gen maleate should be reduced by a radical intermediate mechanism. This mechanistic problem may be explained by assuming either that the $\Delta H^{\ddagger}$ correlation noted previously is fortuitious and the maleate reactions all proceed by a radical mechanism or that the low $\Delta H^{\ddagger}$ and negative $\Delta S^{\ddagger}$ for the maleate dianion bridge are the results of better chelation to the reducing agent with a general resonance-exchange mechanism.

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Kinetics of the Stepwise Aquation of Aquotetraethylenepentaminechromium(III) Cation to Hexaaquochromium(III) Cation[1]

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The stepwise "unwrapping" of the tetraethylenepentamine (tetren) ligand from $Cr(tetren)OH_2^{3+}$ to give $Cr(OH_2)_6^{3+}$ has been investigated spectrophotometrically and chromatographically in 0.1–4 F $HClO_4$ (μ = 2–4 M, $NaClO_4$) from 10° (first stages) to 80° (last stages). The reaction scheme

$$\mathrm{Cr(tetren)OH_2^{3+}} \xrightarrow[\mathrm{H_3O^+}]{550} \mathrm{Cr(tetrenH)(OH_2)_2^{4+}} \xrightarrow[\mathrm{H_3O^+}]{2100} \text{1,2,3-}\mathrm{Cr(tetrenH_2)(OH_2)_3^{5+}} \xrightarrow[\mathrm{H_3O^+}]{24} \mathrm{Cr(tetrenH_3)(OH_2)_4^{6+}} \xrightarrow[\mathrm{H_3O^+}]{1}$$

$$\mathrm{Cr(tetrenH_4)(OH_2)_5^{7+}} \xrightarrow[\mathrm{H_3O^+}]{0.173} \mathrm{Cr(OH_2)_6^{3+}} + \mathrm{H_5tetren^{5+}}$$

with first-order rate constants (10^5k, sec^{-1}) accounts for the observations in 4 F $HClO_4$ at 60°; the tetraaquo complex gave kinetic evidence of being a mixture, probably of geometric isomers, inasmuch as the k value obtained from a consecutive first-order treatment decreased with increasing reaction extent (the value given above is based on initial slopes of the rate plots). Acid dependences of the rates are negligible in the range studied, except for the pentaaquo aquation, for which the apparent first-order rate constant k_5 obeys the relation $k_5 = k_{5a} + (k_5'/[H^+])$. The activation energies increase progressively from 20.7 to 27.7 kcal mol^{-1} with the successive stages of aquation, but the entropies of activation exhibit no regularity. Comparisons are made with amine ligand "unwrapping" for related chromium(III) complexes. The d–d absorption spectra of the tetren complexes are given.

Introduction

Recently this laboratory has been engaged in studies of the kinetics of amine ligand "unwrapping"[2] in the stepwise aquation of tetraaquoethylenediaminechromium(III), $Cr(en)(OH_2)_4^{3+}$,[3] of 1,2,3- and 1,2,6-triaquodiethylenetriaminechromium(III), 1,2,3- and 1,2,6-$Cr(dien)(OH_2)_3^{3+}$,[4] and of 1,2,3- and 1,2,6-triaquo(1-azonia-4,7,10-triazadecane)chromium(III) cations, 1,2,3- and 1,2,6-$Cr(trienH)(OH_2)_3^{3+}$,[5] to hexaaquochromium(III) cation, $Cr(OH_2)_6^{3+}$.

With the recent synthesis and characterization[6] of aquotetraethylenepentaminechromium(III) cation, $Cr(tetren)OH_2^{3+}$ (hereafter referred to as "monoaquo"), in which the tetraethylenepentamine ligand (hereafter referred to as "tetren") has its normal denticity of five, and of the isolable aquation intermediates $Cr(tetrenH)(OH_2)_2^{4+}$ ("diaquo"), 1,2,3-$Cr(tetrenH_2)(OH_2)_3^{5+}$ ("triaquo"), $Cr(tetrenH_3)(OH_2)_4^{6+}$ ("tetraaquo"), and $Cr(tetrenH_4)(OH_2)_5^{7+}$ ("pentaaquo"), in which the tetren ligand is partially "unwrapped" and protonated and has respective denticities of four, three, two, and one, it has become possible to investigate the kinetics of these successive aquations. We report here the results of that study, which allow a more complete examination of the factors affecting the rates of amine ligand "unwrapping" from Cr(III) centers. We also present the complete d–d absorption spectra of these tetren complexes, for which only band maxima and minima were reported earlier.[6]

Experimental Section

Aquo–tetren Complexes.—The above aquo–tetren complexes were individually chromatographically isolated in aqueous $HClO_4$ solutions, free of other chromium species (except possibly for tetraaquo—see below), as described previously.[6] Purity was established by agreement of the d–d electronic band maxima and minima with those reported earlier.[6]

Other Materials and Procedures.—The source or preparation of all other chemicals, the analytical methods, kinetic run procedures, spectrophotometry, and calculation of rate constants from optical absorbance data were essentially as described earlier.[4] Chromatographic procedures were essentially those used in the isolation[6] of the complexes, with tetraaquo and pentaaquo solutions prepared in the more concentrated form described previously.[6] First-order aquation rate constants k_n are defined by $-dC_n/dt = k_nC_n$ where C_n is the molar concentration of the given substrate complex (n = 1 for monoaquo aquation, n = 2 for diaquo aquation, etc.). Kinetic overlap between succes-

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[1] (a) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-18 to the AEC. (b) Abbreviations used: en, ethylenediamine, $H_2N(CH_2)_2NH_2$; dien, diethylenetriamine, $H_2N(CH_2)_2NH(CH_2)_2NH_2$; trien, triethylenetetramine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$; tetren, tetraethylenepentamine, $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$. (c) Based upon the Ph.D. dissertation of S. J. Ranney, UCLA, March, 1971.

