effect to the extent that the vibrations become coupled significantly. Although the shifts of the nicotinamide vibration frequencies in the Cr–nicotinamide complex are perhaps not as dramatic as those observed for urea, they are clearly in the direction indicating a chromium–oxygen bond. The visible

(10) Values previously reported[2] are in error by 5–10%.

(11) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, 79, 1575 (1957).

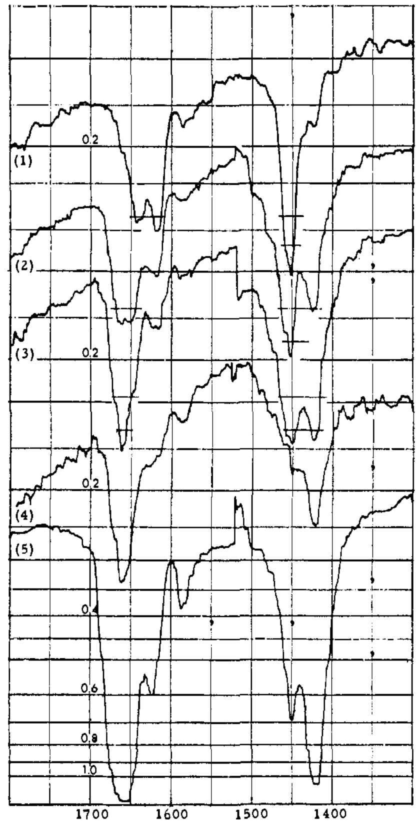
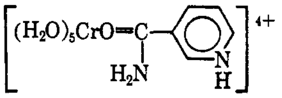


Figure 1. Infrared spectra of the Cr–nicotinamide complex in acidic D_2O: (1–4) spectra of fresh solutions of complex after 5 min, 14 min, 27 min, and 15 hr, respectively; (5) spectrum of nicotinamide.

spectrum of the complex, having maxima at slightly longer wavelengths than those of $Cr(H_2O)_6^{3+}$ (408 and 575 mμ), is consistent with coordination by a weakly basic oxygen. The affinity of the complex for the ion-exchange column implies that it is more highly charged than $Cr(H_2O)_6^{3+}$. All lines of evidence support the conclusion that the Cr–nicotinamide complex has the structure I.



I

The relative importance of an inner-sphere reaction path, producing the Cr–nicotinamide complex, and an outer-sphere path, producing $Cr(H_2O)_6^{3+}$, could be determined by measuring the relative yields of the Cr^{III} products. Yield measurements are complicated, however, by the instability of the Cr–nicotinamide complex. Ion-exchange separations result in partial aquation and, furthermore, the Cr–nicotinamide product in a reaction mixture undergoes significant aquation before reduction of the Co^{III} is complete, except at inconveniently high Co^{III} concentrations. However, knowledge of the visible spectra of both Cr^{III} products was put to use in a spectrophotometric method, and the desired information was obtained by an analysis of absorbance changes accompanying both the reduction and aquation reactions.

The following reaction scheme was hypothesized

$$Co^{III} + Cr^{2+} \xrightarrow{k_{inner}} Co^{2+} + \text{Cr–nicotinamide}$$

$$Co^{III} + Cr^{2+} \xrightarrow{k_{outer}} Co^{2+} + Cr(H_2O)_6^{3+}$$

$$\text{Cr–nicotinamide} \xrightarrow{k_2} Cr(H_2O)_6^{3+}$$

where species having no visible absorption are omitted. Experiments were designed to determine the contribution, if any, of the k_{outer} path to the disappearance of Co^{III}. Large excesses of Cr^{2+} were used in combination with nicotinamidepentaammine in these experiments so that the second-order reactions could be treated as first order, with rate constants $k_1' = k_{inner} \cdot (Cr^{2+})$ and $k_1'' = k_{outer}(Cr^{2+})$. Absorbance data from these experiments were treated by the computer program described in the Experimental Section. The program gave optimized values of k_1', k_1'', k_2, and ϵ_A. Values of k_{inner} and k_{outer} were calculated from k_1' and k_1'' using the average (Cr^{2+}) for each run.

The results of these experiments are shown in Table III. Values of the extinction coefficients of Cr–nicotinamide (22.05 at 25°, 22.20 at 45°), $Cr(H_2O)_6^{3+}$ (13.30 at 25°, 13.65 at 45°), and Co^{2+} (0.68 at 25°, 0.75 at 45°) were used as constants in these computations. The apportionment between k_1' and k_1'' is mainly determined by the difference, $\epsilon_{nic} - \epsilon_{aq}$. This difference was determined directly at 25° in experiments described above. The extinction coefficients of $Cr(H_2O)_6^{3+}$ and Co^{2+} at 44.8° were extrapolated from values at 4.7, 15.3, and 25°. The quantity, $\epsilon_{nic} - \epsilon_{aq}$, was measured only at 25°; its values at 45° were estimated from measurements for the analogous Cr–isonicotinamide complex (to be discussed below), assuming that the temperature dependence is linear and the same for both Cr–amide complexes. The sum of the extinction coefficients of Co^{III} and Cr^{2+}, ϵ_A, was determined by the program, even though its value could be fixed at about 3.2 by independent measurements. A fixed value of ϵ_A would often lead to a poor fit of absorbances at early parts of the reaction. By allowing ϵ_A to be adjusted, good fits and, in most cases, reasonable values of ϵ_A were obtained (*cf.* Table III). The standard deviation of the fit was 0.001 or less absorbance unit for all runs except one that was discarded on this basis.

The rate constants k_{inner} and k_{outer} show no significant variation with (H^+). Their average values are $k_{inner} = 0.033 \pm 0.002\ M^{-1}\ sec^{-1}$ at 25° and $0.112 \pm 0.013\ M^{-1}\ sec^{-1}$ at 44.8; $k_{outer} = 0.014 \pm 0.002\ M^{-1}\ sec^{-1}$ at 25° and 0.034 ± 0.029 at 44.8°. The total specific reduction rates, 0.047 at 25° and 0.146 at 44.8°, agree well with the measurements reported in Tables I and II. These results indicate that about 29% of the reduction reaction proceeds *via* an outer-sphere activated complex which results in $Cr(H_2O)_6^{3+}$ as product.

