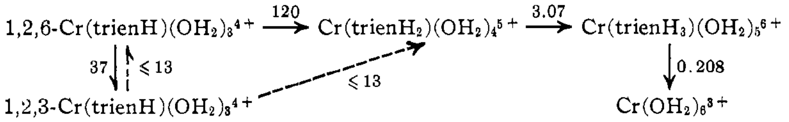
CONTRIBUTION NO. 2701 FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, LOS ANGELES, CALIFORNIA 90024

Kinetics of the Stepwise Aquation of 1,2,3- and 1,2,6-Triaquo(1-azonia-4,7,10-triazadecane)chromium(III) Cations to Hexaaquochromium(III) Cation[1]

BY DAVID A. KAMP, RONALD L. WILDER, S. CONRAD TANG, AND CLIFFORD S. GARNER*

Received August 27, 1970

The stepwise "unwrapping" of the triethylenetetramine (trien) ligand from 1,2,3- and 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$ to give $\text{Cr(OH}_2)_6^{3+}$ has been investigated spectrophotometrically and chromatographically in 0.5–2 F HClO_4 (μ = 2–3 M, NaClO_4) from 20 (first stages) to 80° (last stage). Concurrent aquation and isomerization of 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$ occurs and 1,2,3-$\text{Cr(trienH)(OH}_2)_3^{4+}$ aquates and/or isomerizes in an indeterminant ratio, both complexes aquating to $\text{Cr(trienH}_2)(\text{OH}_2)_4^{5+}$, which aquates to $\text{Cr(trienH}_3)(\text{OH}_2)_5^{6+}$, which in turn aquates to $\text{Cr(OH}_2)_6^{3+}$. The reaction scheme



$$\begin{tikzcd}
\text{1,2,6-Cr(trienH)(OH}_2)_3^{4+} \arrow[r, "120"] \arrow[d, shift right, "37"'] & \text{Cr(trienH}_2)(\text{OH}_2)_4^{5+} \arrow[r, "3.07"] & \text{Cr(trienH}_3)(\text{OH}_2)_5^{6+} \arrow[d, "0.208"] \\
\text{1,2,3-Cr(trienH)(OH}_2)_3^{4+} \arrow[u, shift right, dashed, "\leqslant 13"'] \arrow[ur, dashed, "\leqslant 13"'] & & \text{Cr(OH}_2)_6^{3+}
\end{tikzcd}$$

with first-order rate constants (10^5k, sec^{-1}), accounts for the observations in 2 F HClO_4 at 60°. Acid dependences of the rates are negligible in the range studied. Activation parameters were evaluated; starting with 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$ the activation energies and entropies increase progressively with the successive stages of aquation from 18.0 to 28.1 kcal mol^{-1} and from −20 to −2 cal deg^{-1} mol^{-1}, respectively. Comparisons are made with amine ligand "unwrapping" in aquodiethylenetriamine and aquoethylenediamine complexes of Cr(III). The visible absorption spectra of the complexes are given.

Introduction

The aquation of tetraaquoethylenediaminechromium(III) cation, $\text{Cr(en)(OH}_2)_4^{3+}$, and of its isolated product $\text{Cr(enH)(OH}_2)_5^{4+}$, with a protonated unidentate ethylenediamine ligand, has recently been studied kinetically,[2] as has the stepwise aquation[3] of 1,2,3- and 1,2,6-triaquodiethylenetriaminechromium(III) cations, 1,2,3- and 1,2,6-$\text{Cr(dien)(OH}_2)_3^{3+}$, to the hexaaquochromium(III) cation, $\text{Cr(OH}_2)_6^{3+}$. In the latter aquations, the intermediates $\text{Cr(dienH)(OH}_2)_4^{4+}$ and $\text{Cr(dienH}_2)(\text{OH}_2)_5^{5+}$, with "partially unwrapped" singly protonated bidentate and doubly protonated unidentate diethylenetriamine ligands, respectively, were isolated.[4]

In connection with a continuing program of investigating the "unwrapping" of multidentate amine ligands from chromium(III) centers, we report here the kinetics of the successive aquations 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-$\text{Cr(trienH)(OH}_2)_3$,$^{4+}$, to $\text{Cr(OH}_2)_6^{3+}$ *via* the recently isolated[5] $\text{Cr(trienH}_2)(\text{OH}_2)_4^{5+}$ and $\text{Cr(trienH}_3)(\text{OH}_2)_5^{6+}$ intermediates. The isomerization of 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$, which occurs concurrently with its aquation, was also investigated.