[2] The term "unwrapping" is used here to refer to the successive rupture of M–N bonds between a multidentate amine ligand and a metal center M, without regard to which M–N bonds are broken. Examination of Fisher–Hirschfelder models indicates that rupture of a Cr–N bond between two amino N atoms which are still bound to the Cr atom is very improbable, especially when steric requirements are considered for the proton taken up by the freed amino N atom, and which stabilizes each isolable intermediate.

[3] R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, **7**, 749, 2678 (1968).

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

[5] D. A. Kamp, R. L. Wilder, S. C. Tang, and C. S. Garner, *Inorg. Chem.*, **10**, 1396 (1971).

[6] S. J. Ranney and C. S. Garner, *Syn. Inorg. Metal-Org. Chem.*, **1**, 179 (1971).

sive aquations was present for all sequences except triaquo → tetraaquo and pentaaquo → hexaaquo; a consecutive first-order kinetics treatment was made when kinetic overlap was involved, using the five-variable computer program discussed earlier,[3] with input k values obtained from initial slopes of first-order rate plots for each substrate.

Results

Visible Absorption Spectra of Aquo–tetren Complexes.—The d–d electronic spectra of the complexes in 0.1–4 F $HClO_4$ ($\mu = 4\ M$, $NaClO_4$) are given in Figure 1.

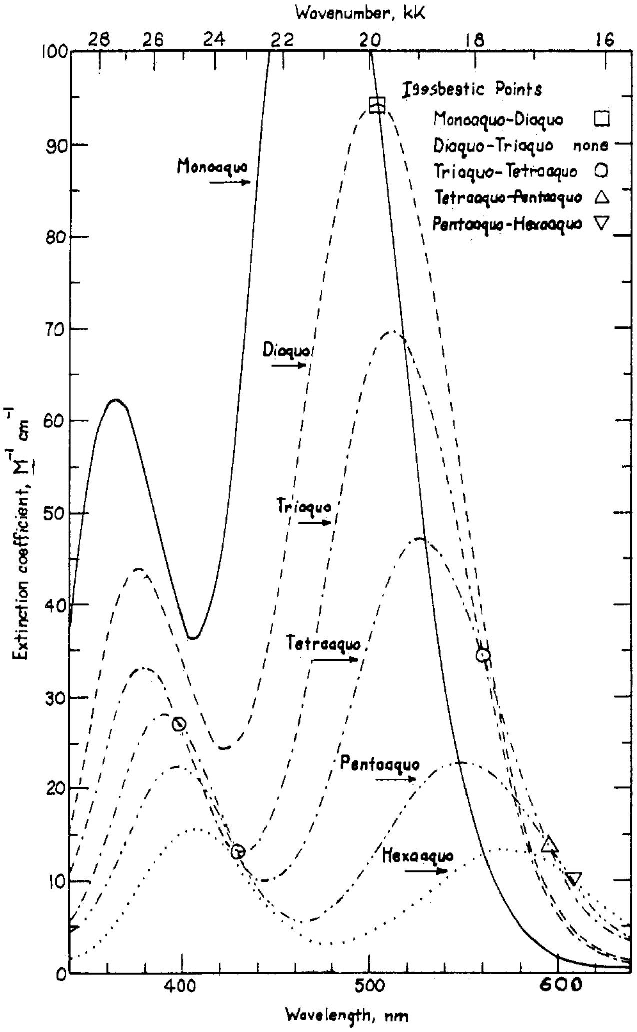

Figure 1.—Visible absorption spectra of aquotetraethylenepentaminechromium(III) complexes and of hexaaquochromium(III) cation in 0.1–4 F $HClO_4$ ($\mu = 4M$, $NaClO_4$): monoaquo, $Cr(tetren)OH_2^{3+}$, with main absorption band at 473 nm and ϵ 134 M^{-1} cm^{-1} (0°); diaquo, $Cr(tetrenH)(OH_2)_2^{4+}$ (0°); triaquo, 1,2,3-$Cr(tetrenH_2)(OH_2)_3^{5+}$ (20–25°); "standard" tetraaquo, $Cr(tetrenH_3)(OH_2)_4^{6+}$ (20–25°; see text); pentaaquo, $Cr(tetrenH_4)(OH_2)_5^{7+}$ (20–25°); hexaaquo, $Cr(OH_2)_6^{3+}$ (20–25°). The molar extinction coefficient ϵ is defined by the relation log $(I_0/I) = A = \epsilon cl$, where c is the molarity of the absorbing complex and l is the optical path length in centimeters.

