Co–N bonds, that steric change is associated with a higher (and positive) $\Delta S°^*$ than is retention of configuration; this pattern seems to apply also to the few related bis(ethylenediamine)chromium(III) complexes so studied.[15] Thus it is probable that aquation of the aquo–tetren complexes proceeds *via* a dissociative mechanism, possibly through a trigonal-bipyramidal intermediate (which predicts steric change) for Cr-tetrenH)$(OH_2)_2^{4+}$ and through tetragonal-pyramidal intermediates (which predict retention) for all the other aquo–tetren complexes. Alternatively, there may be an isomerization intervening in the series at the diaquo step or simply an isomerically abnormal form of the diaquo substrate. An X-ray crystallographic study of all the "partially unwrapped" complexes would be most interesting if crystalline solids could be isolated.

(15) See ref 9, p 206.

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# The Preparation and Kinetics of the Aquation of Pentaaquopyridinechromium(III) Ion

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The pentaaquopyridinechromium(III) ion was prepared by the aquation of a tetraaquobispyridinechromium(III) ion followed by the separation on an ion-exchange column. The rate of aquation of the former complex was studied as a function of acidity and temperature. The rate law is of the form $-\mathrm{d}\ln(\mathrm{Cr(py)}^{3+})/\mathrm{d}t = k_0 + k_{-1}/(\mathrm{H}^+)$. In 1.0 *M* ionic strength ($HClO_4$ + $NaClO_4$) the specific rates extrapolated to 25° and the corresponding activation parameters have the values $k_0 = 1.2 \times 10^{-8}$ sec$^{-1}$, $\Delta H_0^{\ddagger} = 27.2 \pm 0.7$ kcal mol$^{-1}$, $\Delta S_0^{\ddagger} = -3.5 \pm 2.0$ cal mol$^{-1}$ deg$^{-1}$, and $k_{-1} = 9.9 \times 10^{-11}$ sec$^{-1}$ *M*, $\Delta H_{-1}^{\ddagger} = 35.6 \pm 0.3$ kcal mol$^{-1}$, $\Delta S_{-1}^{\ddagger} = 15.2 \pm 0.8$ cal mol$^{-1}$ deg$^{-1}$.

## Introduction

In recent years the aquation of a number of monosubstituted complexes of chromium(III), $CrX^{n+}$, has been studied. Particularly useful information about the reaction mechanism has been gained from correlations of the activation parameters for the series of complexes with $n = 2$.[1,2] The aquation of some complexes with X being a unidentate amine-type ligand was also investigated.[3–6]

In an attempt to prepare a series of monosubstituted complex ions of 3+ charge and to investigate their aquation kinetics, we report in this paper studies on the pentaaquopyridine complex ion. In the acidic media the net equation for the aquation reactions is[7]

$$\mathrm{Cr(H_2O)_5py^{3+} + H^+ + H_2O \longrightarrow Cr(H_2O)_6^{3+} + Hpy^+} \quad (1)$$

## Experimental Section

**Preparation of Pentaaquopyridinechromium(III).**—This complex was prepared in solution by the stepwise aquation of a tetraaquobis(pyridine)chromium(III) cation and by the subsequent separation on an ion-exchange column. Crude $[\mathrm{Cr(py)_2(H_2O)_2(OH)_2}]\mathrm{Cl}$, prepared according to Pfeiffer,[8] was dissolved in aqueous perchloric acid and freed of chloride anion and some other complex species on a Dowex 50W-X8 ion-exchange column with 1 *M* perchloric acid, and a tetraaquobis(pyridine)chromium(III) species was then eluted with 3 *M* perchloric acid. Preliminary experiments showed that this species aquates by a stepwise pathway in acidic media, accumulating the pentaaquopyridine intermediate.[9] At 75° in 1 *M* $HClO_4$ the first-order rate constant for the dissociation of the first pyridine amounts to $1.12 \times 10^{-4}$ sec$^{-1}$ and for the second pyridine $1.06 \times 10^{-5}$ sec$^{-1}$. The aging of the bis-pyridine complex at these conditions for about 700 min leads to about 70% of the chromium(III) in the form of the pentaaquopyridine, 29% in the form of the hexaaquo-, and 1% in the form of the tetraaquobis(pyridine) complex cation. $HClO_4$ (1 *M*) elutes the hexaaquopyridine easier than the pentaaquopyridine, and the latter easier than the tetraaquobis(pyridine)chromium(III) cation on a Dowex 50W-X8 ion-exchange column. After pyridinium and blue-gray hexaaquochromium(III) ions had been washed off the column with 1 *M* $HClO_4$, the middle portion of the bluish red pentaaquopyridine complex was eluted with 3 *M* $HClO_4$. Solutions of the complex, usually obtained in concentrations of (2–6) $\times 10^{-2}$ *M* and stored at −5°, did not change for an extended period of time.