Experimental Section

Aquo–trien Complexes.—The complexes 1,2,3- and 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$, $\text{Cr(trienH}_2)(\text{OH}_2)_4^{5+}$, and $\text{Cr(trienH}_3)(\text{OH}_2)_5^{6+}$ were individually chromatographically isolated in aqueous HClO_4 solutions, free of other chromium species, as described previously.[5] Purity was established by agreement of the visible absorption maxima and minima with those reported earlier.[5]

Other Materials and Procedures.—The source or preparation of all other chemicals and the analytical methods, kinetic run procedures, and calculation of rate constants from optical absorbance data were essentially as described previously.[3] Cation-exchange chromatographic procedures used in the study of the 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$ concurrent isomerization and aquation kinetics were essentially the same methods used in the original solutions of 1,2,6- and 1,2,3-$\text{Cr(trienH)(OH}_2)_3^{4+}$ and of $\text{Cr(trienH}_2)(\text{OH}_2)_4^{5+}$.[5] Observed first-order 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; kinetic overlap of the successive aquations was generally unimportant over the reaction times used. Light was routinely excluded from the reacting solutions, except for the spectrophotometer beam during spectral scans. Visible absorption spectra of fresh solutions of the pure complexes were obtained with a Cary Model 11 spectrophotometer and matched 10-cm silica cells; the reference cell was filled with the same solution without the Cr(III) complex.

Results

Aquation and Isomerization of 1,2,6-Cr(trienH)-$(\mathbf{OH_2})_3^{4+}$.—Attempts to interpret the change in the visible absorption spectrum of 1,2,6-$\text{Cr(trienH)(OH}_2)_3^{4+}$ with reaction time solely in terms of either reaction 1

$$\text{1,2,6-Cr(trienH)(OH}_2)_3^{4+} + \text{H}_3\text{O}^+ \xrightarrow{k_{3t4}} \text{Cr(trienH}_2)(\text{OH}_2)_4^{5+} \quad (1)$$

or reaction 2

$$\text{1,2,6-Cr(trienH)(OH}_2)_3^{4+} \xrightarrow{k_{3t3c}} \text{1,2,3-Cr(trienH)(OH}_2)_3^{4+} \quad (2)$$

were incompatible with the known d–d spectra of these three complexes, and chromatography of the reaction solutions revealed that 1,2,3-$\text{Cr(trienH)(OH}_2)_3^{4+}$ was produced in addition to the expected $\text{Cr(trienH}_2)(\text{OH}_2)_4^{5+}$. The successive spectral scans during the first ~65% reaction exhibited an isosbestic point at 533 ± 1 nm (ϵ 51.9 ± 1.3) at 35° (five runs), 534 ± 2 nm (ϵ 53.4

---

[1] (a) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the university. This paper constitutes Report No. UCLA-34P170-14 to the AEC. (b) Abbreviations used: en, ethylenediamine, $\text{H}_2\text{N(CH}_2)_2\text{NH}_2$; dien, diethylenetriamine, $\text{H}_2\text{N(CH}_2)_2\text{NH}_2$; trien, triethylenetetramine, $\text{H}_2\text{N(CH}_2)_2\text{NH(CH}_2)_2\text{NH}_2$; tetren, tetraethylenepentamine, $\text{H}_2\text{N(CH}_2)_2\text{NH(CH}_2)_2\text{NH(CH}_2)_2\text{NH(CH}_2)_2\text{NH}_2$.

[2] 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).

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

[4] D. K. Lin and C. S. Garner, *Inorg. Nucl. Chem. Lett.*, **5**, 481 (1969).

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

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE REACTIONS $1,2,6\text{-Cr(trienH)(OH}_2)_3{}^{4+} \begin{array}{l} \xrightarrow{+\text{H}_3\text{O}^+,\ k_{3t4}} \text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+} \\ \xrightarrow[k_{3t3c}]{} 1,2,3\text{-Cr(trienH)(OH}_2)_3{}^{4+} \end{array}$

