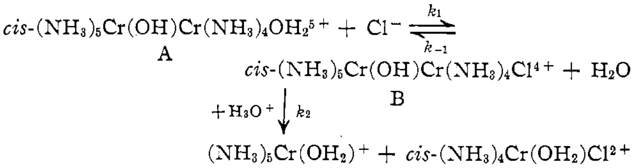
catalyzed cleavage of the aquoerythro ion



$$cis\text{-}(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2^{5+} + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+} + H_2O$$

A B

$$\xrightarrow[+H_3O^+]{k_2} (NH_3)_5Cr(OH_2)^+ + cis\text{-}(NH_3)_4Cr(OH_2)Cl^{2+}$$

The step which is given the rate constant k_2 would probably be the composite of a slow step and one or more rapid steps, including the neutralization of the OH^- which served as the bridge. If the intermediate *cis*-chloroerythro ion is treated as a reactive intermediate, the general rate law for the reaction by this path is

$$\text{rate} = \frac{k_1k_2[A][Cl^-]}{k_{-1} + k_2} \quad (7)$$

Equation 7 is equivalent to the chloride-dependent term of eq 6, where $k' = k_1k_2/(k_{-1} + k_2)$. It seems useless to speculate on the relative magnitudes of the rate constants of the proposed mechanism at this time, since we expect to be able to isolate the *cis*-chloroerythro ion and measure its reaction rates directly.

Absorption maxima and minima for the various monomeric complexes synthesized in the course of this study are given in Table IV.

Acknowledgment.—The authors are grateful to the National Science Foundation for financial support of this research (Grant GP-5425).

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Cyanoaquochromium(III) Complexes. Separation and Identification of the Neutral and Cationic Cyanoaquo Complexes of Chromium(III) and Aquation Kinetics of the Monocyanopentaaquochromium(III) Ion[1]

By D. K. Wakefield[2] and Ward B. Schaap

Received August 16, 1968

The neutral and cationic cyanoaquochromium(III) complexes formed as intermediates in the acid-assisted aquation of hexacyanochromate(III) ion were separated using ion-exchange techniques. Species isolated include the uncharged 1,2,3-tricyanotriaquochromium(III) complex and the *cis*-dicyanotetraaquo- and cyanopentaaquochromium(III) cations. The aquation kinetics of the cyanopentaaquochromium(III) ion were studied in acidic aqueous solutions and were found to proceed *via* an acid-independent pathway and also an acid-catalyzed pathway involving an equilibrium protonation of the complex. The rate of the aquation is described by the rate law $-dC_t/dt = (k_0 + k_HK_{eq}[H^+])C_t/(1 + K_{eq}[H^+])$, where C_t is the total concentration of the cyanopentaaquochromium(III) ion in both protonated and nonprotonated forms. At 25° in perchloric acid–sodium perchlorate solutions of ionic strength 2.0 *M*, the rate parameters are $k_0 = (1.1 \pm 0.1) \times 10^{-5}$ sec^{-1} for the acid-independent path, $k_H = (3.2 \pm 0.1) \times 10^{-3}$ sec^{-1} for the aquation of the protonated species, $K_{eq} = 0.185 \pm 0.006$ l. mol^{-1} (for the protonation equilibrium), and $k_HK_{eq} = (5.90 \pm 0.05) \times 10^{-4}$ sec^{-1} l. mol^{-1}. The aquation was also studied at 15, 35, and 45° and the activation parameters were calculated. For the acid-independent (k_0) pathway, $\Delta H_0^{\ddagger} = 26.9 \pm 0.3$ kcal mol^{-1} and $\Delta S_0^{\ddagger} = 8.9 \pm 1.1$ eu. For the acid-assisted (k_HK_{eq}) pathway, $\Delta H^{\ddagger} = 20.2 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5.5 \pm 0.3$ eu. The pseudo-first-order rate constants calculated from these activation parameters agreed with the experimental values with an average deviation of 1.3%.

Introduction

In acidic aqueous solutions, the hexacyanochromate(III) ion aquates *via* a series of stereospecific reactions to give, finally, the hexaaquochromium(III) cation.[1b,2,3] During the aquation the cyanide ligands are replaced by water molecules in a stepwise manner, forming a previously unknown[4] series of intermediate cyanoaquochromium(III) complexes having the general formula $Cr(CN)_n(H_2O)_{6-n}{}^{3-n}$. Under the proper hydrolysis conditions each of these aquation intermediates can be isolated in solution by ion-exchange techniques. This paper decribes the separation, identification, and spectral properties of the neutral and cationic intermediates and the aquation kinetics of one of them, the monocyanopentaaquochromium(III) ion.

The aquation of monocyanochromium(III) ion (eq 1)

$$Cr(H_2O)_5CN^{2+} + H^+ + H_2O \longrightarrow Cr(H_2O)_6{}^{3+} + HCN \quad (1)$$

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[1] (a) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT(11-1)-256 (Document No. COO-256-84). (b) Presented in part before the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; at the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 1966; and at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Taken in part from a thesis submitted by D. K. Wakefield to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree in chemistry, 1967.

[3] (a) R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); (b) R. Krishnamurthy, Thesis, Indiana University, 1966.

[4] (a) The cyanopentaaquochromium(III) complex was prepared by a different method and previously reported by J. H. Espenson and J. P. Birk, *J. Am. Chem. Soc.*, **87**, 3280 (1965). (b) A method of preparing cyanopentaaquochromium(III) ion at higher concentrations is given by J. P. Birk and J. H. Espenson, *ibid.*, **90**, 2266 (1968).

was studied over a range of hydrogen ion concentrations and at ionic strengths of 1.5 and 2.0. After completion of this work,[1b] Birk and Espenson[5] reported the results of their study of the aquation of monocyanochromium(III) ion which employed somewhat different conditions of acidity and ionic strength than used in the present study.

Monosubstituted pentaaquochromium(III) complexes form an interesting series of compounds in which basic ligands such as azide,[6] fluoride,[7] hypophosphite,[8] sulfate,[9] and acetate[10] show an acid-catalyzed aquation pathway which has a first-order dependence on hydrogen ion concentration, presumably due to protonation of the ligand. Complexes of these ligands, with the exception of hypophosphite, also show an acid-independent pathway which may involve intramolecular proton transfer in the case of more basic ligands such as azide and fluoride. The acid-catalyzed pathway is not present in the case of complexes with less basic anions.[11-16] The monocyano complex is of particular interest because the high basicity of cyanide ion makes it probable that protonated intermediates would be involved in both the acid-catalyzed and acid-independent mechanisms and that their presence might be detected directly as well as inferred from their effects on the parameters of the reaction pathways.