Activation parameters were assigned to inner- and outer-sphere paths by taking a weighted average of all combinations of $\Delta H^{\ddagger}_{outer}$, $\Delta S^{\ddagger}_{outer}$, $\Delta H^{\ddagger}_{inner}$, and $\Delta S^{\ddagger}_{inner}$ which are consistent with both the product distributions at 25 and 44.8° and the rate measurements of Table I. The following values were obtained: $\Delta H^{\ddagger}_{inner} = 10.2 \pm 1$ kcal/mole, $\Delta S^{\ddagger}_{inner} = -31.3 \pm 3.3$ eu; $\Delta H^{\ddagger}_{outer} = 9.2 \pm 2$ kcal/mole, $\Delta S^{\ddagger}_{outer} = -36 \pm 7$ eu.

Table III. Kinetic Results for the Reactions in the Nicotinamidepentaamminecobalt(III) System[a]

Temp, °C	$(\text{Co}^{\text{III}})_0 \times 10^3$, M	$(\text{Cr}^{\text{II}})_\infty \times 10^2$, M	$(\text{H}^+)_\infty$, M	k_{inner}, M^{-1} sec^{-1}	k_{outer}, M^{-1} sec^{-1}	$k_2 \times 10^3$, sec^{-1}	ϵ_{A}
25.0	9.03	6.12	0.046	0.0363	0.0120	1.54	3.55
25.0	9.03	6.10	0.146	0.0344	0.0130	0.546	3.46
25.0	9.17	6.08	0.574	0.0377	0.0135	0.173	3.63
25.0	11.1	5.65	0.57	0.0344	0.0200	0.168	4.46
25.0	9.48	5.96	0.44	0.0291	0.0129	0.221	3.83
25.0	9.13	6.13	0.20	0.0330	0.0143	0.485	3.73
25.0	8.86	5.97	0.44	0.0321	0.0140	0.201	3.50
25.0	9.08	6.17	0.58	0.0332	0.0140	0.192	3.34
25.0	8.97	6.10	0.28	0.0328	0.0130	0.353	3.36
25.0	8.95	6.15	0.19	0.0354	0.0154	0.402	3.67
25.0	9.13	12.7	0.27	0.0308	0.0097	0.658	3.51
25.0	8.99	14.6	0.18	0.0313	0.0132	1.013	3.13
25.0	4.63	6.39	0.46	0.0317	0.0135	0.258	3.52
44.8	9.17	6.13	0.045	0.115	0.043	10.43	0.64
44.8	9.17	6.13	0.145	0.117	0.010	4.80	1.23
44.8	9.09	6.14	0.575	0.099	0.032	1.60	1.17
44.8	9.08	6.14	0.045	0.116	0.052	11.08	−0.10

[a] All runs were followed at 575 mμ.

The aquation of the Cr^{III}-nicotinamide complex was studied in experiments described in Table IV. The first two experiments were with reaction mixtures of Cr^{2+} and an excess of Co^{III} in which the disappearance of the Cr^{III}-nicotinamide complex was observed after the reduction was complete. Other experiments were performed with complex obtained from the ion-exchange separations.

Table IV. Specific Rates of the Aquation of the Cr-Nicotinamide Complex[a]

Temp, °C	(H^+), M	$k \times 10^6$, sec^{-1}
24.9	0.81	4.93
24.9	0.04	4.95
25.0	0.92	5.27
34.8	0.90	16.8
44.6	0.90	53.3
44.6	0.90	52.2

[a] All runs have ionic strength = 1 M and were followed at 580 mμ.

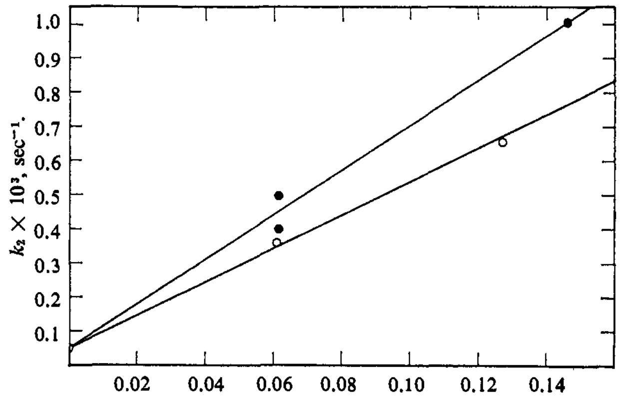


Figure 2. Plot of k_2 vs. (Cr^{II}) for aquation of the Cr-nicotinamide complex: solid points at 0.19 M H^+; open points at 0.27 M H^+.

The specific rates at 25° exhibit no H^+ dependence. The values $\Delta H^\ddagger = 21.8 \pm 0.4$ kcal/mole and $\Delta S^\ddagger = -5.0 \pm 1.3$ eu were obtained from the data of Table IV.

The rate constants, k_2, in Table III represent the aquation of the Cr^{III}-nicotinamide complex in the presence of Cr^{2+}. Comparison of these values with those obtained in the absence of Cr^{2+} (Table IV) shows that the aquation is Cr^{2+}-catalyzed. Plots of k_2 vs. (Cr^{2+}) at fixed (H^+) (Figure 2) show that there is a term in the rate law first order in Cr^{2+}. This term is characterized by a second-order rate constant which is H^+ dependent (specific rate = 6.53×10^{-3} M^{-1} sec^{-1} at 0.19 M H^+ and 4.9×10^{-3} M^{-1} sec^{-1} at 0.27 M H^+). The H^+ dependence may be most easily considered by plotting k_2 vs. $(\text{H}^+)^{-1}$ at a fixed (Cr^{2+}) as in Figure 3.