Aquation of $Cr(tetren)OH_2^{3+}$ and $Cr(tetrenH)(OH_2)_2^{4+}$.—The reaction sequence

$$Cr(tetren)OH_2^{3+} + H_3O^+ \xrightarrow{k_1} Cr(tetrenH)(OH_2)_2^{4+} \quad (1)$$

$$Cr(tetrenH)(OH_2)_2^{4+} + H_3O^+ \xrightarrow{k_2} 1,2,3\text{-}Cr(tetrenH_2)(OH_2)_3^{5+} \quad (2)$$

was investigated by starting with a solution of monoaquo (contaminated with diaquo) and following the change in optical absorbance with time as the system generated triaquo, for which the aquation is *ca.* 100-fold slower than diaquo aquation at 10–30°. Figure 1 predicts one isosbestic point at 503 ± 3 nm (ϵ 94 ± 3 M^{-1} cm^{-1}) for reaction 1 and no isosbestic points for reaction 2. Experimentally, kinetic runs gave an initial isosbestic point in the range 507–514 nm (ϵ 77–70), which is in satisfactory agreement with the kinetically overlapping reactions 1 and 2 in view of the fact that the initial monoaquo solution always contained some diaquo (the chromatographic separation time for isolation of monoaquo was about $^1/_3$ half-life for monoaquo aquation). This initial isosbestic point was soon lost due to the kinetic overlap (a single run starting with diaquo gave the expected absence of isosbestic points). A consecutive first-order analysis of the absorbance data at 470 nm gave the values of k_1 and k_2 given in Table I.

Table I

First-Order Rate Constants for the Reactions

monoaquo $\xrightarrow{k_1}$ diaquo $\xrightarrow{k_2}$ triaquo

Temp,[a] °C	[$HClO_4$], F	C_0,[b] mM	μ,[c] M	10^5k_1,[d] sec^{-1}	10^5k_2,[d] sec^{-1}
10.00	0.134	1.59	3.8	2.9 ± 0.1	6.5 ± 0.3
10.00	0.198	1.53	3.8	3.0 ± 0.1	6.4 ± 0.3
10.00	3.89	1.39	3.89	2.28 ± 0.08	4.3 ± 0.2
19.90	0.252	1.51	3.8	9.7 ± 0.7	25.7 ± 0.3
19.90	3.59	1.51	3.59	8.3 ± 0.3	18.3 ± 1.0
30.10	0.222	1.59	3.8	30 ± 3	98 ± 2
30.10	3.86	1.51	3.86	25 ± 2	67.8 ± 0.8
30.10	1.78	1.50	1.78	48 ± 2	98.3 ± 0.7

[a] Deviation ±0.05°. [b] Initial concentration of substrate. [c] Ionic strength, controlled with $NaClO_4$. [d] Errors are standard deviations.

At ionic strength 4 M the effect of varying hydrogen ion concentration in the ranges shown in Table I is relatively small below 0.3 F $HClO_4$; there appears to be some acid dependence of both k_1 and k_2 when the 3.6–3.9 F $HClO_4$ values are included, but this effect could easily arise from the replacement of Na^+ by H^+ at the very high ionic strength involved. No systematic study of the effect of ionic strength was made, but in view of the presumably small acid dependence the 30° data suggest no major effect on k_1 or k_2 in changing ionic strength from 3.8 to 1.8 M.

Good linear Arrhenius plots were obtained for the two ranges of acid concentration, 0.20–0.25 (0.20–0.35 for k_2) and 3.6–3.9 F $HClO_4$ (μ = 3.6–3.9 M). Least-squares analysis gave activation parameters agreeing within the experimental errors, and only the 4 F $HClO_4$ values are given here: for reaction 1, $E_a = 20.7 \pm 0.6$ kcal mol^{-1}, log PZ (sec^{-1}) = 11.4 ± 0.5, $\Delta S^\circ_{298}{}^* = -9 \pm 2$ cal deg^{-1} mol^{-1}; for reaction 2, $E_a = 23.1 \pm 0.6$ kcal mol^{-1}, log PZ (sec^{-1}) = 13.5 ± 0.5, $\Delta S^\circ_{298}{}^* = 1 \pm 2$ cal deg^{-1} mol^{-1}. Interpolated values for 10^4k_1 and 10^4k_2 at 25° are 1.4 and 3.5 sec^{-1}, respectively, in 4 F $HClO_4$.

Aquation of 1,2,3-$Cr(tetrenH_2)(OH_2)_3^{5+}$.—This triaquo complex aquates in acid solution to tetraaquo

$$1,2,3\text{-}Cr(tetrenH_2)(OH_2)_3^{5+} + H_3O^+ \xrightarrow{k_3} Cr(tetrenH_3)(OH_2)_4^{6+} \quad (3)$$

as shown by cation-exchange chromatography and the existence of three isosbestic points during spectral scans over at least 3 half-lives in agreement within experimental error with the values 400 ± 1 (ϵ 26.5 ± 0.5), 429 ± 1 (ϵ 13.1 ± 0.5), and 561 ± 3 nm (ϵ 30 ± 2 M^{-1} cm^{-1}) predicted for reaction 3 from Figure 1. Absorbance *vs.* time data analyzed at 500 nm gave good first-order rate plots (aquation of the tetraaquo product is *ca.* 50-fold slower under the conditions studied), from which values of the first-order rate constant k_3 were obtained. These are presented in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF 1,2,3-$Cr(tetrenH_2)(OH_2)_3^{5+}$ [a]

Temp, °C	[$HClO_4$], *F*	C_0, m*M*	μ, *M*	10^5k_3, sec^{-1}
40.00	4.03	1.86	4.03	2.08 ± 0.06
50.10	4.03	1.86	4.03	7.0 ± 0.2
60.10	0.101	1.33	3.8	27.6 ± 1.1
60.10	0.223	2.05	3.8	27.9 ± 1.3
60.10	0.271	1.63	3.8	27.2 ± 0.8
60.10	3.90	1.37	3.90	23.9 ± 0.7
60.10	2.03	1.85	2.03	31.4 ± 0.9

[a] The footnotes of Table I apply to the analogous columns here.

These results suggest that acid concentration and ionic strength effects on k_3 are small at 60°.