Experimental Section

Reagents.—Deionized water and reagent grade chemicals were used in all procedures. Stock solutions of sodium perchlorate used to adjust the ionic strength were prepared from sodium carbonate and perchloric acid. Potassium hexacyanochromate(III) was synthesized and purified by the method given by Bigelow.[17] Analytical grade anion-exchange resin (Bio-Rad, AG 1-X4, 100–200 mesh), converted to the perchlorate form by washing with 1.0 *M* sodium perchlorate solution, and analytical grade cation-exchange resin (Bio-Rad, AG 50W-X4, 100–200 mesh) in the sodium form were used in the separation procedures. The pH of the cation-exchange resin was adjusted to about 2.2 by equilibrating the resin in a beaker with a little 0.01 *M* perchloric acid solution, which served to convert a small fraction of the resin to the hydrogen cycle. The acidified sodium-form resin was washed with deionized water and its pH was tested by immersing a pH electrode into the wet resin.

Hydrolysis Mixture.—A solution containing the neutral and cationic cyanoaquochromium(III) complexes was prepared by combining potassium hexacyanochromate with perchloric acid in a molar ratio of 1:5. In a typical experiment, 0.65 g (2.00 mmol) of potassium hexacyanochromate was dissolved in 250 ml of 0.04 *M* perchloric acid. The hydrolysis solution was kept in the dark at room temperature until the pH of the solution rose to 2.2, which took approximately 44 hr. A stream of nitrogen was continuously bubbled through the solution to sweep out the liberated molecular hydrogen cyanide. The deep red solution was cooled to 0° and the precipitated potassium perchlorate was removed by filtration.

Separation and Identification of Species.—The chilled hydrolysis mixture was first passed through an anion-exchange column to remove any possible anionic cyanoaquochromium(III) complexes. No colored anionic complexes were detected on the resin, indicating their absence from the mixture. The various neutral and cationic complexes in the effluent from the anion-exchange column were loaded onto a cation-exchange column with resin-bed dimensions of about 1.5 × 20 cm. Both columns were jacketed and cooled below 1.0° by means of circulating ice water and both were shielded from the light wtih aluminum foil. As the cationic species were adsorbed onto the cation-exchange column, brightly colored bands were formed at the top of the column. A deep orange uncharged species was not adsorbed and moved through the column with the solution. The lowest adsorbed band at the top of the column was peach colored, above this was a small yellow one, next a pink-violet band, and then a purple band at the top. These bands could be separated and eluted individually from the column by gradually increasing the concentration of sodium perchlorate used as the eluting agent. The effluent from the cation column was collected in 25- or 50-ml fractions, the pH was measured, and the fractions were stored in the dark at 0° for spectral and chemical analysis. Each fraction collected was analyzed for chromium(III) ion concentration in order to obtain the elution curve for the separation shown in Figure 1. The separation and identification of the individual species are described below.

(1) **Tricyanotriaquochromium(III), $Cr(CN)_3(H_2O)_3$.**—This uncharged complex is not retained by either an anion or a cation-exchange resin and emerges from the cation-exchange column as a deep-orange solution, the last traces of which can be washed off the column with 0.05 *M* sodium perchlorate adjusted to pH 3. The composition of this species was confirmed by chromium and cyanide analyses (see below) which consistently gave chromium to cyanide ratios in the range 1:3.11 to 1:2.92. In the visible and ultraviolet regions the absorption spectrum of tricyanotriaquochromium(III) is independent of pH in the range 3.0–4.5 and has absorption maxima (in mμ) and corresponding molar absorbancy indices (in l. mol^{-1}) as follows: 687 (0.2), 620 (0.3), 467 (115), 360 (25.2), 236 (2.1×10^3); and 227 (2.1×10^3). The tricyano complex is extremely soluble in water but usually forms insoluble orange solids, thought to be polymers, when solutions are concentrated by evaporation, by freeze-drying techniques, or even by repeated freezing and thawing. The optimum pH range for storing the tricyano complex appears to be 3.5–4.5. The tricyano complex was found to constitute apout 38% of the hydrolysis mixture prepared as described above.

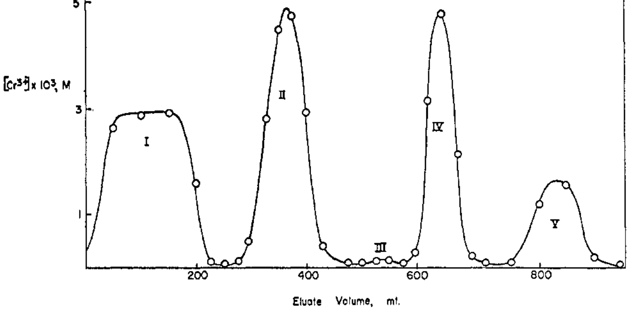

Figure 1.—Elution curve for the ion-exchange separation of neutral and cationic cyanoaquochromium(III) complexes: I, $Cr(CN)_3(H_2O)_3$; II, $Cr(CN)_2(H_2O)_4^+$; III, unidentified species; IV, $Cr(CN)(H_2O)_5^{2+}$; V, $Cr(H_2O)_6^{3+}$.

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(5) J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968).
(6) T. W. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964).
(7) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965).
(8) J. H. Espenson and D. E. Binau, *ibid.*, **5**, 1305 (1966).
(9) J. Finholt and S. N. Deming, *ibid.*, **6**, 1533 (1967).
(10) E. Deutsch and H. Taube, *ibid.*, **7**, 1532 (1968).
(11) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).
(12) F. H. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).
(13) J. H. Espenson, *ibid.*, **3**, 968 (1964).
(14) M. Ardon, *ibid.*, **4**, 372 (1965).
(15) K. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).
(16) T. W. Swaddle, *J. Am. Chem. Soc.*, **89**, 4338 (1967).
(17) J. H. Bigelow, *Inorg. Syn.*, **2**, 203 (1946).