Temp,[a] °C	[HClO$_4$], *F*	C_0,[b] m*M*	μ,[c] *M*	10^4k_{obsd},[d,e] sec^{-1}	R[e,f]	10^4k_{3t4},[e] sec^{-1}	10^4k_{3t3c},[e] sec^{-1}
35.00	2.0	2.64	2.0	2.08 ± 0.10	2.34 ± 0.26	1.46 ± 0.11	0.624 ± 0.050
35.00	0.50	2.07	2.0	2.32 ± 0.06	2.34 ± 0.26	1.62 ± 0.09	0.695 ± 0.067
35.00	0.50	1.36	2.0	2.21 ± 0.06	2.34 ± 0.26	1.55 ± 0.09	0.662 ± 0.064
35.00	0.10	1.99	2.0	2.39 ± 0.06	2.34 ± 0.26	1.67 ± 0.10	0.715 ± 0.068
35.00	2.0	3.34	3.0	2.54 ± 0.10	2.34 ± 0.26	1.78 ± 0.12	0.761 ± 0.067
30.05	2.0	1.56	2.0	1.27 ± 0.03	2.13 ± 0.25	0.857 ± 0.056	0.402 ± 0.039
30.05	1.0	0.888	2.0	1.27 ± 0.03	2.13 ± 0.25	0.862 ± 0.051	0.405 ± 0.042
30.05	0.42	1.58	2.0	1.32 ± 0.04	2.13 ± 0.25	0.899 ± 0.049	0.422 ± 0.044
30.05	0.089	1.38	2.0	1.26 ± 0.04	2.13 ± 0.25	0.859 ± 0.057	0.404 ± 0.040
20.05	1.9	1.56	1.9	0.502 ± 0.04	1.86 ± 0.33	0.326 ± 0.040	0.176 ± 0.012

[a] Deviations: ±0.10° at 35°; ±0.08° at 30°; ±0.05° at 20°. [b] Initial concentration of substrate. [c] Ionic strength, controlled with NaClO$_4$. [d] First-order rate constant for disappearance of 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ by all paths; spectral data analyzed at 490 nm. [e] Errors are standard deviations. [f] Chromatographically determined mole ratio of product Cr(trienH$_2$)(OH$_2$)$_4$$^{5+}$ to product 1,2,3-Cr(trienH)(OH$_2$)$_3$$^{4+}$.

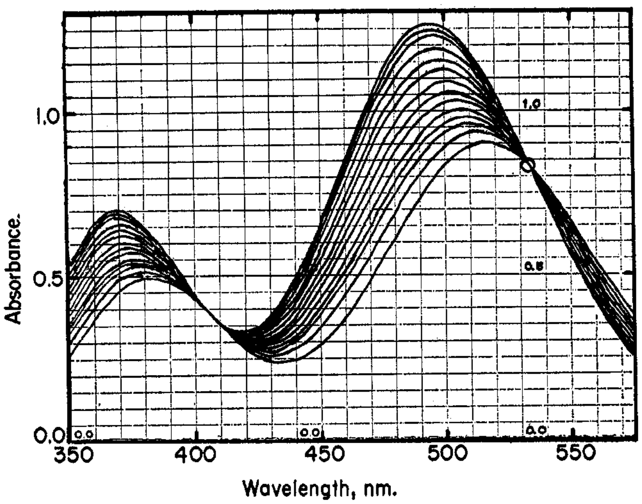


Figure 1.—Change in absorption spectra during concurrent aquation and isomerization of 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ (C_0 = 1.56 m*M*) in 2.0 *F* HClO$_4$ at 30.05°; reading downward at 490 nm, reaction times are zero, 5, 10, 20, 30, 40, 55, 70, 85, 105, 125, 145, 180, 260 min.