An excellent linear Arrhenius plot was obtained for the 3.9–4.0 *F* $HClO_4$ data, leading to least-squares values of E_a = 25.1 ± 0.7 kcal mol^{-1}, log *PZ* (sec^{-1}) = 12.9 ± 0.5, and $\Delta S^{\circ}_{298}{}^{*}$ = −2 ± 2 cal deg^{-1} mol^{-1}. The value of k_3 at 25° (extrapolated) is 2.7×10^{-6} sec^{-1}.

Aquation of $Cr(tetrenH_3)(OH_2)_4^{6+}$.—Figure 1 predicts one isosbestic point, at 594 ± 4 nm (ϵ 14 ± 2 M^{-1} cm^{-1}), with a region of near tangency at *ca.* 430 nm (ϵ ~13), for the reaction

$$Cr(tetrenH_3)(OH_2)_4^{6+} + H_3O^+ \xrightarrow{k_4} Cr(tetrenH_4)(OH_2)_5^{7+} \quad (4)$$

Experimentally most kinetic runs starting with tetraaquo exhibited an initial isosbestic point and a region of near tangency located within the above ranges, with the apparent isosbestic point moving to higher wavelengths as kinetic overlap with aquation of pentaaquo set in. Nevertheless, attempts to interpret the spectral changes with time (at 520 nm) by consecutive first-order kinetics failed, except for two runs.

When simple first-order plots were made, using the "infinite-time" absorbance A_∞ from the known spectrum of pentaaquo, most of the runs gave reasonably linear plots for *ca.* 0.3–1 half-time from which "initial slope" apparent k_4 values could be obtained. These k_4 values are given in Table III. As shown by runs 4, 5, 8, 9, 19, and 20, in which k_4 is calculated from the per cent tetraaquo remaining at 5 hr and at 25 hr as directly determined by chromatographic isolation, k_4 is substantially smaller at the greater reaction time. The possibility of a rechelation reaction of pentaaquo to tetraaquo was ruled out by heating pentaaquo in 4 *F* $HClO_4$ at 70° for 5 and 25 hr and chromatographing; no trace of tetraaquo was found. Since the spectral, chromatographic, and other evidence upon which the original characterization[6] of the tetraaquo complex was based is wholly consistent with the formulation of this complex as $Cr(tetrenH_3)(OH_2)_4^{6+}$, we are inclined to view the apparent falloff in k_4 values with increasing reaction extent and the failure to obtain in most cases a satisfactory consecutive first-order analysis of the spectral kinetic runs as suggesting standard tetraaquo as previously synthesized[6] is a mixture of two or more geometric isomers whose aquation rates under the experimental conditions differ somewhat. Since all attempts to separate these apparent isomers chromatographically have failed, attempts were made to reduce the percentage of the more labile isomer by aging it out of the isomeric mixture under various conditions and then following the aquation rate (see Table III, runs 2, 6, 10–14, 17, and 21). In most cases this did result in a smaller value of k_4. In run 13 especially there was a substantial drop in k_4 associated with using a tetraaquo substrate which was standard tetraaquo[6] aged for an extended period in 4 *F* $HClO_4$ at 60° and then reisolated chromatographically; it is interesting that the kinetic data for this run did fit satisfactorily a consecutive first-order treatment. Tetraaquo made by this lengthy aging procedure might be expected to be chiefly (but not necessarily pure) "slow" isomer, and the d–d absorption spectrum was found to differ from that of standard tetraaquo in the 525-nm region (band at 529 nm and ϵ 45 *vs.* 525 nm and ϵ 47.1 for standard tetraaquo) but not significantly in the 390-nm region of the other absorption band. If one takes the d–d spectrum of this lengthily aged tetraaquo as that of the hypothesized "slow" isomer, then mathematical analysis of the change

TABLE III

INITIAL-SLOPE FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Cr(tetrenH_3)(OH_2)_4^{6+}$ [a]

Run no.	Temp, °C	[$HClO_4$], *F*	C_0, m*M*	μ, *M*	10^6k_4, sec^{-1}
1[b]	60.10	3.90	3.42	3.90	10
2[c]	60.10	3.90	2.81	3.90	7
3[b]	69.90	0.108	3.44	3.8	37[d,e]
4[b]	69.90	0.108	3.44	3.8	36[e]
5[b]	69.90	0.108	3.44	3.8	29[f]
6[c]	70.00	0.110	3.28	3.8	25
7[b]	69.90	0.208	2.81	3.8	36
8[b]	69.90	0.208	2.81	3.8	31[e]
9[b]	69.90	0.208	2.81	3.8	20[f]
10[g]	70.03	0.210	3.12	3.8	11
11[h]	70.00	3.67	2.42	3.67	39[i]
12[j]	70.00	3.80	2.66	3.80	39
13[k]	70.03	3.83	2.15	3.83	7[c,d]
14[c]	70.00	3.87	2.81	3.87	19
15[b]	70.20	3.90	3.42	3.90	34
16[b]	70.11	3.94	3.72	3.94	30
17[c]	70.00	4.02	2.77	4.02	28
18[b]	69.90	2.05	2.71	2.05	42
19[b]	69.90	2.05	2.71	2.05	30[e]
20[b]	69.90	2.05	2.71	2.05	13[f]
21[c]	69.90	1.94	2.60	1.94	35
22[b]	80.00	3.90	3.42	3.90	92