(2) **Dicyanotetraaquochromium(III) ion, $Cr(CN)_2(H_2O)_4^+$.**—The peach-colored band containing this species was eluted from the cation-exchange column with 0.10 *M* sodium perchlorate solution at pH 2.5. Analysis of these solutions gave chromium to cyanide ratios of 1:1.99, 1:2.03, and 1:1.96 in three trials. The visible and ultraviolet absorption spectrum of the dicyano complex is independent of pH in the region from 2.0 to 4.0. The position of the maxima (in mμ) and corresponding molar absorbancy indices (in l. mol^{-1} cm^{-1}) in dilute sodium perchlorate are 535 (30.2) sh, 474 (45.3), 464 (45.5), and 378 (25.8), with strong absorption in the ultraviolet region. On freeze-drying a solution of the dicyano complex, a powder was obtained which was readily soluble in water, methanol, and ethanol. The optimum pH for storing this complex appears to be about 3. For the hydrolysis procedure described above, about 30% of the product was in the form of the dicyanotetraaquochromium(III) ion.

(3) **Unknown Species.**—When the eluent concentration was increased in successive steps from 0.1 to 0.4 *M* sodium perchlorate, a small concentration of an unknown species was eluted from the column which contained 0.6% of the total chromium present in the hydrolysis mixture. Separations carried out at various initial concentrations of potassium hexacyanochromate ranging from 10^{-3} to 10^{-1} *M* showed that the amount of this species formed depends greatly on the initial concentration of hexacyanochromate used, which may be taken as evidence of its polymeric nature. The species is not produced in detectable amounts if very dilute solutions and long reaction times are used. The ultraviolet and visible spectral characteristics of the species are intermediate between those of the dicyano and tricyano complexes, though the cyanide to chromium ratio appears to be 2.0:1. Because it is eluted just before the cyanopentaaquo complex, we believe that the species probably has an over-all charge of +2 and that it is most likely a dimer. Application of previously discussed spectral criteria for distinguishing between *cis* and *trans* isomers of chromium complexes[3] clearly indicates that this yellow species is not the *trans*-dicyanotetraaquochromium(III) ion.

(4) **Cyanopentaaquochromium(III) Ion, $Cr(CN)(H_2O)_5^{2+}$.**—This complex was found to constitute 20% of the hydrolysis mixture and could be eluted from the column with 0.6 *M* sodium perchlorate solution adjusted to pH 2.0. Chromium to cyanide ratios of 1:0.992, 1:1.103, and 1:1.009 were determined in separate experiments for this pink, permanganate-colored species. The visible and ultraviolet spectra of cyanopentaaquochromium(III) ion are independent of pH in the regions from 2 to 3.5. The positions of the maxima (in mμ) and corresponding molar absorbancy indices (in l. mol^{-1} cm^{-1}) in 0.6 *M* sodium perchlorate are: 800 (0.30), 525 (26.0), and 393 (20.5). The strong absorption band in the ultraviolet shows a point of inflection (a_m = 268 l. mol^{-1} cm^{-1}) at 235 mμ. The positons of the absorption maxima are identical with those reported by Espenson.[4] Dilute solutions (pH 2) of the monocyano complex can be stored at 0° for several weeks without serious decomposition.

(5) **Hexaaquochromium(III) Ion, $Cr(H_2O)_6^{3+}$.**—The hydrated chromium(III) cation was washed off the column with a solution containing 0.5 *M* perchloric acid and 2.5 *M* sodium perchlorate. It was identified by its typical three-band ultraviolet and visible absorption spectrum and comprised about 11% of the hydrolysis mixture.

Traces of hydrolytic polymers[18,19] were left on the column. The total amount of chromium(III) ion eluted from the cation column amounted to more than 98% of that originally loaded onto the column.

Kinetic Measurements.—The aquation of monocyanochromium(III) ion was followed spectophotometrically using a Cary Model 14 recording spectrophotometer for all measurements. Reactions were carried out directly in a 10-cm water-jacketed silica spectrophotometer cell. As a usual procedure an aliquot of the stock solution of the monocyanochromium(III) ion and a solution containing perchloric acid and enough sodium perchlorate to achieve the desired ionic strength were mixed in a darkened constant-temperature water bath and then transferred to the spectrophotometric cell with a fast draining pipet. In all experiments the hydrogen ion concentration was at least 50 times the concentration of the complex, which was kept low and in the range 5×10^{-4} to 3×10^{-3} *M*.

Reactions were followed at either 525 or 240 mμ. The molar absorbancy indices of monocyanochromium(III) ion and of hexaaquochromium(III) ion at 525 mμ are 25.9 and 7.34 l. mol^{-1} cm^{-1}, respectively. At 240 mμ the molar absorbancy index of the monocyanochromium(III) complex changes with acidity and ionic strength and is approximately 182 l. mol^{-1} cm^{-1}. The corresponding index for hexaaquochromium(III) ion is 5.1 l. mol^{-1} cm^{-1}. The rate of aquation was found to be independent of the length of time the aquation solutions were exposed to monochromatic light at 525 mμ. When reactions were followed at 240 mμ the wavelength and slit settings were not changed during the experiment because in this region of the spectrum the absorbance changes sharply with wavelength. Reaction rates determined at these two wavelengths were in good agreement.

In all experiments the reactions went to completion and gave, after 8 or more half-lives, a final spectrum identical with that of the hexaaquochromium(III) ion. All reactions were followed for 3 or 4 half-lives and gave good pseudo-first-order rate plots of log ($A_t - A_\infty$) *vs.* time, where A_t is the absorbance at time *t* and A_∞ is the absorbance after more than 8 half-lives. A computer program[20] which was adapted to the available CDC 3600 computer was used to calculate the least-squares best slopes for the straight-line plots of ln ($A_t - A_\infty$) *vs.* time and was used to obtain the pseudo-first-order rate constants. The rate constants were calculated for the first, for the first and second, and for the first, second, and third half-lives. All three calculations were in good agreement and the rate constant reported for each experiment is the average of the three values obtained.

Chemical Analysis.—The aquated solutions were analyzed for the hydrogen ion concentration, for the total ionic strength, and periodically for the chromium(III) ion concentration. The concentrations of the chromium complexes in solution were determined by analyzing the solutions for chromium spectrophotometrically following oxidation of the chromium(III) to chromate ion with hot alkaline hydrogen peroxide ($a_m = 4.83 \times 10^3$ l. mol^{-1} cm^{-1} for CrO_4^{2-} at 372 mμ).[21]

The amount of bound cyanide in the cyanoaquochromium(III) complexes was determined by the modified Liebig titration method. In order to do this, the compounds were first decomposed in 0.8 *M* sodium hydroxide and boiled to precipitate chromic hydroxide, which was subsequently removed by filtration prior to the titration of the filtrate for cyanide ion.