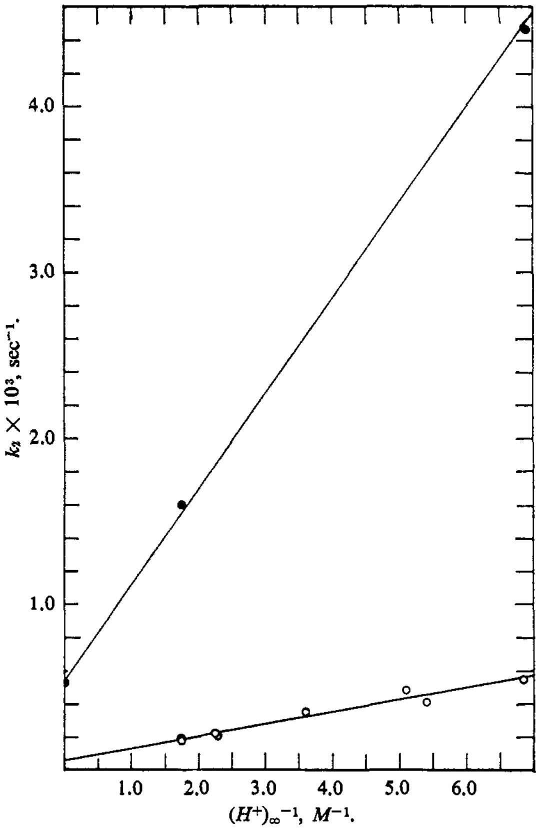


Figure 3. Plot of k_2 vs. $(\text{H}^+)^{-1}$ for the aquation of the Cr-nicotinamide complex in the presence of chromium(II): solid points at 0.0613 M Cr^{2+} and 44.8°; open points at 0.0608 M Cr^{2+} and 25°.

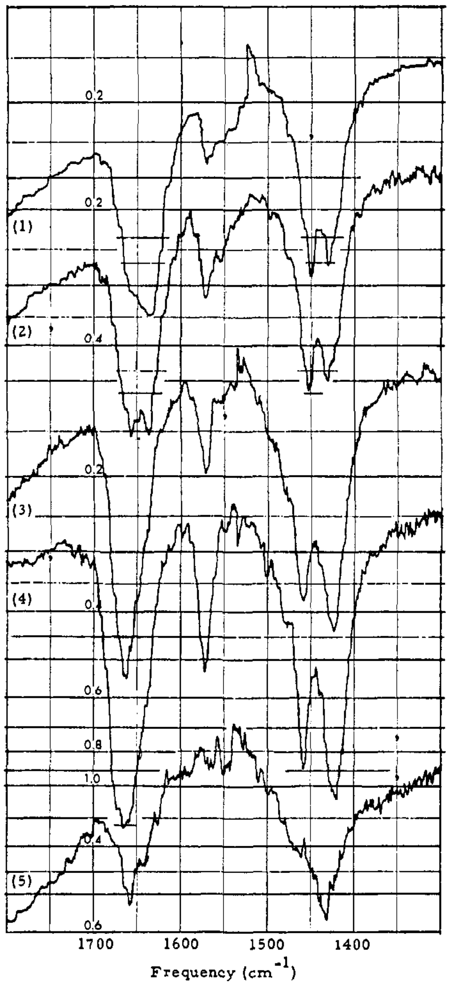


Figure 4. Infrared spectra of the isonicotinamide–chromium(III) complexes in acidic D_2O: (1 and 2), spectra of fresh solutions of amide form of the complex obtained as quickly as possible (within 3–5 min); (3) spectrum of solution 2 after 60 min; (4) spectrum of isonicotinamide; (5) spectrum of pyridine form of the complex.

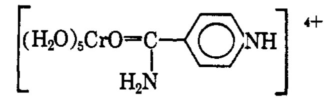
The plot is described by the equation $k_2 = 0.0575 + 0.073(\mathrm{H}^+)^{-1}$ at 0.608 M Cr^{2+}. The agreement of this intercept with the Cr^{2+}-independent rate sets an upper limit of 10^{-4} M^{-1} sec^{-1} on a Cr^{2+}-dependent path which is independent of (H^+). The rate of disappearance of the $\mathrm{Cr}^{\mathrm{III}}$–nicotinamide complex may be described by the equation

$$\text{rate} = [k^0 + k^{\mathrm{i}}(\mathrm{Cr}^{2+}) + k^{\mathrm{ii}}(\mathrm{Cr}^{2+})(\mathrm{H}^+)^{-1}](\mathrm{Cr}^{\mathrm{III}}\text{–nicotinamide})$$

where $k^0 = 5.0 \pm 0.2 \times 10^{-5}$ sec^{-1}, $k^{\mathrm{i}} < 2 \times 10^{-4}$ M^{-1} sec^{-1}, and $k^{\mathrm{ii}} = 1.3 \pm 0.1 \times 10^{-3}$ sec^{-1} at 25°. From the measurements of k_2 at 45°, k^{ii} was found to be 9.38×10^{-3} sec^{-1}. An enthalpy of activation was calculated as 19 ± 1 kcal/mole with an entropy of activation of -8 ± 3 eu for the Cr^{2+}-catalyzed k^{ii} path.

$\mathrm{Cr}^{\mathrm{III}}$ Products from Isonicotinamidepentaammine Reduction. The reaction of the isonicotinamide complex with Cr^{2+} is rapid enough to reach completion before decomposition of the $\mathrm{Cr}^{\mathrm{III}}$ products is appreciable. $\mathrm{Cr}^{\mathrm{III}}$ product spectra could readily be computed from the spectra of reaction mixtures. Runs with $(\mathrm{H}^+) > 0.5$ M and an excess of $\mathrm{Co}^{\mathrm{III}}$ over Cr^{2+} have $\mathrm{Cr}^{\mathrm{III}}$ product spectra with maxima at 584 mμ ($\epsilon \sim 21$). Thus the $\mathrm{Cr}^{\mathrm{III}}$ product has a spectrum similar to that of the $\mathrm{Cr}^{\mathrm{III}}$–nicotinamide complex. Reaction mixtures having $(\mathrm{H}^+) \leq 0.02$ or an excess of Cr^{2+} over $\mathrm{Co}^{\mathrm{III}}$ have $\mathrm{Cr}^{\mathrm{III}}$ product spectra with maxima at shorter wavelengths, in some cases as low as 565 mμ. The latter observations imply that a second $\mathrm{Cr}^{\mathrm{III}}$ product is formed on the time scale of the $\mathrm{Co}^{\mathrm{III}}$ reduction. Since the maximum sometimes occurs at wavelengths shorter than 575 mμ, a complex other than $\mathrm{Cr(H_2O)_6}^{3+}$ must be present. Ion-exchange chromatography performed on an appropriate reaction mixture served to isolate two $\mathrm{Cr}^{\mathrm{III}}$ complexes of isonicotinamide.