[a] The footnotes of Table I apply to the analogous columns here; see text for discussion of initial-slope k_4, obtained by spectral analysis at 520 nm unless noted otherwise. [b] Tetraaquo substrate chromatographically isolated from base hydrolysis solution after first making it 4 *F* in $HClO_4$ and aging in the dark for 2 hr at 70°, the standard method as described previously.[6] [c] Tetraaquo substrate isolated from "standard" tetraaquo[b] after first aging in 4 *F* $HClO_4$ at 70° for 0, 1, 2, 3, 4, and 5 hr (equal amounts of each). [d] Consecutive first-order treatment also satisfactory. [e] Based on amount of tetraaquo chromatographically isolated from reaction solution at 5 hr. [f] Same as footnote *e*, except 25 hr. [g] Same as footnote *b*, except aged 70 hr at 60°. [h] Same as footnote *b*, except aged 11 min at 100°. [i] Same value from 490-nm data also. [j] Same as footnote *b*, except aged 79 hr at 35°. [k] Tetraaquo substrate isolated as for footnote *b* and then aged in 4 *F* $HClO_4$ an additional 152 hr at 60° and chromatographically reisolated.

in spectrum with time of the parallel consecutive first-order sequence

$$\begin{tikzcd} T_f \arrow[dr, "k_{4f}"] & & \\ & P \arrow[r, "k_5"] & H \\ T_s \arrow[ur, "k_{4s}"'] & & \end{tikzcd} \qquad (5)$$

where T_f and T_s refer to the more labile ("fast") and less labile ("slow") isomers and P[7] and H refer to the pentaaquo and hexaaquo complexes shows that a first-order rate law could be found at early stages of the reactions (and consecutive first-order for later stages) within certain ranges of k_{4f}/k_{4s} and of $[T_f]_0/[T_s]_0$. The isosbestic point results can also be accommodated. However, in the absence of any reliable method for determining the ratio $[T_f]_0/[T_s]_0$, the fixing of the ratio k_{4f}/k_{4s} becomes essentially impossible. If scheme 5 is valid, then the initial-slope values of k_4 given in Table III are related to k_{4f} and k_{4s} by the equation $k_4[T]_0 = k_{4f}[T_f]_0 + k_{4s}[T_s]_0$. Of course, the scheme may be still more complicated, possibly with a concurrent isomerization or with more than two isomers. For this reason and because obtaining enough "slow" isomer for a single kinetic run and making the run would require about 2 months, further study of the tetraaquo aquation was abandoned. Even if it were possible to handle the problem of the "slow" isomer by this approach, the problem of the more labile isomer would not be solved.

At 70° initial-slope k_4 values (Table III) are the same within experimental error for 0.1, 0.2, and 3.9 *F* $HClO_4$ ($\mu = 4$ *M*). For order of magnitude purposes, an Arrhenius plot was made of the initial-slope k_4 values in 3.7–4.0 *F* $HClO_4$, despite the apparent composite nature of k_4. This plot was linear, giving the apparent activation parameters $E_a = 25.9 \pm 2.4$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 12.0 ± 1.6, and $\Delta S^{\circ}_{298}{}^* = -6 \pm 7$ cal^{-1} mol^{-1}; k_4 at 25° is 3×10^{-8} sec^{-1} by extrapolation.

Aquation of $Cr(tetrenH_4)(OH_2)_5{}^{7+}$.—The d–d spectra of pentaaquo and of hexaaquo (Figure 1) predict for the reaction

$$Cr(tetrenH_4)(OH_2)_5{}^{7+} + H_3O^+ \xrightarrow{k_5} Cr(OH_2)_6{}^{3+} + H_5tetren^{5+} \qquad (6)$$

one isosbestic point at 608 ± 3 nm (ϵ 10.0 ± 2.0 M^{-1} cm^{-1}) and a region of near tangency centered at 440 nm (ϵ 9). Spectral scans made during the aquation of pentaaquo exhibited for at least 2 half-times one isosbestic point at 608 ± 2 nm (ϵ 9.7 ± 0.6) and the expected region of tangency, in good agreement with expectations for reaction 6. Good linear first-order plots of log $(A - A_\infty)$ *vs.* *t* were obtained at 440 nm over 2 or more half-times. The values of k_5 are tabulated in Table IV.

There appears to be a small dependence of k_5 on $HClO_4$ formality. Plots of k_5 *vs.* $1/[H^+]$, with $[H^+]$ taken equal to the $HClO_4$ formality ($\mu = 4$ *M*), are linear for the 70 and 80° data of Table IV but curved for the 60° runs. The acid dependence at 70 and 80° is best interpreted, for reasons described[4] for the analogous aquation of $Cr(dienH_2)(OH_2)_5{}^{5+}$, in terms of the relation $k_5 = k_{5a} + (k_{5h}K_a/[H^+])$, where k_{5a} is the first-order rate constant for aquation of the species $Cr(tetrenH_4)(OH_2)_5{}^{7+}$, k_{5h} is the first-order rate constant for aquation of $Cr(tetrenH_4)(OH_2)_4OH^{6+}$, and K_a is the first acid dissociation constant of $Cr(tetrenH_4)(OH_2)_5{}^{7+}$. Failure of this relation to fit the 60° data may possibly mean that the second acid dissociation of the substrate is also involved. Judging from the single kinetic run made in ionic strength 1.98 *M* at 80°, there is a small ionic strength dependence of k_5 relative to 4 *M* ionic strength; such effects are not uncommon at such high ionic strengths.