The ionic strength was determined from the total electrolyte concentration using standard ion-exchange techniques involving a cation-exchange resin in the hydrogen form. Concentration values are given at room temperature in all cases.

Results

Separation.—Under the hydrolysis conditions described in the previous section, at least five different chromium(III)-containing species exist in the final solution. These species can be cleanly separated by means of a cation-exchange resin, as shown by the elution curve given in Figure 1. Successive fractions of each peak of the elution curve, including leading and trailing fractions, exhibited visible and ultraviolet absorption spectra with identical molar absorbancy indices

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[18] M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

[19] J. S. Laswick and R. A. Plane, *ibid.*, **81**, 3564 (1959).

[20] K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 554.

[21] G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

over the wavelength scanned. For example, successive fractions of the first peak, corresponding to the tricyanochromium(III) complex, gave molar indices of 115.6, 115.6, 114.8, and 114.9 at a wavelength of 467 mμ. Successive fractions of the second peak, corresponding to removal of the dicyanochromium(III) complex, gave indices of 45.6, 45.6, 45.8, and 45.3 at 464 mμ. This reproducibility indicates that only one species is included in each peak of the elution curve and, more specifically, that only one of the two possible geometric isomers of $Cr(CN)_3(H_2O)_3$ and of $Cr(CN)_2(H_2O)_4{}^+$ are formed. On the basis of their spectra and the reaction rate data obtained for each step in the acid-catalyzed aquation of hexacyanochromate(III) ion, these complexes have been assigned a *cis* configuration. The arguments for these assignments are presented in detail elsewhere.[3]

Spectra.—The visible and ultraviolet absorption spectra for 1,2,3-$Cr(CN)_3(H_2O)_3$ or *cis*-$Cr(CN)_3(H_2O)_3$, *cis*-$Cr(CN)_2(H_2O)_4{}^+$, and $Cr(CN)(H_2O)_5{}^{2+}$ are shown in Figure 2. The spectrum of $Cr(H_2O)_6{}^{3+}$ is also included for the sake of comparison. As cyanide ligands are successively replaced by water molecules, the frequencies of both absorption bands attributed to d–d transitions shift markedly toward lower energies. The observable absorption spectrum of 1,2,3-$Cr(CN)_3(H_2O)_3$ consists of two relatively narrow ligand field bands which are symmetrical without apparent broadening or splitting, in agreement with the ligand field predictions for a pseudo-cubic, trigonal (C_{3v}) field.[3] The sums of the dipole moments of the ligands are identical along each of the cartesian axes in a 1,2,3-trisubstituted complex and the five d orbitals maintain the same relative energies that they possess in fields of cubic (O_h) symmetry.

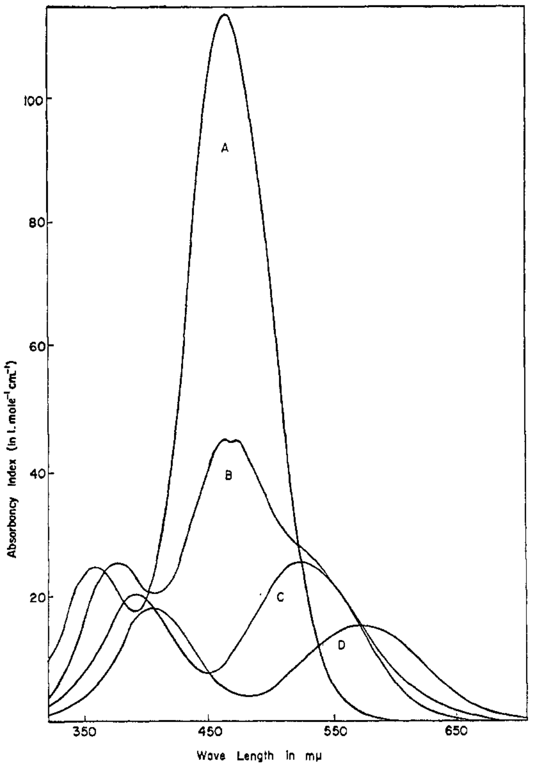

Figure 2.—Visible and near-ultraviolet spectra of chromium(III) complexes at 25°: A, 1,2,3-$Cr(CN)_3(H_2O)_3$; B, *cis*-$Cr(CN)_2(H_2O)_4{}^+$; C, $Cr(CN)(H_2O)_5{}^{2+}$; D, $Cr(H_2O)_6{}^{3+}$.

Because the ligand field strengths of cyanide and water differ greatly, the other mixed cyanoaquochromium(III) complexes exhibit noticeable splitting or broadening of the first (lowest energy) spin-allowed d–d band.[3,22] In the case of *cis*-$Cr(CN)_2(H_2O)_4{}^+$, the first band shows a well-resolved shoulder, and it is the only *cis*-chromium(III) complex known which exhibits such splitting. In the case of $Cr(CN)(H_2O)_5{}^{2+}$, on the other hand, the first band shows no splitting but is instead broadened and unsymmetrical. The explanations and implications of these observations are presented elsewhere,[3] together with a discussion of criteria for predicting the spectra of isomers of various chromium(III) complexes.

Aquation of Cyanopentaaquochromium(III) Ion.—The aquation of monocyanochromium(III) ion was studied over a range of acidities from 0.05 to 1.6 *M* perchloric acid at an ionic strength of 2.0 adjusted with sodium perchlorate. Repetitive scans of the absorption spectrum of the aquating solution showed the presence of three isosbestic points in the visible region of the spectrum which remain throughout the reaction. In a solution containing 1.0 *M* perchloric acid and 1.0 *M* sodium perchlorate, the isosbestic points are located at 577, 447, and 417 mμ. The positions of the points near 577 and 417 mμ, however, vary slightly with acidity, indicating a slight acid dependence of the absorption spectrum of the monocyanochromium(III) ion.