Acidic stock solutions of pentaaquopyridinechromium(III) ion (hereafter pyridinechromium(III)) with a more favorable complex to perchloric acid ratio (low acidity), used for kinetic runs at low acidities, were obtained by extracting the pure complex from a cation-exchange resin with a solution containing 1 *M* sodium perchlorate and $5 \times 10^{-3}$ *M* perchloric acid. Solutions of the complex (2–5) $\times 10^{-3}$ *M* were obtained in this way. Attempts were made to reduce acid concentration in more concentrated stock solutions of the complex containing 3 or 6 *M* perchloric acid by titration with KOH at 0°. However, aquation of the complex to a significant degree was observed.

**Other Materials.**—All solutions were prepared with double distilled water. All chemicals used were analytical grade. Perchloric acid, pyridine, and chromium(III) chloride (all Merck) were used without further purification. Sodium perchlorate was prepared by neutralizing sodium carbonate with perchloric acid. Sodium carbonate (Merck) was recrystallized three times from water.

**Analytical Methods.**—Chromium(III) was determined spectrophotometrically as chromate ion ($\epsilon$ $4.83 \times 10^3$ at 372 nm) after decomposition of the complex and oxidation with alkaline peroxide.[10] Pyridine was determined spectrophotometrically ($\epsilon$ $5.29 \times 10^3$ at 255.7 mm)[11] in 0.1 *M* hydrochloric or perchloric acid after aquation of the complex for 10 or more half-lives. The concentration of free perchloric acid in pyridinechromium-

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(1) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).

(2) T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 4338 (1967).

(3) E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

(4) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

(5) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *ibid.*, **7**, 749 (1968).

(6) D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.*, **91**, 6637 (1969).

(7) Abbreviation: py = pyridine.

(8) P. Pfeiffer, *Z. Anorg. Allg. Chem.*, **31**, 401 (1902).

(9) Detailed kinetic studies of this reaction and attempts for stereochemical characterization of the bis-pyridine species are in progress.

(10) G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 2331 (1952).

(11) H. C. Brown and X. B. Mihm, *J. Amer. Chem. Soc.*, **77**, 1723 (1955).

(III) perchlorate solutions was determined by the method of King and Neptune.[12] All absorbance measurements were performed on Beckman DU-2 and Hilger H 700 spectrophotometers.

**Kinetic Measurements.**—The aquation of $Cr(py)^{3+}$ was followed spectrophotometrically at 250 and 213 nm ($\epsilon$ values of the complex ion at these wavelengths are about $2.1 \times 10^3$ and $3.5 \times 10^3$, of pyridinium ion about $4.7 \times 10^3$ and $7.2 \times 10^2$, and of hexaaquochromium(III) ion 3.3 and 16.5). Some runs at high acidity were followed also at 400 and 550 nm. The reaction solutions were sealed in glass ampoules, heated shortly in a bath of a higher temperature to bring them close to the temperature of the reaction, and then kept in a thermostated bath controlled to ±0.05°. Ampoules were taken at known times, quenched in ice or liquid air (faster runs), and stored at −5° until the run was over, and the optical absorbance was measured at room temperature. The "zero-time" ampoule was removed after 5 min of thermostating. In faster runs a significant part of the reaction occurred prior to "zero-time" reading, and in several cases only the last 40–60% of the reactions were followed. First-order rate constants were calculated from the slopes of the straight lines obtained by plotting log $(D_t - D_\infty)$ *vs.* time, where $D_t$ and $D_\infty$ are the optical densities at time $t$ and 10 half-lives of the reaction, respectively. Good linearity was obtained as far as the kinetics was followed (to about 90% of the reaction). Similar results were obtained at the different wavelengths used.