TABLE IV

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Cr(tetrenH_4)(OH_2)_5{}^{7+}$ [a]

Temp, °C	$[HClO_4]$, *F*	C_0, m*M*	μ, *M*	10^6k_5, sec^{-1}
60.20	0.118	3.19	3.8	2.33 ± 0.03
60.20	0.215	3.38	3.8	2.20 ± 0.03
60.20	0.218	3.79	3.8	2.24 ± 0.03
60.20	3.96	3.00	3.96	1.73 ± 0.03
70.05	0.118	3.19	3.8	8.4 ± 0.1
70.10	0.215	3.38	3.8	7.17 ± 0.09
70.10	3.96	3.00	3.96	5.81 ± 0.02
80.20	0.118	3.19	3.8	28.3 ± 0.4
80.10	0.215	3.38	3.8	24.8 ± 0.5
80.10	3.96	3.00	3.96	19.3 ± 0.6
80.10	1.98	2.78	1.98	32.5 ± 0.8

[a] The footnotes of Table I apply to the analogous columns here.

At ionic strength 3.6–4 *M*, Arrhenius plots for k_{5a} and $k_{5h}K_a$ are approximately linear, despite the failure of the $1/[H^+]$ relation at 60°. Treating the acid-independent path (k_{5a}) only, the activation parameters are $E_a = 29.5 \pm 0.6$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 13.5 ± 0.4, and $\Delta S^{\circ}_{298}{}^* = 2 \pm 2$ cal deg^{-1} mol^{-1}. In 4 *F* $HClO_4$, $k_5 \approx 8 \times 10^{-9}$ sec^{-1} at 25° by extrapolation.

Discussion

As discussed elsewhere,[6] the parent compound $[Cr(tetren)Cl]Cl_2$ used in the synthesis of the aquo–tetren complexes probably has the $\alpha\beta R$ configuration of $\alpha\beta R$-$[Co(tetren)Cl](ClO_4)_2$.[8] The latter has been reported to convert substantially in basic aqueous solution to the $\alpha\beta S$ form.[8] Thus the $Cr(tetren)OH_2{}^{3+}$ involved in our work is probably one of the two diastereoisomers of I, Figure 2. As mentioned earlier,[2] Fisher–Hirschfelder models suggest that aquation *via* rupture of a Cr–N bond between two amino N atoms which are still bound to the Cr atom is very improbable. On this assumption and the assumption that no geometric isomerizations occur (although relatively little is known about isomerization rates of octahedral Cr(III) complexes, aquation of Cr(III) amine complexes commonly is so much faster than isomerization that the latter is often not observed[9]), the probable sequence of aquation steps starting with monoaquo is shown in Figure 2. Spectral evidence[6] suggests that the diaquo complex has a cis diaquo configuration and the triaquo complex has the 1,2,3 (facial) configuration, as shown. Except for tetraaquo (see above), neither the chromatographic nor kinetic results suggest that more than one geometric isomer of each complex is involved, and where pathways leading to more than one isomer are shown in Figure 2, these are presumed to be alternative and not concurrent routes. However, we must admit that some isomers

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[7] Neither spectral nor kinetic evidence for the production of more than one isomer of pentaaquo from the two apparent isomers of tetraaquo was obtained.

[8] M. R. Snow, D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 981 (1969).

[9] C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 221 (1970).