The pseudo-first-order rate constants for the aquation reaction at 15, 25, 35, and 40° were determined as described in the Experimental Section and are presented in Table I. Although the aquation is acid catalyzed, the rate of the reaction exhibits less than a simple first-order dependence upon the hydrogen ion concentration, as shown in Figure 3. In the concentration range studied, the hydrogen ion dependence of the pseudo-first-order constants, k_{obsd}, indicates the presence of two reaction pathways for the aquation. The positive extrapolated value of k_{obsd} at zero hydrogen ion concentration (Figure 3) indicates the presence of a reaction pathway whose rate law does not involve hydrogen ion from the solution and whose stoichiometry can be represented by

$$Cr(H_2O)_5CN^{2+} + 2H_2O \xrightarrow{k_0} Cr(H_2O)_6{}^{3+} + HCN + OH^- \quad (2)$$

The rate of the other pathway depends on the hydrogen concentration in a limiting way which is consistent with a two-step mechanism involving a rapid and reversible equilibrium protonation followed by a rate-limiting aquation of the protonated species

$$Cr(H_2O)_5CN^{2+} + H^+ \underset{\text{fast}}{\overset{K_{eq}}{\rightleftarrows}} Cr(H_2O)_5CNH^{3+} \quad (3)$$

$$Cr(H_2O)_5CNH^{3+} + H_2O \xrightarrow{k_H} Cr(H_2O)_6{}^{3+} + HCN \quad (4)$$

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[22] (a) J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967); (b) J. R. Perumareddi, *ibid.*, **71**, 3155 (1967).

TABLE I

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANT MEASURED AT AN IONIC STRENGTH OF 2.0

15.0°, $I = 2.0\ M^a$		25.0°, $I = 2.06\ M^a$		35.0°, $I = 2.01\ M^a$		40.0°, $I = 2.02\ M^a$	
$[H^+]$, M	$10^4 k_{obsd}$, sec^{-1}	$[H^+]$, M	$10^4 k_{obsd}$, sec^{-1}	$[H^+]$, M	$10^4 k_{obsd}$, sec^{-1}	$[H^+]$, M	$10^4 k_{obsd}$ sec^{-1}
0.990	1.58	0.106	0.717	0.109	2.41	0.0521^b	2.65
1.18	1.74	0.208	1.30	0.210	4.10	0.108	4.40
1.40	2.00	0.413	2.34	0.407	7.39	0.112^b	4.64
1.56	2.26	0.591	3.26	0.596	10.2	0.209	7.29
1.83	2.44	0.609	3.39	0.811	13.2	0.316	10.2
		0.813	4.24	1.00	15.4	0.410	13.3
		0.994	4.97	1.01	15.6	0.523^b	15.0
		1.21	5.89	1.21^b	18.5	0.607	17.8
		1.22	6.07	1.21	17.6	0.805	22.0
		1.41	6.73			0.993	26.4
		1.44	6.86			1.200^b	30.9
		1.61	7.40				
		1.61	7.28				
		1.70	7.79				

Summary[c]

Constants	25.0°	35.0°	40.0°
$10^5 k_0$, sec^{-1}	1.1 ± 0.1	4.0 ± 0.4	10.8 ± 0.8
$10^3 k_H$, sec^{-1}	3.2 ± 0.1	7.5 ± 0.5	13 ± 2.0
K_{eq}, l. mol^{-1}	0.185 ± 0.006	0.25 ± 0.02	0.25 ± 0.05
$10^4 k_H K_{eq}$, sec^{-1} l. mol^{-1}	5.90 ± 0.05	18.9 ± 0.03	31.7 ± 0.8

[a] The ionic strength was maintained at 2.0 with sodium perchlorate. [b] $[Cr(H_2O)_5CN^{2+}]_0 = 6 \times 10^{-4}\ M$. In all other experiments, the initial concentration was $2.6 \times 10^{-3}\ M$. [c] The confidence interval is determined from the appropriate variance calculation for the slope and intercept of the reciprocal plot at 1.0 unit of standard deviation.

Under pseudo-first-order conditions of constant hydrogen ion concentration, combination of eq 2–4 leads to the rate law

$$\frac{-C_t}{dt} = \frac{k_0 + k_H K_{eq}[H^+]}{1 + K_{eq}[H^+]} C_t = k_{obsd} C_t \qquad (5)$$

where C_t represents the total concentration of the monocyanochromium(III) complex in both the protonated and nonprotonated forms, k_0 and k_H are the first-order rate constants for reactions 2 and 4, respectively, and K_{eq} is the equilibrium constant for the protonation reaction (eq 3).

Equation 5 can be rearranged to give

$$\frac{1}{k_{obsd} - k_0} = \frac{1}{k_H - k_0} + \frac{1}{(k_H - k_0)K_{eq}} \frac{1}{[H^+]} \qquad (6)$$

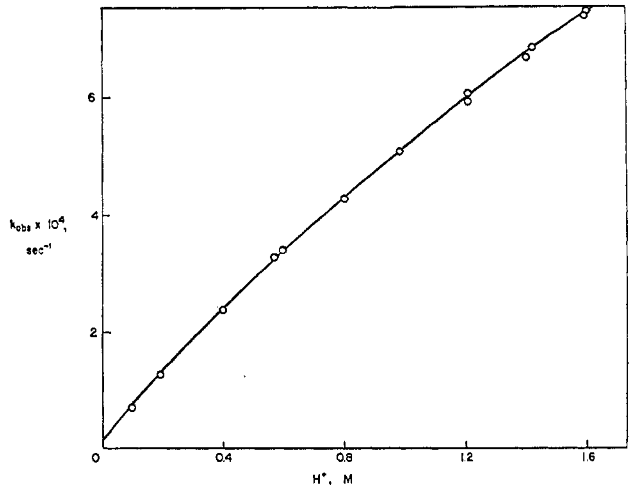

Figure 3.—Dependence on hydrogen ion concentration of the pseudo-first-order rate constant for the aquation of $Cr(H_2O)_5CN^{2+}$ at 25.0° and an ionic strength of 2.06 M.

A plot of $1/(k_{obsd} - k_0)$ *vs.* $1/[H^+]$, which should be linear, can be used to evaluate the individual rate parameters, k_0, k_H, and K_{eq}. If k_0 is known, K_{eq} can be evaluated from the ratio of the intercept to the slope of the plot, and k_H can be calculated from the intercept. An iterative calculation method was used to obtain the rate parameters.