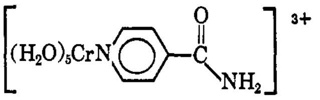
The $\mathrm{Cr}^{\mathrm{III}}$ complex similar to that described for the nicotinamidepentaammine reaction was obtained from a reaction mixture of isonicotinamidepentaammine and a sevenfold excess of Cr^{2+} at 0.61 M H^+. The excess Cr^{2+} was quenched with $\mathrm{FeCl_3}$ immediately following the rapid reduction of the $\mathrm{Co}^{\mathrm{III}}$. Exposure to Cr^{2+} was minimized because isonicotinamide itself is slowly reduced by this reagent. The $\mathrm{Cr}^{\mathrm{III}}$ complex was isolated and investigated using procedures identical with those used for the $\mathrm{Cr}^{\mathrm{III}}$–nicotinamide complex. The corresponding blank experiment was also performed using isonicotinamide. The $\mathrm{Cr}^{\mathrm{III}}$ complex was found to have visible absorption maxima at 411 mμ (ϵ 22.7) and 585 mμ (ϵ 22.0) at 25°. Repeated ir scans of a solution of the complex in D_2O are shown in Figure 4. The final spectrum is that of isonicotinamide shown in the same figure. The infrared spectra show that the peak in the C=O stretching region is shifted down from 1664 to 1639 cm^{-1}, whereas peaks in the C—N stretching region are shifted to longer wavelengths upon coordination. According to the arguments presented for the nicotinamide case, these shifts indicate $\mathrm{Cr}^{\mathrm{III}}$ coordination of the amide oxygen as shown in structure II. This complex will henceforth be referred to as the $\mathrm{Cr}^{\mathrm{III}}$–amide complex of isonicotinamide.



II

The second $\mathrm{Cr}^{\mathrm{III}}$ complex was obtained from a reaction mixture of isonicotinamidepentaammine and Cr^{2+} in 0.01 M H^+. The reaction mixture was quenched with $\mathrm{FeCl_3}$, buffered, and applied to a column of Chelex-100 as was described for the $\mathrm{Cr}^{\mathrm{III}}$–nicotinamide complex. The column was eluted with phosphate buffer solutions of pH 2.4. A solution of ionic strength 0.05 N was used to remove all colored ion except the purple $\mathrm{Cr(H_2O)_6}^{3+}$ and the more violet complex of isonicotinamide. Elution with the ionic strength 0.2 M buffer effected a partial separation of the two $\mathrm{Cr}^{\mathrm{III}}$ ions, removing some of the $\mathrm{Cr(H_2O)_6}^{3+}$ from the column while leaving the violet band behind. The technique of eluting with 0.5 M $\mathrm{HClO_4}$ (or 0.05 M DCl), as described for the $\mathrm{Cr}^{\mathrm{III}}$–nicotinamide complex, was used to remove the $\mathrm{Cr}^{\mathrm{III}}$ complex from the column. The visible spectrum of this complex was, as before, calculated from the absorbance change attending the aquation, eliminating the need to consider the absorbance of the $\mathrm{Cr(H_2O)_6}^{3+}$ present initially. At 25° visible maxima are located at 555 mμ (ϵ 18.6) and 401 mμ (ϵ 20.9). An infrared spectrum in D_2O is shown in Figure 4.

Comparison of the spectrum of the complex with that of free isonicotinamide shows that peaks at 1664 and 1428 cm^{-1} are shifted to 1660 and 1435 cm^{-1} upon complexation. These shifts are small compared to those observed for the Cr^{III}–amide complex of isonicotinamide and imply that the amide group is uncoordinated. The Cr^{III} must therefore be bound to the pyridinyl nitrogen of isonicotinamide as shown in structure III. This structure is consistent with the



III

observed spectral and ion-exchange properties. The visible maxima lie at shorter wavelengths than those of Cr(H$_2$O)$_6$$^{3+}$, as would be expected because pyridine lies beyond water in the spectrochemical series. This isonicotinamide complex was retained by the ion-exchange column only slightly more strongly than Cr(H$_2$O)$_6$$^{3+}$, indicating that it probably has the same charge. Hereafter this complex will be referred to as the Cr^{III}–pyridine complex to distinguish it from the Cr^{III}–amide complex of isonicotinamide.

It was next desired to elucidate the reaction steps leading to the variable distribution of Cr^{III} products. The rate of reduction of Co^{III} is not dependent on (H$^+$), yet the Cr^{III} product distribution does have an acid dependence. It follows that the distribution must be determined by reaction steps subsequent to the activated complex leading to Co^{III} reduction. In the hope that the subsequent step would be observable spectrophotometrically, the investigation was begun by studying the absorbance changes at wavelengths sensitive to the Cr^{III} products.

For mixtures of nicotinamidepentaammine and excess Cr^{2+} the absorbance increase at 600 mμ attending the production of Cr^{III} was followed by a smaller decrease. The size of the absorbance decrease was inversely related to (H$^+$) and was very small for (H$^+$) $\sim$ 1.0 *M*. The data collected from such experiments were treated by plotting ln $(A_t - A_\infty)$ *vs.* t and ignoring the initial points which are distorted by the first reaction. A straight line was drawn through the linear portion of the plot, and the slope of this line was taken to be the rate constant for the second reaction, k_{obsd}. The results of these experiments are shown in Table V. The spectrophotometer was equipped with a 0.0–0.1 and 0.1–0.2 absorbance range slidewire.

Table V. Kinetic Data for the Intraconversion of Cr^{III}–Isonicotinamide Complexes[a]

Temp, °C	(Cr^{II})$_\infty$ × 10^3, *M*	(H$^+$)$_\infty$, *M*	k_{obsd} × 10^3, sec^{-1}
4.6	4.0	0.97	3.74[b]
4.6	4.0	0.97	3.85
4.6	4.0	0.50	4.00
4.6	4.0	0.30	4.88
4.6	4.0	0.20	5.82
4.6	4.0	0.10	7.70
4.6	4.0	0.05	10.7
4.6	4.0	0.50	3.27
4.6	10.0	0.50	7.88
4.6	15.0	0.50	14.7
4.6	25.0	0.50	24[c]
4.6	39.0	0.50	21[d]
4.6	4.0	0.50	4.15
4.6	15.0	0.50	12.84
4.6	39.0	0.50	...[e]
4.6	1.0	0.10	2.1
4.6	2.0	0.10	4.23
4.6	4.0	0.10	7.37
4.6	6.0	0.10	10.6
4.6	10.0	0.10	17.8
4.6	15.0	0.10	25.8
15.3	4.0	0.97	4[d]
15.3	4.0	0.10	12.2
15.3	4.0	0.20	8.56
15.3	4.0	0.30	6.7[d]
15.3	4.0	0.50	5.2[d]
15.3	4.0	0.97	...[e]
25.0	4.0	0.97	...[e]
25.0	4.0	0.10	19.8
25.0	4.0	0.20	13.0[d]
25.0	4.0	0.30	12.3[d]
25.0	4.0	0.50	...[e]
25.0	4.0	0.97	...[e]
25.0	4.0	0.97	9.15[d,f]
25.0	4.0	0.50	9.56[d,f]
25.0	4.0	0.20	12[d,f]
25.0	4.0	0.30	9.63[d,f]
25.0	4.0	0.50	9.63[d,f]
25.0	4.0	0.97	8.83[d,f]
25.0	4.0	0.10	20.8[g,h]
25.0	4.0	0.10	17.0
25.0	4.0	0.15	17.8
25.0	4.0	0.30	11.3[d]
25.0	4.0	0.30	10[d,f]