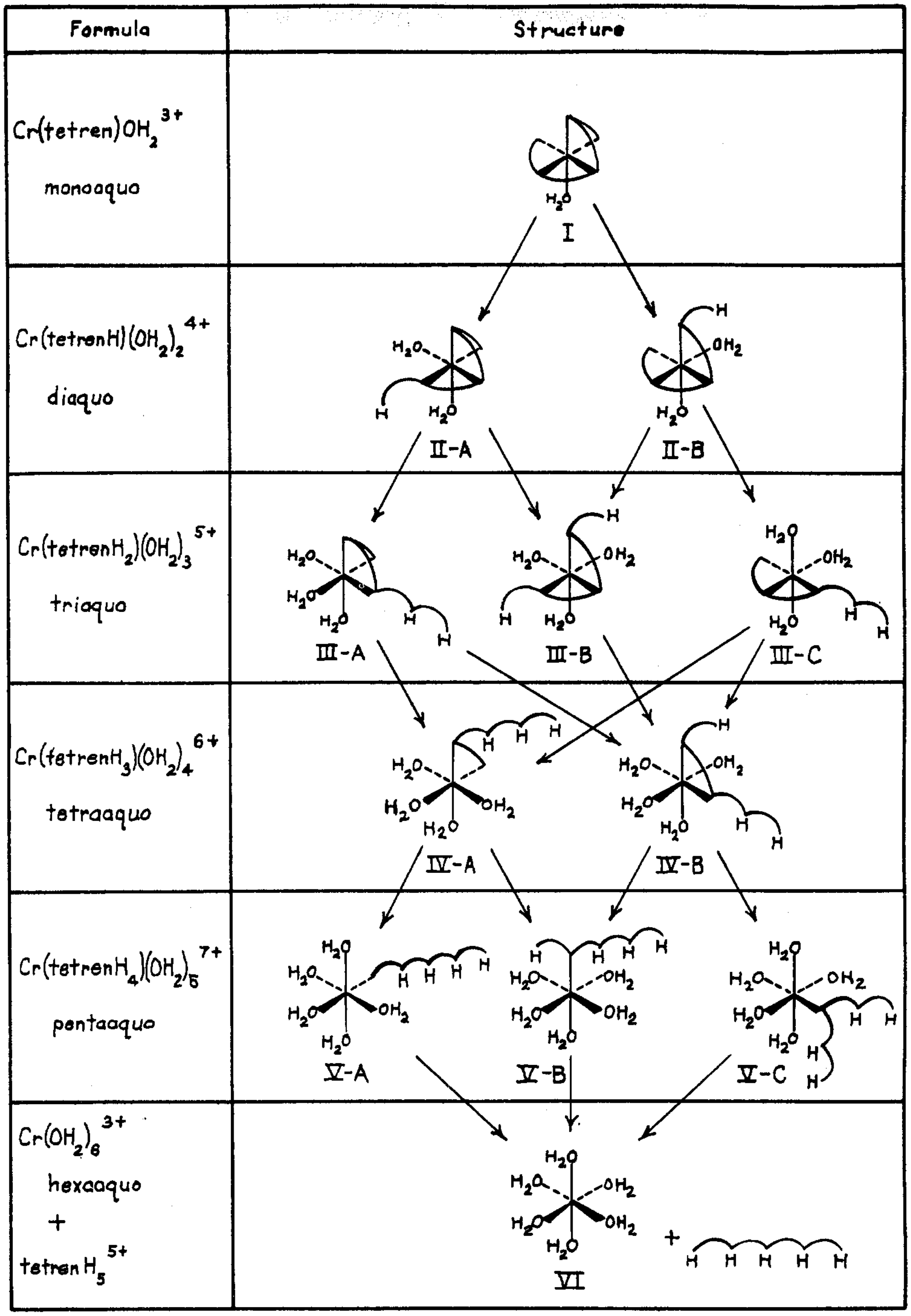

Figure 2.—Probable successive steps in the aquation of Cr(tetren)OH_2^{3+} (applicable to isomers with either *R* or *S* configuration about the asymmetric N atom; charges of species not shown).

may conceivably have such closely related kinetic and spectral parameters that our techniques would not distinguish among them.

Table V compares the rate parameters for multidentate amine "unwrapping" from Cr(III) centers for all such aquoamine complexes investigated so far. As in aquation of the aquo–en, aquo–dien, and aquo–trien analogs, the "unwrapping" of the amine ligand becomes progressively slower with each successive stage for the aquo–tetren complexes (except for an abnormally high aquation rate for Cr(tetrenH)$(OH_2)_2^{4+}$). Two hypotheses have been advanced to account for this trend toward decreasing aquation rates with increased ligand unwrapping. In the first,[4] it is argued that there is considerable ring strain associated with the several chelate rings in the complex, which strain is partly relieved as the ligand unwraps. In the second,[5] an additional consideration is the "grease" effect of the ligand ethylene bridges, which would be expected to hinder solvation in the aqueous medium in both the ground state and transition state, but presumably more so in the latter because of the greater solvation demanded by the separating charges of the Cr(III) center and the charged protonated free portion of the partly unwrapped ligand. The "grease" effect of *chelated* ethylene groups has been used[10] to rationalize the decreasing aquation rate of a

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(10) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

TABLE V

RATE PARAMETERS FOR AQUATION OF SOME CHROMIUM(III)–AQUOAMINE COMPLEXES

Complex	No. of chelate rings	$[HClO_4]$, F	10^5k,[n] sec^{-1}	E_a, kcal mol^{-1}	$\Delta S^\circ_{298}{}^*$, cal deg^{-1} mol^{-1}
$Cr(tetren)OH_2^{3+}$ [a]	4	4	550[b]	20.7 ± 0.6	-9 ± 2
$Cr(trien)(OH_2)_2^{3+}$ [c]	3	...	...	...	...
1,2,6-$Cr(dien)(OH_2)_3^{3+}$ [d]	2	1	1600[e]	19.2 ± 0.6	-11 ± 2
1,2,3-$Cr(dien)(OH_2)_3^{3+}$ [d]	2	1	5.89	24.3 ± 0.7	-7 ± 3
Pink $Cr(en)(NH_3)(OH_2)_3^{3+}$ [f]	1	3	13.3	27.5 ± 0.3	$+4 \pm 1$
$Cr(en)(OH_2)_4^{3+}$ [g]	1	3	0.30	27.7 ± 1.5	-3 ± 5
$Cr(tetrenH)(OH_2)_2^{4+}$ [a]	3	4	2100[b]	23.1 ± 0.6	$+1 \pm 2$
1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ [h]	2	2	1200[i]	18.0 ± 2.6	-20 ± 9
1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ [h]	2	2	$\leqslant 13$[j,k]	21.2 ± 2.2[k]	-15 ± 7[k]
$Cr(dienH)(OH_2)_4^{4+}$ [d]	1	1	2.16	24.0 ± 0.6	-10 ± 2
$Cr(enH)(OH_2)_5^{4+}$ [g]	0	3	0.19	24.5 ± 2.3	-11 ± 7
1,2,3-$Cr(tetrenH_2)(OH_2)_3^{5+}$ [a]	2	4	24	25.1 ± 0.7	-2 ± 2
$Cr(trienH_2)(OH_2)_4^{5+}$ [h]	1	2	3.07	24.2 ± 0.7	-9 ± 7
$Cr(dienH_2)(OH_2)_5^{5+}$ [d]	0	1	0.26[l]	26.5 ± 0.8[l]	-6 ± 3[l]
$Cr(tetrenH_3)(OH_2)_4^{6+}$ [a,m]	1	4	1	25.9 ± 2.4	-6 ± 7
$Cr(trienH_3)(OH_2)_5^{6+}$ [h]	0	2	0.208	28.1 ± 0.8	-2 ± 2
$Cr(tetrenH_4)(OH_2)_5^{7+}$ [a]	0	4	0.173[l]	27.7 ± 0.7[l]	-4 ± 2[l]