A computer program was developed which calculates the least-squares best line for a plot of $1/(k_{obsd} - k_0)$ *vs.* $1/[H^+]$ and also varies k_0 to find the straight line which has the minimum standard deviation. Trial values of k_0 were obtained from plots of k_{obsd} *vs.* $[H^+]$ (Figure 3). The relative per cent errors in the pseudo-first-order rate constants were judged to be constant and the data points were weighted according to the squares of the corresponding hydrogen ion concentrations. Plots of $1/(k_{obsd} - k_0)$ *vs.* $1/[H^+]$ using the best value of k_0 obtained from the iterative calculations were excellent straight lines. The values of k_0, k_H, K_{eq}, and $k_H K_{eq}$ calculated for the aquation of monocyanochromium(III) ion at 25, 35, and 40° using all data points at each temperature are summarized in Table I.

The activation parameters corresponding to the individual rate coefficients k_0 and k_H and to the product of $k_H K_{eq}$ were determined using the Eyring transition-state equation ($\kappa = 1$). The pseudo-first-order rate constants calculated from the activation parameters agree well with the experimental values, the average deviation being only 1.3%.

Effect of Ionic Strength on the Aquation Rate.—The rate of aquation of monocyanochromium(III) ion at a given hydrogen ion concentration was found to increase significantly with increasing ionic strength. The pseudo-first-order rate constant for the aquation reaction was measured at various concentrations of hydrogen ion at

25° and at an ionic strength of 1.5. The data are presented in Table II. Although the actual ionic strengths of the aquating solutions (determined by analysis) deviated slightly from 1.50, the pseudo-first-order rate constants (k_{obsd}) were corrected to an ionic strength of 1.50 by linear interpolation between the experimental values of k_{obsd} and the corresponding values of k_{obsd} calculated from the rate parameters determined at an ionic strength of 2.06 (Table I). The rate parameters k_0, k_{H}, and K_{eq} calculated for the aquation reaction at 25° were 9.2×10^{-6} sec^{-1}, 3.2×10^{-3} sec^{-1}, and 0.14 l. mol^{-1}, respectively, at $I = 1.50$, and were 1.1×10^{-5} sec^{-1}, 3.2×10^{-3} sec^{-1}, and 0.185 l. mol^{-1}, respectively, at $I = 2.06$. Whereas the first-order rate constants k_0 and k_{H} appear to be constant within experimental error in this range of ionic strength, the concentration equilibrium constant for the protonation reaction appears to vary, presumably owing to changes in the activity coefficient quotient with changes in ionic strength in the expression $K_c = K_a(\gamma_{\mathrm{CrCN}^{2+}})(\gamma_{\mathrm{H}^+})/(\gamma_{\mathrm{CrCNH}^{3+}})$.

TABLE II

VALUES OF THE PSEUDO-FIRST-ORDER RATE CONSTANT MEASURED AT A VARIETY OF IONIC STRENGTHS[a] FOR $[\mathrm{Cr(H_2O)_5CN^{2+}}]_0 = 2.6 \times 10^{-3}\ M$

I^c	$[\mathrm{H}^+]$, M	10^4k_{obsd}, sec^{-1}	I^c	$[\mathrm{H}^+]$, M	10^4k_{obsd}, sec^{-1}
1.55	0.412	1.95	2.67	0.212	1.74
(1.50)		(1.90)[b]	2.60	0.112	0.919
1.55	0.611	2.73	2.60	0.411	2.87
(1.50)		(2.68)[b]	2.51	0.614	3.94
1.52	0.010	4.17	2.44	0.818	4.95
(1.50)		(4.17)[b]	2.37	1.03	5.72
1.50	1.00	4.20	2.32	1.02	5.56
1.48	0.106	0.562	2.21	1.42	6.83
(1.50)		(0.568)[b]	0.961	0.381	1.22
1.46	0.973	3.88			
(1.50)		(3.93)[b]			

[a] All measurements made at 25°. [b] Value interpolated to an ionic strength of 1.50. [c] Ionic strength maintained with sodium perchlorate.

The aquation reaction was also studied at 25° at a variety of other ionic strengths ranging from 0.9 to 2.7. The pseudo-first-order rate constants obtained are included in Table II. If the rate coefficients k_0 and k_{H} are assumed to be constant over this range of ionic strengths, as the data indicate, the equilibrium constant can be calculated by solving eq 5 for K_{eq}. The values of K_{eq} obtained in this manner describe a fairly smooth curve when plotted *vs.* ionic strength (Figure 4). (A similar increase in the value of K_{eq} for the protonation of the acetatopentaaquochromium(III) ion with increased ionic strength was observed by Deutsch and Taube[10] in lithium perchlorate solutions.)

Discussion

In the acidity range studied, the aquation of monocyanochromium(III) ion proceeds *via* two pathways,[23] an acid-catalyzed and an acid-independent pathway. The hydrogen ion dependence of the acid-catalyzed pathway is less than first order, as seen in Figure 3. This lack of linearity is interpreted in terms of an equilibrium protonation of the complex followed by the aquation of the protonated complex, reactions 3 and 4. It has also been suggested[5] that such a lack of first-order dependence might be due to medium effects arising from variations in activity coefficients as sodium perchlorate is replaced by perchloric acid in solutions of constant ionic strength. This possibility is discussed more fully below.

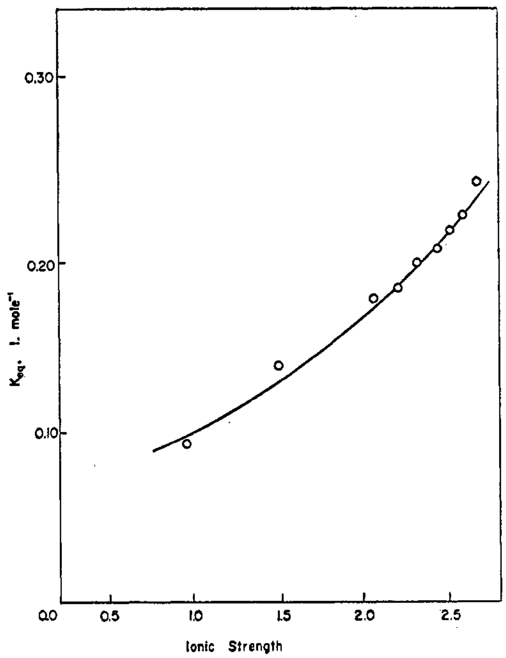

Figure 4.—The equilibrium constant for the protonation reaction $\mathrm{Cr(H_2O)_5CN^{2+} + H^+ \rightleftarrows Cr(H_2O)_5CNH^{3+}}$ as a function of ionic strength at 25.0°.