The initial concentration of pyridinechromium(III) was in the range $1.95 \times 10^{-5}$ to $5.23 \times 10^{-3}$ $M$. The ionic strength was maintained constant with sodium perchlorate and perchloric acid. The change of the perchloric acid concentration during a run due to the protonation of the liberated pyridine was negligible.

Stoichiometry of the reaction, assumed to be as given in eq 1, was checked by measuring uv–visible spectra of the reaction products. Uv spectra agreed with the spectra of the appropriate pyridine blank solutions, while the visible spectra (for runs in 1.0 $M$ $HClO_4$) agreed with that of the hexaaquochromium(III) ion.[5]

Table I

d–d Absorption Band Wavelengths of Some Pentaaquo(ligand)chromium(III) Ions

| Ligand | $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ cm$^{-1}$) | | Ligand | $\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ cm$^{-1}$) | |
|---|---|---|---|---|---|
| $H_2O$[a] | 573 (13.0) | 407 (15.3) | $dienH_2^{2+}$ [c,d] | 551 (22.4) | 396 (23.4) |
| $NCS^-$ [b] | 570 (31.4) | 410 (33.5) | $enH^+$ [a,d] | 549 (22.2) | 396 (21.5) |
| py | 560 (18.2) | 402 (20.8) | $NH_3$[e] | 545 (22.1) | 397 (21.8) |

[a] Reference 5. [b] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966). [c] Reference 6. [d] Abbreviations: $dienH_2^{2+}$, unidentate diethylenetriamine with two amino groups protonated; enH, unidentate ethylenediamine with one amino group protonated. [e] M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

Table II

First-Order Rate Constants for the Aquation of $Cr(H_2O)_5py^{3+}$ at Constant Ionic Strength ($HClO_4$ + $NaClO_4$)

| 90°, $\mu$ = 1.0 $M$ | | 85°, $\mu$ = 1.0 $M$ | | 80°, $\mu$ = 1.0 $M$ | | 75°, $\mu$ = 1.0 $M$ | | 90°, $\mu$ = 4.0 $M$ | |
|---|---|---|---|---|---|---|---|---|---|
| [H$^+$], m$M$ | $10^4k_{obsd}$, sec$^{-1}$ | [H$^+$], m$M$ | $10^4k_{obsd}$, sec$^{-1}$ | [H$^+$], m$M$ | $10^4k_{obsd}$, sec$^{-1}$ | [H$^+$], m$M$ | $10^4k_{obsd}$, sec$^{-1}$ | [H$^+$], m$M$ | $10^4k_{obsd}$, sec$^{-1}$ |
| 1000[a] | 0.57 | 1014 | 0.33 | 990 | 0.20 | 1020[a] | 0.106 | 4130 | 0.324 |
| 102 | 1.14 | 30.0 | 1.20 | 30.4 | 0.63 | 30.0 | 0.30 | 2040 | 0.364 |
| 30.0 | 2.48 | 3.54 | 8.20 | 6.07 | 2.38 | 6.07 | 1.13 | 1010 | 0.371 |
| 8.65 | 7.40 | 2.53 | 11.5 | 3.33 | 4.40 | 3.54 | 1.90 | 30.0 | 0.910 |
| 6.07 | 9.75 | 2.01 | 14.7 | 2.53 | 5.75 | 2.53 | 2.58 | 4.04 | 4.65 |
| 3.54 | 15.9 | 1.52 | 18.5 | 2.02 | 7.00 | 2.02 | 3.25 | 2.02 | 9.00 |
| 2.53 | 22.8 | | | 1.52 | 9.48 | 1.52 | 4.38 | 1.37 | 13.3 |
| 2.02 | 28.0 | | | 1.24 | 11.6 | 1.24 | 5.49 | 1.01 | 18.6 |
| | | | | 1.01 | 14.3 | 1.01 | 6.48 | | |

[a] Concentration of $Cr(H_2O)_5py^{3+}$ varied in the range $8.2 \times 10^{-5}$–$5.2 \times 10^{-3}$ $M$; at other acidities, $2.0 \times 10^{-5}$–$1.6 \times 10^{-4}$ $M$.