[a] All runs at (Co^{III})$_0$ = 1 × 10^{-3} *M* and ionic strength 1.00 *M*. [b] Average of four runs followed at different wavelengths; all other runs followed at 600 mμ. [c] Uncertainty in A_∞ is ±10%. [d] Corrected for downward absorbance drift. [e] Irregularities in data make first-order plot impossible. [f] Reaction followed in the reverse direction by injecting acid into an equilibrium mixture. [g] Corrected for upward absorbance drift. [h] Reaction followed in the forward direction by diluting an equilibrated mixture.

The precision for the results of these experiments was poorer than usual. This was not unexpected because the absorbance changes were small (as little as 0.0006 change being used for the plot) and were likely to be influenced by factors such as dust, temperature variations, and incomplete mixing which go undetected in experiments with larger absorbance changes. An additional complication was that aquation of the Cr^{III}–amide complex produces a steady decrease in absorbance which under some conditions becomes appreciable during the course of the second reaction. This is especially true at higher temperatures because the aquation reaction has the larger temperature dependence. In these cases the absorbance was followed for an extended period of time to determine the rate of drift, and the absorbance values were corrected accordingly. Such a correction leaves additional uncertainty in the data, especially in the value of A_∞. Data treated in this way are noted as such.

The data of Table V yield information about the Cr^{2+} and H$^+$ dependence of the second reaction. Plots of k_{obsd} *vs.* (Cr^{2+}) at fixed (H$^+$) (Figure 5) are reasonably linear indicating a first-order Cr^{2+} dependence. A plot of k_{obsd} *vs.* (H$^+$)$^{-1}$ at fixed (Cr^{2+}) (Figure 6) gives a straight line with a nonzero intercept indicating that one of two paths is inverse in H$^+$.

These observations suggest a mechanism which is supported by further experiments described below. In this mechanism, the immediate product of the reduction of isonicotinamidepentaammine by Cr^{2+} is the Cr^{III}–amide complex which may react by a Cr^{2+}-catalyzed path to form an equilibrium concentration

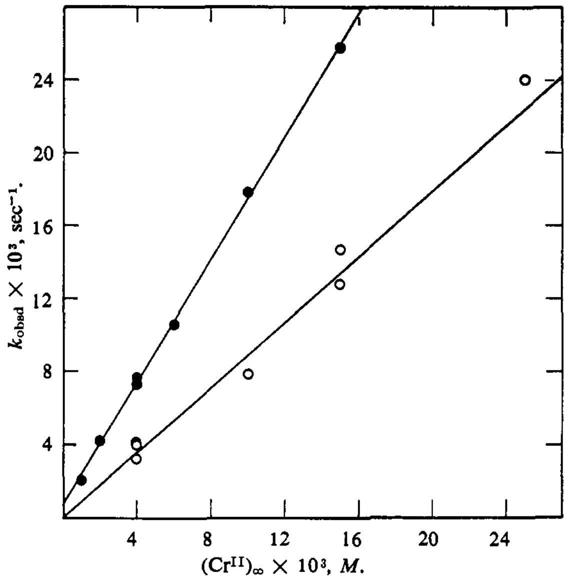


Figure 5. Plot of k_{obsd} *vs.* (Cr^{2+}) for the intraconversion of the Cr^{III}-isonicotinamide complexes in the presence of chromium(II): solid points at 0.1 M H^+, 4.7°; open points at 0.5 M H^+, 4.7°.

of the Cr–pyridine complex. The Cr–pyridine and Cr–amide complexes have extinction coefficients of 11.6 and 21.2, respectively, at 600 mμ. These are consistent with the decrease of absorbance which accompanies the second reaction. Moreover, the Cr^{2+}-catalyzed equilibrium

$$Cr^{2+} + \text{Cr–amide} \underset{k_R}{\overset{k_F}{\rightleftharpoons}} \text{Cr–pyridine} + Cr^{2+} + H^+$$

involves H^+ which accounts for the increased production of Cr–pyridine and the increased absorbance changes at lower (H^+). The rate equations for this equilibrium would be

$$\text{rate forward} = k_F(Cr^{2+})(\text{Cr–amide})(H^+)^{-1}$$

$$\text{rate reverse} = k_R(Cr^{2+})(\text{Cr–pyridine})$$

Under conditions where (Cr^{2+}) and (H^+) are constant throughout the reaction, the rates of the forward and reverse reactions would be pseudo-first order in Cr^{III} complex, having the first-order rate constants

$$k_{\text{forward}} = k_F(Cr^{2+})(H^+)^{-1}$$

$$k_{\text{reverse}} = k_R(Cr^{2+})$$

Approach to equilibrium for a first-order reaction has an apparent rate constant equal to the sum of the constants for the forward and reverse directions[12]

$$k_{obsd} = k_{\text{forward}} + k_{\text{reverse}} = k_R(Cr^{2+}) + k_F(Cr^{2+})(H^+)^{-1}$$

This rate law is in qualitative agreement with considerations of the (Cr^{2+}) and (H^+) dependence and reproduces the data within experimental error where $k_R = 0.81 \pm 0.03$ M^{-1} sec^{-1} and $k_F = 0.106 \pm 0.01$ sec^{-1} at 4.6°.