In a preequilibrium protonation mechanism, a significant portion of the monocyanochromium(III) complex might be present in the protonated form at higher acid concentrations. Since the spectrum of the protonated complex should differ from that of the unprotonated complex, spectral changes should occur as the hydrogen ion concentration is increased and were in fact observed. Variations in activity coefficients alone should not cause such spectral changes in the absence of protonation. In the case of the monocyano complex, unfortunately, the spectral changes upon addition of acid, though definite, were too small to allow a precise value to be measured for the protonation equilibrium constant. In other experiments, changes in spectra with variations in acidity were found to be more pronounced for the dicyanotetraaquochromium(III) and the tricyanotriaquochromium(III) complexes, where proton association is expected to be greater because of the decreased positive charge. For these latter two complexes, the protonation equilibrium constants were determined from the changes in their spectra with hydrogen ion concentration[2] and were found to be 0.55 ± 0.22 l. mol^{-1} for the dicyanochromium(III)

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[23] A third pathway with inverse hydrogen ion dependence has been detected by Espenson,[5] who carried out studies at lower hydrogen ion concentrations. This pathway is negligible in the acidity range covered in this study.

TABLE III

RATE AND ACTIVATION PARAMETERS FOR THE AQUATION OF $Cr(H_2O)_5CN^{2+}$

Ionic strength, medium	Rate parameters at 25°	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	Ref
1.0 *M*, $LiClO_4$^{a}	$k_0 = 1.3 \times 10^{-5}$ sec^{-1}	27.9 ± 1.4	$+12.7 \pm 4.2$	5
	$k_1 = 5.2 \times 10^{-4}$ l. mol^{-1} sec^{-1}	17.05 ± 0.73	-16.4 ± 2.2	5
1.0 *M*, $NaClO_4$^{a}	$k_0 = 1.6 \times 10^{-5}$ sec^{-1}	25.6 ± 1.0	$+5.4 \pm 3.1$	5
	$k_1 = 3.1 \times 10^{-4}$ l. mol^{-1} sec^{-1}	19.76 ± 0.48	-8.3 ± 1.5	5
2.0 *M*, $NaClO_4$	$k_0 = 1.1 \times 10^{-5}$ sec^{-1}	26.9 ± 0.3	$+8.9 \pm 1.1$	This study
	$k_HK_{eq} = k_1 = 5.9 \times 10^{-4}$ l. mol^{-1} sec^{-1}	20.2 ± 0.1	-5.5 ± 0.3	
	$k_H = 3.2 \times 10^{-3}$ sec^{-1}	16.2 ± 2.0	-16.0 ± 4.0	

[a] The rate parameters are extrapolated to 25° from higher temperatures.

ion and 1.1 ± 0.4 l. mol^{-1} for the tricyano complex at 25° and an ionic strength of 2.0 (sodium perchlorate). The corresponding value of 0.19 l. mol^{-1} for the monocyanochromium(III) ion, determined from the kinetic data, is reasonable in comparison with the values for the higher cyanide complexes.

The aquation of monocyanochromium(III) ion has also been studied by Birk and Espenson[5] at an ionic strength of 1.0 maintained with both $LiClO_4$ and $NaClO_4$. A summary of their rate and activation parameters is included in Table III, together with those from this study. Using our data (Figure 4), the value of K_{eq} for the monocyanochromium(III) ion is estimated to be 0.1 l. mol^{-1} at an ionic strength of 1.0 maintained with sodium perchlorate. The corresponding product k_HK_{eq} (*i.e.*, k_1) was calculated from our data to be 3.2×10^{-4} l. mol^{-1} sec^{-1}, which is in good agreement with Birk and Espenson's value of k_1 of 3.1×10^{-4} l. mol^{-1} sec^{-1} (Table III).

Birk and Espenson treated the acid-catalyzed pathway in terms of a linear first-order dependence on hydrogen ion concentration. Assuming that K_{eq} is 0.1 l. mol^{-1} at an ionic strength of 1.0, a maximum deviation from linearity of only 10% would be predicted at the highest hydrogen ion concentration used in their studies. It is not surprising, therefore, that such a small deviation from linearity was not observed or considered significant.[24] Furthermore, Deutsch and Taube[10] showed that a plot of k_{obsd} *vs.* $[H^+]$ does not vary significantly from linearity in the acid-assisted aquation of the acetatopentaaquochromium(III) ion at an ionic strength of 1.0 (lithium perchlorate), whereas a very significant deviation is observed at an ionic strength of 4.0. At this ionic strength, they were able to calculate concordant values of the protonation equilibrium constant from both kinetic and spectral data.

For the acid-catalyzed pathway, significant differences exist between the rate and activation parameters determined in the $NaClO_4$–$HClO_4$ medium and those in $LiClO_4$–$HClO_4$ solution (Table III). In both studies, the assumption that the activity coefficients of the reacting species remain constant as perchloric acid replaces the perchlorate salt is not rigorously correct and would be expected to hold true only when the proportion of the salt replaced by the acid is small. Biedermann and Sillén[25] have shown that the activity coefficients of a number of cations do remain constant in a medium of ionic strength 3.0 as sodium perchlorate is replaced by perchloric acid up to an acid concentration of 0.6 *M*.

To test our data for possible medium effects as the salt is replaced by acid, the rate parameters were calculated using the data from only the five lowest acidity points, then from the six lowest, and so on, until all of the acidity points were included. (For the data at 40°, this would mean that only those points below 0.4 *M* H^+ would be included in the first calculation.) At a given temperature the values of k_0, k_H, and K_{eq} were found to vary randomly as more points at higher acidities were included in the calculations and the values of the product k_HK_{eq} remained essentially constant throughout the range of acidities, varying less than 2%. We conclude, therefore, that there is no serious lack of constancy in the activity coefficients under the experimental conditions used ($I = 2.0$) and that the curvature in the plot of k_{obsd} *vs.* $[H^+]$ is actually the result of a protonation of the complex which increases with increasing ionic strength.