[a] This research. [b] Extrapolated from 10–35° values. [c] Repeated attempts to synthesize this complex were unsuccessful: R. L. Wilder, D. A. Kamp, and C. S. Garner, *Inorg. Chem.*, **10**, 1393 (1971). [d] Reference 4. [e] Extrapolated from 15–30° values. [f] T. J. Williams and C. S. Garner, *Inorg. Chem.*, **8**, 1639 (1969); complex has unknown configuration. [g] Reference 3. [h] Reference 5. [i] Extrapolated from 20–35° values. [j] Extrapolated from 40–50° values. [k] Reaction may include concurrent isomerization. [l] Acid-independent path. [m] Probably an isomeric mixture; rate parameters from initial-slope k_4 values of "standard" tetraaquo (see text). [n] Rate constants at 60°.

chloro ligand with increasing chelation in some Co(III) complexes, such as the series *cis*-$Co(NH_3)_4Cl_2^+$, *cis*-$Co(en)(NH_3)_2Cl_2^+$, *cis*-$Co(en)_2Cl_2^+$, and *cis*-α-$Co(trien)Cl_2^+$.[11] Sargeson and Searle[12] questioned the validity of this solvation argument inasmuch as *cis*-β-$Co(trien)Cl_2^+$ does not fit the pattern.

The rate parameters in Table V may be examined to shed some light on which of the effects listed above may be more important. In Table V the substrates are grouped together by charge, since complexes with a given charge have potentially the same unwrapped ligand ends "dangling" from the Cr(III) center. For example, the substrates of charge 5+ may have either one $(CH_2)_2NH_2(CH_2)_2NH_3^{2+}$ group or two $(CH_2)_2NH_3^+$ groups or a mixture of the two types, depending on the isomeric mixture involved in the reaction. Within each charge group of Table V the number of chelate rings is decreasing. Each charge group shows a trend toward lower aquation rate with decreasing number of chelate rings (the two 1,2,6-triaquo species appear to have abnormally large rate constants, and possible reasons presented earlier[4,5] will not be repeated here, since the triaquo complex in the tetren series appears to be the 1,2,3 isomer, with no 1,2,6 isomer known). The activation energies appear to be increasing within each charge group, if one ignores the two 1,2,6-triaquo complexes; two apparent reversals of this order could be due to experimental errors. These trends in E_a are what one would expect if the ring strain effect were predominant, since decreasing numbers of chelated ethylene groups would have been expected to favor solvation and thus decrease activation energies and increase rate constants. This conclusion must be regarded as tentative, however, in light of the small differences found in E_a values and the relatively large experimental errors. Entropies of activation show no regular pattern; inasmuch as $\Delta S^{\circ *}$ values calculated from transition-state theory in the usual way assume unit activity coefficient ratios or, stated equivalently, assume a standard state of a hypothetical ideal 1 M solution in "solvent" consisting of everything except the reactant or transition-state solutes, as well as assuming unit transmission coefficients, part of the randomness of $\Delta S^{\circ *}$ may be due to the considerably different acid and ionic strengths in which different substrates were investigated.

The data of Table V show also that there are no large differences in rate constant from one amine system to another for a given aquation step. For example, 10^5k (sec^{-1}) values for aquation of the pentaaquo complexes range only from 0.17 to 0.26. Those for tetraaquo aquation range from 0.3 to 3, while the 1,2,3-triaquo aquations range from 6 to 24. In none of these three cases does there appear to be a correlation, within the small range found, of aquation rate with length or charge of ligand chain already unwrapped.

Finally it remains to consider the unusually high reactivity of the diaquo–tetren complex relative to the other aquo–tetren species. This reactivity may also exist in the aquo–trien system, for repeated attempts to synthesize $Cr(trien)(OH_2)_2^{3+}$ were unsuccessful.[11] Activation energies show no discontinuity for the diaquo–tetren complex, instead showing an apparently smooth increase (within the sometimes large experimental errors) with the successive aquation steps, namely, $20.7 < 23.1 < 25.1 < 25.9 < 27.7$ kcal mol^{-1}. The entropies of activation appear to be small and positive for $Cr(tetrenH)(OH_2)_2^{4+}$ and apparently negative for all the other aquo–tetren complexes, although the experimental errors are very large. Thus the diaquo complex has next to the smallest E_a value and apparently the largest $\Delta S^{\circ *}$ value and, hence, an abnormally large k value. Although the aquation mechanisms for Cr(III) and Co(III) octahedral substrates are still not fully understood, the evidence strongly favors dissociative mechanisms.[13] Tobe[14] has suggested, as a result of an extensive study of $\Delta S^{\circ *}$ and per cent steric change for a series of cobalt(III)–amine complexes having four

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[11] R. L. Wilder, D. A. Kamp, and C. S. Garner, *Inorg. Chem.*, **10**, 1393 (1971).

[12] A. M. Sargeson and G. A. Searle, *ibid.*, **6**, 2172 (1967).

[13] See ref 9, p 204.

[14] M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

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.

CONTRIBUTION FROM THE INSTITUTE "RUDER BOŠKOVIĆ,"
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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 1.12×10^{-4} sec^{-1} and for the second pyridine 1.06×10^{-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 5×10^{-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 (ϵ 4.83×10^3 at 372 nm) after decomposition of the complex and oxidation with alkaline peroxide.[10] Pyridine was determined spectrophotometrically (ϵ 5.29×10^3 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).