An experiment in which the approach to equilibrium was observed from the opposite direction eliminated the possibility that the second reaction corresponded to competing irreversible steps.[13] A reaction mixture of isonicotinamide and Cr^{2+} was prepared with $(H^+) = 0.05$ M, conditions under which the Cr–pyridine product would predominate. The decrease of absorbance at 600 mμ was observed until the second reaction was complete. Then a solution of perchloric acid was added to increase the (H^+) to 0.50 at 0.01 M Cr^{2+}. This increase in (H^+) would shift the equilibrium to favor the Cr–amide form. An increase in absorbance was observed. A first-order plot of this change gives a rate constant of about 10×10^{-3} sec^{-1}. This is in good agreement with the calculated value of 10.2×10^{-3} sec^{-1} at 4.6°.

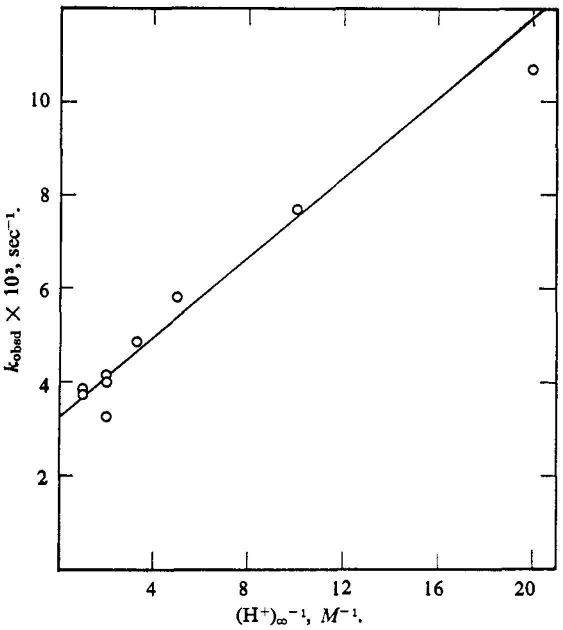


Figure 6. Plot of k_{obsd} *vs.* $(H^+)^{-1}$ for the intraconversion of the Cr^{III}-isonicotinamide complexes at 4.00×10^{-3} M chromium(II) and 4.7°.

As mentioned previously, rate measurements at higher temperatures were complicated by interfering aquation reactions. Some measurements were made at 15°, but a greater effort was made to obtain good data at 25°. The reaction was followed in the reverse direction (using the technique mentioned above) when appropriate in order to get a more easily measurable absorbance change. These experiments are noted as such in Table V. The rate constants $k_R = 1.8 \pm 0.2$ M^{-1} sec^{-1} and $k_F = 0.30 \pm 0.04$ sec^{-1} were obtained at 25°. The values of k_R at 4.6 and 25° were used to calculate $\Delta H^{\ddagger} = 5.8 \pm 1.2$ kcal/mole and $\Delta S^{\ddagger} = -38 \pm 4$ eu for the reverse reaction.

Experiments were done to determine the fraction of isonicotinamide transferred from Co^{III} to Cr^{III} in the oxidation–reduction reaction. Isonicotinamidepentaammine in excess was brought into reaction with Cr^{2+} at high (H^+). Under these conditions very little of the Cr–pyridine is produced. The amount of Cr–amide complex produced was determined from its absorbance. The Cr–amide complex was found to constitute at least 95% of the Cr^{III} product.

The kinetic study of formation of Cr^{III} products shows that in the presence of Cr^{2+} an equilibrium exists between the Cr–amide and the Cr–pyridine complex.

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(12) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 186.

(13) A conclusion to this effect reached previously[2] was the result of an improper interpretation of preliminary results.

Observation of the equilibrium by measurements of the Cr–amide and Cr–pyridine complex concentrations reinforce this conclusion and provide an independent measurement of the formal equilibrium constant. The concentration measurements were made spectrophotometrically.

Mixtures of isonicotinamidepentaammine, a small excess of Cr^{2+}, and various concentrations of H^+ were prepared and given time for the Cr^{III}–isonicotinamide complexes to come to equilibrium at the desired temperature. The spectra of the reaction mixtures were measured from 470 to 660 mμ. These spectra were analyzed by a computer program. The absorbance of Co^{2+} and Cr^{2+} present in the reaction mixture was subtracted. The remaining absorbance was ascribed to amounts of Cr–amide and Cr–pyridine complexes, whose individual spectra were previously measured. The concentrations of Cr^{III} species that gave the least-squares fit of the absorbance data were determined by an ALGOL procedure supplied by Brauman and described by him in a recent publication.[14] The total computed concentration of Cr^{III} (Cr–amide plus Cr–pyridine) was generally within a few per cent of the actual concentration. The standard deviations of the fit for the experiments were about 1% of the absorbance at the maximum. The formal equilibrium constant was calculated from the equilibrium concentrations of each experiment according to the equation

$$K = \frac{(\text{Cr–pyridine})(H^+)}{(\text{Cr–amide})}$$

These results are shown in Table VI and compared with the value of K calculated from the kinetic measurements; the values of K are reasonably constant for the runs at 4.7°. The average value of 0.17 is in fair agreement with the value 0.13, obtained from kinetic measurements at the same temperature. Trends in the equilibrium constant with (H^+) become quite pronounced at higher temperatures. These trends may be ascribed partly to aquation of the mixture of Cr–isonicotinamide complexes which tends to lower the values of K especially at low (H^+).

Table VI. Evaluation of the Formal Equilibrium Constant for the Cr–Amide = Cr–Pyridine + H^+ Reaction

Temp,	K at (H^+) =			
°C	0.05 M	0.10 M	0.20 M	k_F/k_R
4.7	0.162	0.171	0.176	0.131 ± 0.013
15.3	0.130	0.168	0.183	0.19 ± 0.04
25.0	0.116	0.156	0.177	0.17 ± 0.03

First-order rate constants for the aquation of the Cr–amide complex were measured under various conditions (Table VII). All runs except those at 25.0° were performed using excess isonicotinamidepentaammine in reaction with Cr^{2+} and observing the absorbance changes at 580 mμ after the Cr^{2+} was consumed. The runs at 25° were performed on samples of Cr–amide purified by ion exchange. A slight increase in rate with decreasing (H^+) is apparent at all temperatures, but the effect seems more pronounced at higher temperatures. The functional dependence upon (H^+) cannot be determined from the limited amount of data. It appears, however, that the dominant path at high (H^+) is an H^+-independent path. The temperature dependence of the specific rates at *ca.* 1 M H^+ gives $\Delta H^{\ddagger} = 21.9 \pm 0.5$ kcal/mole and $\Delta S^{\ddagger} = -4.3 \pm 1.7$ eu.