## Results and Discussion

**Characterization of Pyridinechromium(III) Ion.**—Bluish red $Cr(H_2O)_5py^{3+}$ was identified by the way in which it was formed (aquation of a red $Cr(H_2O)_4(py)_2^{3+}$ species), by the pyridine to chromium ratio (1.01), and by its behavior on a cation-exchange column (consistent with a 3+ charge). In 0.1–3 $M$ $HClO_4$ and in $6 \times 10^{-3}$ to 1 $M$ $HClO_4$ solutions with 1.0 $M$ ionic strength ($NaClO_4$) the visible and uv absorption spectra of the complex ion show maxima at 560 nm ($\epsilon$ 18.2 $M^{-1}$ cm$^{-1}$), 402 nm ($\epsilon$ 20.8 $M^{-1}$ cm$^{-1}$), and 260 nm ($\epsilon$ $3.46 \times 10^3$ $M^{-1}$ cm$^{-1}$). Table I gives d–d transition band wavelengths for hexaaquochromium(III) ion and several nitrogen-bonded monosubstituted complex ions.

The substitution of one aquo by one pyridine ligand in hexaaquochromium(III) ion shows an expected hypsochromic effect. First the d–d transition band of the pyridine complex lies between those of the isothiocyanato and ammine complexes. Thus, the ligand-field strength of the pyridine ligand for $Cr(H_2O)_5^{3+}$ is compatible with the general position of pyridine in the spectrochemical series.[13]

**Aquation of $Cr(H_2O)_5py^{3+}$ Ion.**—The first-order rate constants obtained for the aquation of pyridinechromium(III) at different hydrogen ion concentrations, different temperatures, and two ionic strengths are given in Table II. The rate constants at a particular temperature increase with decreasing perchloric acid concentration. A straight line is obtained when plotting $k_{obsd}$ *vs.* $1/(H^+)$ and the dependence is expressed in the equation

$$k_{obsd} = k_0 + k_{-1}/(H^+) \tag{2}$$

Assuming the two terms in expression 2 are associated with two distinct reaction pathways, the rate constants for ionic strength 1.0 $M$ given in Table II were treated simultaneously for all hydrogen ion concentrations and temperatures according to the expression

$$k_{obsd} = (kT/h)\sum_i (H^+)^i e^{\Delta S_i^\ddagger/R} e^{-\Delta H_i^\ddagger/RT} \tag{3}$$

with $i$ = 0 and −1. A CAE 90-40 computer and a nonlinear least-squares program[14] were used to calculate the best values of the enthalpies and entropies of activation as well as the values of the rate constants at different temperatures for the two terms in the rate law. Each rate constant was weighted according to the reciprocal of its square. The calculated values of the rate constants agree with the experimentally observed values with an average deviation of 2.6% and a maximum individual deviation of 5.5%. The activation parameters obtained in this way are $\Delta H_0^\ddagger = 27.2 \pm 0.7$ kcal mol$^{-1}$, $\Delta S_0^\ddagger = -3.5 \pm 2.0$ cal mol$^{-1}$ deg$^{-1}$, $\Delta H_{-1}^\ddagger = 35.6 \pm 0.3$ kcal mol$^{-1}$, and $\Delta S_{-1}^\ddagger = 15.2 \pm 0.8$ cal mol$^{-1}$

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[12] E. L. King and J. A. Neptune, *J. Amer. Chem. Soc.*, **77**, 3186 (1955).

[13] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y., 1964, p 109.

[14] We are grateful to Dr. N. Sutin for supplying this program and to Dr. L. Klasinc for adapting it for CAE 90-40 computer.

deg$^{-1}$. At 25° $k_0 = 1.2 \times 10^{-8}$ sec$^{-1}$ and $k_{-1} = 9.9 \times 10^{-11}$ $M$ sec$^{-1}$.

The rates given in Table II for 90° and ionic strength 4.0 $M$ were treated according to expression 2. The calculated values of the function agreed with the experimental values of $k_{\text{obsd}}$ with an average deviation of 2.9%. The computed rate constants for the two terms in the rate law have the value $k_0 = (3.40 \pm 0.08) \times 10^{-5}$ sec$^{-1}$ and $k_{-1} = (1.77 \pm 0.04) \times 10^{-6}$ $M$ sec$^{-1}$. Corresponding values for 1.0 $M$ ionic strength at 90° are $k_0 = (5.18 \pm 0.13) \times 10^{-5}$ sec$^{-1}$ and $k_{-1} = (5.60 \pm 0.07) \times 10^{-6}$ $M$ sec$^{-1}$.