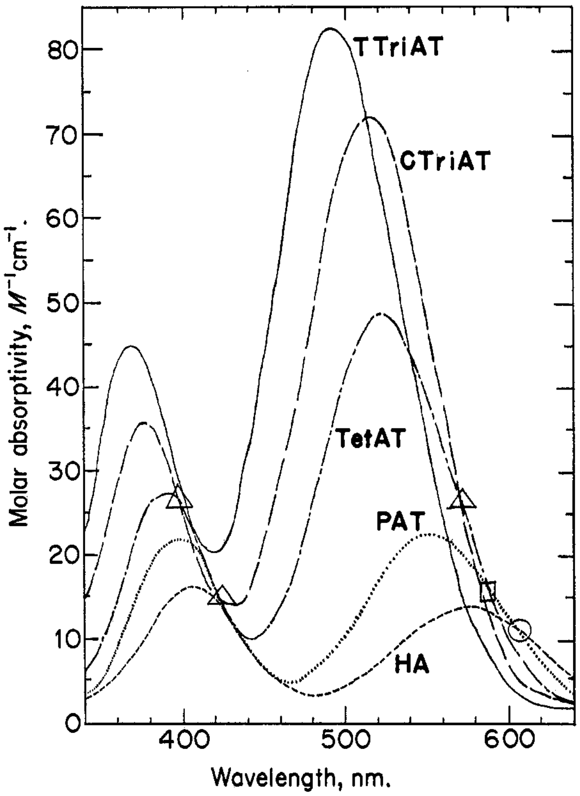


Figure 2.—Visible absorption spectra of aquotriethylenetetramine complexes of chromium(III) at 20–25°: TTriAT, *trans-* or 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ in 2 *F* HClO$_4$; CTriAT, *cis-* or 1,2,3-Cr(trienH)(OH$_2$)$_3$$^{4+}$ in 2 *F* HClO$_4$; TetAT, Cr(trienH$_2$)(OH$_2$)$_4$$^{5+}$ in 2 *F* HClO$_4$; PAT, Cr(trienH$_3$)(OH$_2$)$_5$$^{6+}$ in 3 *F* HClO$_4$; HA, Cr(OH$_2$)$_6$$^{3+}$ in 2 *F* HClO$_4$. The molar absorptivity or molar extinction coefficient ϵ is defined by the relation log (I_0/I) = A = ϵCl, where C is the molarity of the absorbing complex and l is the optical path in centimeters.

± 1.7) at 30° (four runs), and 534 ± 1 nm (ϵ 50.6 ± 1.5) at 20° (one run); a typical set of scans at 30° is shown in Figure 1. From the previously unreported[6] visible absorption spectra of these aquotriethylenetetramine complexes (Figure 2), it is seen that an isosbestic point would occur at 541 nm (ϵ 44) if reaction 1 were the sole reaction and at 515 nm (ϵ 72) if reaction 2 were the only reaction, each in disagreement with the observed isosbestic point.

Accordingly, two methods were developed to determine the essentially constant mole ratio R of product Cr(trienH$_2$)(OH$_2$)$_4$$^{5+}$ to product 1,2,3-Cr(trienH)(OH$_2$)$_3$$^{4+}$ formed from 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ at each temperature. In the first method, chromatographic separation of these three species, with 95% or better recovery of each, was carried out on reaction solutions at *ca.* 30, 50, and 65% reaction for sample kinetic runs, allowing the determination of the total rate of disappearance of 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ and of R. Values of R ($R = k_{3t4}/k_{3t3c}$)[7] are given in Table I; these values are averages for the three extents of reaction, since the increase in R with increasing reaction extent is small (the increase is caused by one or more reactions of the product 1,2,3-Cr(trienH)(OH$_2$)$_3$$^{4+}$ which become more important as the concentration of the 1,2,3-triaquo species builds up, as discussed below). In the second method, ϵ *vs.* λ plots were computed and graphed for various known values of R from the ϵ *vs.* λ plots of the pure products (Figure 2), and these were overlaid on an ϵ *vs.* λ plot of 1,2,6-Cr(trienH)(OH$_2$)$_3$$^{4+}$ and the "predicted" isosbestic point was noted for each value of R.

---

(6) Only the absorption maxima and minima have been reported previously.[5]

(7) k_{3t4} is the rate constant for the direct production of species 4 (tetraaquo complex) from species 3*t* (1,2,6- or "*trans*"-triaquo complex) in Figure 3 of the Discussion; this notation system is used for all other k quantities given.

This trial-and-error procedure was continued until the "predicted" isosbestic point was in agreement with the experimentally observed isosbestic point. Values of R so obtained were the same as those from the chromatographic method within the estimated errors and served to support the validity of the spectral interpretation. In particular, it was then possible to analyze the spectral changes kinetically using "infinite-time" absorbance A_∞ values based on the average R values to obtain the observed first-order rate constant k_{obsd} ($k_{\text{obsd}} = k_{3t4} + k_{3t3c}$) for the disappearance of 1,2,6-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ by both aquation and isomerization. The first-order rate plots were linear to 50–70% reaction.

These values of k_{obsd}, which are more precise than the generally concordant values obtained by the chromatographic method, are presented in Table I, along with the values of the aquation and isomerization rate constants resolved from k_{obsd} and R. At 30 and 35° the values of k_{3t4} and k_{3t3c} are essentially constant within the experimental errors over the acid range 0.1–2.0 F HClO_4 ($\mu = 2.0\ M$). At 35° and 2 F HClO_4, k_{3t4} and k_{3t3c} are increased *ca.* 20% by increasing the ionic strength from 2.0 to 3.0 M, which is within a normal salt effect at such high ionic strengths.