Table VII. Specific Rates of Aquation of the Cr–Amide Complex of Isonicotinamide[a]

Temp, °C	(H^+), M	$k \times 10^6$, sec^{-1}
24.8	0.99	6.33
24.8	0.005	12.9
24.8	0.10	6.37
24.8	0.965	6.62
25.0	0.95	6.63[b]
25.0	0.15	6.47[b]
34.8	1.00	21.2
34.8	0.10	27.0
44.6	1.00	72.5
44.6	1.00	67.5
44.6	0.10	80.0
44.6	0.10	81.7

[a] All runs at ionic strength = 1.0 M. [b] These runs were followed at 600 mμ; all other runs were followed at 580 mμ.

The rate of aquation of the Cr–pyridine complex of isonicotinamide was measured at 70° and at 1.0 M ionic strength.[15] Samples were obtained from the ion-exchange separations described earlier. First-order rate constants of 4.33×10^{-5} sec^{-1} at 1 M $HClO_4$ and 4.63×10^{-5} sec^{-1} at 0.15 M $HClO_4$ were obtained. Uncertainties in temperature make the difference between these values nonsignificant.

Measurements of the rates of aquation of the Cr–isonicotinamide complexes in the presence of Cr^{2+} were complicated by the reduction of isonicotinamide itself by Cr^{2+}. For this reason, the rate law for the Cr^{2+}-catalyzed aquation was not determined. From qualitative observations it is clear that the aquation of the Cr^{III} complexes is accelerated by Cr^{2+}.

Discussion

The specific rate constants for the outer-sphere reduction of the hexaammine-, the pyridinepentaammine-, and the nicotinamidepentaamminecobalt(III) ions are 9×10^{-5},[16] 4×10^{-3}, and 1.4×10^{-2} M^{-1} sec^{-1}, respectively, at 25°. The differences in the rates may be understood in terms of the relative base strengths of the respective ligands. The pK_a's for the protonated forms of the bases NH_3, pyridine,[17] and nicotinamide[17] are 9.2, 5.2, and 3.4, respectively. A less basic ligand would stabilize the activated complex in which negative charge is transferred to the cobalt atom.

The isonicotinamidepentaamminecobalt(III) ion reacts with Cr^{2+} to produce the amide-bound Cr–isonicotinamide complex. The transfer of the ligand to the Cr^{III} demonstrates that this reaction proceeds *via* an inner-sphere activated complex. Results for the nicotinamidepentaaammine–Cr^{2+} reaction at 25°

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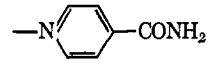
[14] J. I. Brauman, *Anal. Chem.*, **38**, 607 (1966).

[15] The cells containing the reaction mixtures were maintained at 70° in a constant-temperature water bath. Absorbance measurements were made using a Beckman DU with the cell compartment thermostated near 70°. For the two runs the absorbance was followed at 565 and 540 mμ, respectively.

[16] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961).

[17] A. Albert in "Physical Methods in Heterocyclic Chemistry," Vol. 1, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, pp 67, 68, 72.

Table VIII. Comparisons of Specific Rates of the Reaction of Cr^{2+} with Pentaamminecobalt(III) and Pentaaquochromium(III) Complexes

Ligand	Specific rates, M^{-1} sec^{-1}			
	$(NH_3)_5CoL$	$(H_2O)_5CrL$	k_{Co}/k_{Cr}	Ref
F^-	9×10^5	2.64×10^{-2}	3.4×10^7	*b, c*
OH^-	1.6×10^6	0.7	2.3×10^6	*d, e*
NCS^-	19	1.4×10^{-4}	1.4×10^5	*c, f*
Cl^-	2.6×10^6	$\sim 90^a$	$\sim 3 \times 10^4$	*b, c*
$CH_3CO_2^-$	3×10^{-1}	$<10^{-4}$	$>3 \times 10^3$	*g, h*
	17.4	1.8	10	This work

[a] Extrapolated from 0 to 25°; all specific rates at 25° and ionic strength = 1.0 *M*. [b] J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965). [c] D. L. Ball and E. L. King, *J. Am. Chem. Soc.*, **80**, 1091 (1958). [d] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959). [e] A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954). [f] J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964). [g] M. Barrett and E. A. Deutsch, private communication. [h] E. A. Deutsch, private communication.

show that about 71% of the nicotinamide is transferred to the Cr^{III}. Moreover, examination of the structures of these complexes shows that Cr^{2+} attacks the Co^{III} complex at a remote amide oxygen. Since the cobalt atom is coordinated to the pyridinyl nitrogen,[2] in both cases the electron must have been transmitted through the pyridine ring.

The specific rates for the inner-sphere reduction of isonicotinamidepentaammine is 500 times that of the nicotinamidepentaammine at 25°. It is interesting to compare the kinetic data for these complexes with the results that would be predicted from recently proposed models for electron-transfer reactions of this type.

The activation required to bring about energy matching at the two metal ion centers is expected to be nearly the same for the nicotinamide and isonicotinamide complexes. The probability of the electron transition from Cr to Co would be greater with isonicotinamide because electronic interactions are transmitted more efficiently across *para* positions of the bridging ligand than across *meta* positions, and this is in accord with the observations. It would seem, therefore, that the quantum mechanical exchange mechanism[18] requires that the isonicotinamide complex should react more rapidly because of a greater probability of electron transfer, not because any activation step requires less energy. In terms of the activation parameters this means that the isonicotinamide should have a less negative $\Delta S^{\ddagger}$ than the nicotinamide complex, whereas the $\Delta H^{\ddagger}$'s would not necessarily be much different. This is contrary to the observed behavior, and we are led to believe then that at least one of these complexes must react by a mechanism other than the exchange mechanism.

According to the radical intermediate mechanism,[19] the reducing electron is transferred from Cr^{2+} to produce the ligand radical which in turn reduces Co^{III}. Observations made in this study show that the reduction of free isonicotinamide by Cr^{2+} is at least 50 times faster than the reduction of free nicotinamide (which was so slow as not to be observed) under the same conditions. Since the transfer of an electron from Cr^{2+} to the ligand is probably the initial step of the reduction, one might expect the rates of ligand reduction to parallel the rates at which the ligand radical is produced. Thus the radical intermediate mechanism in which the production of the ligand radical is rate determining correctly accounts for the more rapid reduction of the isonicotinamidepentaammine. It is difficult to predict the activation parameters of the electron-transfer reaction for this mechanism; however, it is reasonable that the nicotinamide complex has the larger $\Delta H^{\ddagger}$.