The moderate ionic strength effect on the rate constant for an acid-independent path gives a support to the assumption that the parameters in expression 2 describe chemically significant reaction paths, though a medium effect caused by varying hydrogen ion concentrations at constant ionic strength cannot be ruled out.

A good conformity of data given in Table II with expressions 2 and 3 is seen from the relatively small average deviation of the calculated from the experimentally observed values of the functions. At a constant ionic strength and temperature, the concentration of hydrogen ions was varied for a factor of $\sim 10^3$ causing a $\sim$60-fold change in the rate of aquation. At the temperatures used in 1 $M$ perchloric acid 90–95% of the reaction proceeds *via* the acid-independent path and in the low acidities used almost completely *via* the acid-inverse path.

The rate law is consistent with $k_0$ in expression 2 being the rate constant for the aquation of $Cr(H_2O)_5py^{3+}$ and $k_{-1}/K_h$ the rate constant for the aquation of the conjugate base, $Cr(H_2O)_4(OH)py^{2+}$, where $K_h$ is the equilibrium constant for the acid dissociation reaction

$$Cr(H_2O)_5py^{3+} \rightleftharpoons Cr(H_2O)_4(OH)py^{2+} + H^+$$

Similar rate law terms with respect to hydrogen ion concentration were observed for $Cr(H_2O)_5X^{n+}$ complexes where X represents an acidic ligand.[15-18] An additional term, of first power in the hydrogen ion concentration due to a pathway involving protonated ligand in the transition state, was observed when X was a more basic ligand such as fluoride,[16] azide,[19] cyanide,[20] sulfate,[21] and acetate.[22] Pyridinechromium(III) shows a "normal" behavior in this respect. Though basic as the free ligand, pyridine does not possess a residual basicity in the complex since it is coordinated through the nitrogen atom. Analogous rate laws were found for ammine[23] and unidentate diethylenetriamine[6] complexes of monosubstituted chromium(III), while the unidentate ethylenediamine complex showed only an acid-independent path in the acidity range studied.[5] The rates of aquation of these unidentate amine complexes[5,6] and of the pyridine complex *via* the acid-independent path have very similar values in the temperature range studied.

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(22) E. Deutsch and H. Taube, *ibid.*, **7**, 1532 (1968).
(23) Based on rough estimates of rates in perchlorate media given in ref 4.

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# The Rate of Aquation of *trans*-Difluorobis(ethylenediamine)chromium(III) through an Isolable Monodentate Ethylenediamine Complex

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The stoichiometry and rate of aquation of *trans*-$Cr(en)_2F_2^+$ have been determined. The sole product (>98%) is Cr(en)-$(enH)H_2OF_2^{2+}$ which is a monodentate ethylenediamine complex with the two fluorides probably trans to one another. This complex is isolated in solution by ion-exchange chromatography. It aquates in turn to form *cis*-$Cr(en)_2H_2OF^{2+}$ and $Cr(en)(H_2O)_2F_2^+$ (which is assigned the stereochemistry 1,6-difluoro-2,3-diaquoethylenediaminechromium(III)) in a ratio of 1.0:3.25. The rate constant for aquation of *trans*-$Cr(en)_2F_2^+$ is $(1.23 \pm 0.02) \times 10^{-5}$ sec$^{-1}$ at 25.0° and $I = 1.0$ $M$. The activation parameters are $\Delta H^{\ddagger} = 24.1 \pm 0.1$ kcal mol$^{-1}$ and $\Delta S^{\ddagger} = -0.3 \pm 0.5$ cal mol$^{-1}$ deg$^{-1}$. The values at $I = 0.12$ $M$ are also reported. These data are compared with those for analogous systems and the implications are discussed.

## Introduction

We have been interested for some time in the nature of the lowest lying $\sigma$-antibonding orbital in metal complexes.[1,2] There is now ample spectroscopic evidence that fluorine in fluorochromium(III) complexes is a strong $\sigma$-bonding ligand.[3-5] This feature makes molecules such as *trans*-$Cr(en)_2F_2^+$ of importance in electron-transfer studies and in photochemical investigations of Cr(III) complexes. In order to investigate these systems, we felt it was of importance to understand the thermal aquation of *trans*-$Cr(en)_2F_2^+$. In this paper we report on that aquation.

A recent development in studies of the aquation of Cr(III) complexes involving multidentate amine ligands has been the isolation of products in which multidentate ligands are partially unwrapped.[6-9] In this study we

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