On the basis of kinetic studies, monosubstituted chromium(III) complexes, $Cr(H_2O)_5X^{2+}$, can be divided into two groups, one of which includes complexes with a basic ligand such as cyanide, fluoride,[7] azide,[6] hypophosphite,[8] sulfate,[9] and acetate,[10] while the other includes complexes with a nonbasic ligand such as chloride,[7] iodide,[7,13,14] isothiocyanate,[11] nitrate,[16] and perchlorate.[15] The complexes in the former group exhibit an acid-catalyzed aquation pathway, whereas those in the latter group are not acid catalyzed. Except for the cyanide complex, the complexes with a basic ligand exhibit an acid-catalyzed pathway with a linear first-order dependence on $[H^+]$. For the cyanide complex the rate for this pathway is equal to $\{k_HK_{eq} \cdot [H^+]/(1 + K_{eq}[H^+])\}C_t$ which reduces to $k_HK_{eq}[H^+] \cdot C_t$ when $K_{eq}[H^+] \ll 1$. The latter expression probably applies in the cases of the fluoro-, azido-, sulfato-, and hypophosphitopentaaquochromium(III) complexes. Only for the cyano complex and for the acetato complex at higher ionic strengths is the equilibrium constant for protonation sufficiently large so that a

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(24) Separate experiments presently in progress in this laboratory by C. DeVine indicate that a significant deviation from linearity is also observed in a plot of k_{obsd} *vs.* $[H^+]$ for the monocyano complex at $I = 2.0$ maintained with lithium perchlorate. The value of K_{eq} appears to be about the same as that in sodium perchlorate at the same ionic strength.

(25) G. Biedermann and L. G. Sillén, *Arkiv Kemi*, **4**, 425 (1953).

detectable amount of the protonated species is present under the experimental conditions studied and a deviation from a simple, first-order dependence on $[H^+]$ is observed.

An acid-independent pathway, k_0, has been observed for all complexes in both groups, with the exception of the hypophosphite complex. For the monosubstituted chromium(III) complexes containing nonbasic or weakly basic ligands, there is a good linear correlation between $\Delta S_0^{\ddagger}$ and the molar entropy of the free ligand.[7] The $\Delta S_0^{\ddagger}$ values for the fluoro, azido, and cyano complexes all show a positive deviation from this linear relationship, and for this reason it has been suggested[5-7] that the transition state for the acid-independent pathway for these complexes involves the transfer of a proton from a coordinated water molecule to the strongly basic ligand, forming a hydroxochromium(III) ion and a neutral acid molecule rather than an aquochromium(III) ion and an anionic leaving group. In addition, the value of k_0 for an internal proton-transfer mechanism should not depend greatly on the ionic strength of the medium because the leaving group would be a neutral molecule and there would be no change of charge in the transition state. In agreement with this expectation, the k_0 values shown in Table III for the monocyano complex in the three different media are all in good agreement.

For monosubstituted pentaaquochromium(III) complexes containing the less basic halogen or halogenoid ligands, *i.e.*, iodide, bromide, chloride, azide, or thiocyanate, the rate parameter k_0 for the acid-independent pathway decreases with increasing ligand field strength and a fairly good correlation exists between the $\Delta G_0^{\ddagger}$ and $\Delta H_0^{\ddagger}$ values for the aquation reactions and the frequency of the lowest energy d–d absorption band. (A similar correlation exists over a wide range of ligand field strengths for the monosubstituted pentaaminecobalt(III) complexes.[26]) In contrast with the trends observed with the other monosubstituted chromium(III) complexes, the free energy of activation for the acid-independent aquation of the monocyano complex is surprisingly low, being slightly less than that of the monobromo complex.[12] We believe that the intramolecular transfer of a proton to the ligand, which becomes more probable with the increasing basicity of the ligand, can account for this relatively low activation energy and that this provides additional support for the proposal that the acid-independent pathway involves an intramolecular proton transfer.

Acknowledgment.—We are indebted to Dr. R. Krishnamurthy, whose research opened up this area of study, for many helpful discussions and suggestions, and to Mr. Donn Darsow, who prepared the potassium hexacyanochromate(III) used in this work.

[26] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, p 65.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ, PISA, ITALY,
AND FROM THE ISTITUTO DI CHIMICA GENERALE DELL'UNIVERSITÀ, PADUA, ITALY

Salt Effects on Substitution Reactions of Platinum(II) Complexes

BY A. GIACOMELLI, A. INDELLI, AND U. BELLUCO

Received July 8, 1968

Rate data for the reaction of $Pt(NO_2)_4^{2-}$ with SCN^- in the presence of various cations and at different ionic strength values (ranging from 0.1 to 0.01 *M*) are reported. Reaction occurs in at least three steps, the first one being the substitution of two NO_2^- groups by two thiocyanate ions. The results are discussed in terms of the specific salt effect. The nucleophilic attack is accelerated specifically by the various cations.

Introduction

It has long been recognized that rate constants for nucleophilic substitutions of four-coordinated planar platinum(II) complexes follow the two-term rate law: rate = k_1[complex] + k_2[complex][L] (L = entering group). Accordingly, the processes represented by the two terms are thought of as bimolecular attacks on the substrate by either the solvent (k_1 path) or the entering group (k_2 path). In either case, formation of a labile five-coordination intermediate (which may just as well be an activated complex) is postulated.[1,2]

This work is concerned with the reaction between $Pt(NO_2)_4^{2-}$ and SCN^- in the presence of Li^+, K^+, $N(C_2H_5)_4^+$, and Ba^{2+}. These cations were present as thiocyanate, tetranitroplatinate(II), and perchlorate salts, added in order to keep the ionic strength constant at the desired value. We limited ourselves to the study of the first stage of the reaction involving substitution of two NO_2^- groups.

Experimental Section

Materials.—The complex $K_2[Pt(NO_2)_4]$ was prepared following the methods of the literature.[3] The corresponding salts of Li^+, Ba^{2+}, and $N(C_2H_5)_4^+$ were obtained by ion exchange from $K_2[Pt(NO_2)_4]$ on a Dowex 50-X8 resin. The solution of H_2-

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[1] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 2.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, Chapter 4; see also U. Belluco, R. Ettorre, F. Basolo, R. G. Pearson, and A. Turco, *Inorg. Chem.*, **5**, 591 (1966).

[3] "Gmelins Handbuch der Anorganischen Chemie," Vol. 68, Verlag Chemie, G.m.b.H., Berlin, 1942, part C, p 166.