One basic difference between the radical intermediate mechanism and the exchange mechanism suggests an experimental test of these mechanisms. For the radical intermediate mechanism when the production of the radical is rate determining, the activated complex involves transfer of an electron to the bridging ligand. The cobalt atom should have little influence on the stability of this activated complex, or, at any rate, there should be little change in replacing Co^{III} by another metal of like charge. The activated complex for the exchange mechanism involves transfer of an electron through the bridging ligand and to the cobalt atom. The cobalt atom is intimately involved in this activation process. These two possible mechanisms may be distinguished experimentally. For a given bridging ligand the pentaamminecobalt(III) may be replaced by a similar trivalent metal ion, or by a different cobalt(III) group. If the rate of the Cr^{2+} reduction is not sensitive to these replacements, one may conclude that the primary activation process involves electron transfer to the ligand rather than to the metal atom.

This kind of comparison may be made for isonicotinamide. The reduction rate of the pentaamminecobalt(III) complex may be compared to that of the pentaaquochromium(III) complex for isonicotinamide and other bridging ligands. These and related data are presented in Table VIII.

The ratio k_{Co}/k_{Cr} is large for the bridging ligands F^- and OH^-. This indicates that for these bridging ligands the activation process is mainly that of electron transfer to the metal atom. For other bridging ligands the ratio k_{Co}/k_{Cr} is smaller, indicating the increased importance of transfer to the ligand in the activated complex. Isonicotinamide has a remarkably small value of k_{Co}/k_{Cr} indicating the transfer to the ligand is most important in this case. From these comparisons we are led to conclude that the radical ion mechanism predominates with isonicotinamide as the bridging ligand.

The rates of the reaction of Cr^{2+} with the isonicotinamide complexes of Co^{III} and Cr^{III} do still differ by a factor of 10. This is not inconsistent with a purely radical intermediate mechanism since the decomposition of the radical intermediate to form reactants may com-

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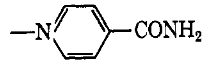
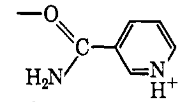
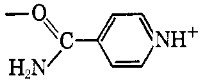
(18) J. Halpern and L. E. Orgel, *Discussions Faraday Soc.*, **29**, 32 (1960).

(19) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

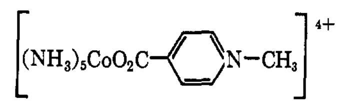
Table IX. Rate Data on the Spontaneous Aquation of Pentaaquochromium(III) Complexes[a]

Ligand	k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	Ref
NH_3	~7 × 10^{-8} (45°)			*c*
	4.5 × 10^{-6} (70°)			This work
$^-O_2CCH_3$	3.3 × 10^{-7}	. . .[b]	. . .[b]	*d*
H_2O	31 × 10^{-6}	27		*e*
	5.0 × 10^{-6}	21.8	−5.0	This work
	6.5 × 10^{-6}	21.9	−4.3	This work

[a] All rates at 25° except where noted otherwise. [b] Rate data for this complex gave a curved Eyring plot. [c] J. H. Espenson and D. W. Carlyle, *Inorg. Chem.* **5**, 586 (1966). [d] E. A. Deutsch, private communication. [e] J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

pete with the decomposition to form products. If this is the case, the over-all reaction rate will reflect the properties of the acceptor metal atom. The decomposition to form reactants might understandably compete with decomposition to form products when the donor and acceptor atoms are both chromium.

This conclusion is in agreement with that of Gould and Taube,[19] who suggest that the complex



reacts with chromium(II) according to a radical intermediate mechanism.

Comparisons of the type in Table VIII cannot be made for the nicotinamide bridging ligand because the chromium(II)-catalyzed isomerization of the nicotinamidechromium(III) complex was not observed. The rate data obtained for the nicotinamidepentaammine do not lead to a conclusion on the mechanism by which nicotinamide acts as an electron mediating ligand.

The kinetics of the spontaneous aquation of nicotinamide- and isonicotinamidechromium(III) may be compared with those of other chromium complexes (Table IX). The nitrogen-bound isonicotinamide is released from chromium(III) more rapidly than the ammine group (assuming that $\Delta H^{\ddagger}$ is $\leq$ 30 kcal, the specific rate the pyridine form of the isonicotinamide complex would be >7 × 10^{-7} sec^{-1} at 45°). It is reasonable that the weaker base be the better leaving group.

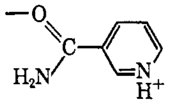
It is to be expected that the amide-bound nicotinamide- and isonicotinamidechromium complexes show almost identical kinetic behavior. They both react faster than other more basic oxygen-bound ligands. The amide group of the isonicotinamide is located in a position *para* to the electron-withdrawing pyridinium nitrogen, and it would be less basic than the amide group of nicotinamide. This explains why the isonicotinamide is released from chromium(III) slightly faster than the nicotinamide. The enthalpies of activation are large; this is characteristic of reactions in which chromium–ligand bonds are broken.

The chromium(II)-catalyzed path for aquation which obeys the rate equation

$$\text{rate} = k''\frac{(\text{Cr}^{\text{II}})}{(\text{H}^+)}(\text{Cr}^{\text{III}}\text{-amide})$$

was studied only for the nicotinamide complex. The kinetic results are listed in Table X, along with the rate data for other complexes of oxygen-donor ligands The order of reactivity is readily understood in terms of the basicity and charge of the sixth ligand. Progression through the series acetato-, aquo-, and nicotinamidechromium(III) ions would be accompanied by increasing acidity of the chromium(III) complex, decreasing electrostatic repulsion between the reacting ions, and increasing ease of transfer of negative charge to chromium(III). Each of these factors may contribute to the observed rate differences.

Table X. Rate Data on the Chromium(II)-Catalyzed Aquation of Pentaaquochromium(III) Complexes[a]

Ligand	k'', sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	Ref
$^-O_2CCH_3$	2.4 × 10^{-5}	22.1	−5	*b*
H_2O	1.2 × 10^{-4}	22		*c*
	1.3 × 10^{-3}	19	−8	This work

[a] All rates at 25°. [b] See footnote *h*, Table VIII. [c] See footnote *e*, Table VIII.

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