Satisfactory, slightly curved Arrhenius plots were obtained from the temperature dependences of k_{3t4} and k_{3t3c} for the 2 F HClO_4 ($\mu = 2\ M$) runs, from which the following activation parameters were calculated: 1,2,6-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ aquation, $E_a = 18.0 \pm 2.6$ kcal mol^{-1}, $\log [PZ\ (\text{sec}^{-1})] = 8.9 \pm 1.9$, $\Delta S°_{298}{}^{\ddagger} = -20 \pm 9$ cal deg^{-1} mol^{-1}; 1,2,6-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ isomerization, $E_a = 15.3 \pm 1.8$ kcal mol^{-1}, $\log [PZ\ (\text{sec}^{-1})] = 6.6 \pm 1.3$, $\Delta S°_{298}{}^{\ddagger} = -30 \pm 6$ cal deg^{-1} mol^{-1}. At 25° interpolated values of k_{3t4} and k_{3t3c} are $(5 \pm 5) \times 10^{-5}$ sec^{-1} and $(3 \pm 2) \times 10^{-5}$ sec^{-1}, respectively.

Aquation and/or Isomerization of 1,2,3-$\mathbf{Cr(trienH)(OH_2)_3{}^{4+}}$.—Chromatographically and spectrophotometrically the only product observed during the first half-time in the reaction of 1,2,3-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ in 0.5–1.8 F HClO_4 ($\mu = 1.8\ M$, NaClO_4) at 40–50° is $\text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+}$. Up to 75% reaction, successive spectral scans gave sharp isosbestic points at 398 ± 2 (ϵ 26.9 ± 0.6), 430 ± 2 (ϵ 13.7 ± 0.4), and 568 ± 2 nm (ϵ 29.4 ± 0.9), in good agreement with the values 399 ± 2 (25.9 ± 1.3), 426 ± 2 (ϵ 14.0 ± 0.7), and 569 ± 2 nm (ϵ 28.8 ± 1.4) predicted from Figure 2 for the reaction

$$\text{1,2,3-Cr(trienH)(OH}_2)_3{}^{4+} + \text{H}_3\text{O}^+ \xrightarrow{k_{3c4}} \text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+} \quad (3)$$

and in disagreement with the prediction from Figure 2 for the reaction

$$\text{1,2,3-Cr(trienH)(OH}_2)_3{}^{4+} \xrightarrow{k_{3c3t}} \text{1,2,6-Cr(trienH)(OH}_2)_3{}^{4+} \quad (4)$$

namely, a single isosbestic point at 515 nm (ϵ 72). Accordingly, the spectral scans were analyzed kinetically (at 500 nm) using A_∞ values calculated from the spectrum of pure $\text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+}$ to obtain the total first-order rate constant k_{3c} for the disappearance of the 1,2,3-triaquo substrate. Values of k_{3c}, given in Table II, actually represent upper limits for the aquation rate constant k_{3c4} and the isomerization rate constant k_{3c3t}; *i.e.*, $k_{3c} = k_{3c4} + k_{3c3t}$, as shown by the following argument. Aquation of 1,2,6-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ (reaction 1) is fast relative to the maximum possible rate (k_{3c}) of the isomerization of 1,2,3-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$. Consequently, even if all 1,2,3-triaquo substrate were to disappear *via* isomerization (reaction 4), this would be followed by the much faster aquation of the 1,2,6-triaquo intermediate (reaction 1), and formation of the tetraaquo product found experimentally as the sole product would be controlled by the isomerization rate of the 1,2,3-triaquo substrate. Experimentally the same result would be achieved if all 1,2,3-triaquo substrate were to aquate directly to the tetraaquo product (reaction 3); such reaction may be considered more probable, since the values of k_{3c} and the activation parameters appear to be approximately what would be expected from trends considered in the Discussion, assuming the reaction is aquation. Calculations based on relative rates show that only a few per cent at most of 1,2,6-triaquo intermediate could be present in the reaction solutions. This is the reason why reaction 3 or 4 perturbs the reaction scheme given at the top of Table I negligibly except at long reaction times, as noted earlier. In fact, one can use the integrated rate equation of Van der Borg[8]

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE DISAPPEARANCE OF 1,2,3-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ BY AQUATION AND/OR ISOMERIZATION

Temp,[a] °C	$[\text{HClO}_4]$, F	C_0,[b] mM	μ,[c] M	10^4k_{3c},[d] sec^{-1}
49.97	1.80	1.66	1.80	0.517 ± 0.018
45.10	1.83	1.80	1.83	0.307 ± 0.032
45.10	0.49	1.71	1.80	0.267 ± 0.040
45.00	1.79	1.72	3.00	0.259 ± 0.020
40.03	1.77	2.07	1.77	0.187 ± 0.014

[a] Deviations: ±0.10° at 50 and 45.10°; ±0.05° at 45.00 and 40°. [b] Initial concentration of substrate. [c] Ionic strength, controlled with NaClO_4. [d] Errors are standard deviations.

$$X_C = \frac{k_2}{k_3 - (k_1 + k_2)}\{\exp[-(k_1 + k_2)t] - \exp[-k_3t]\} \quad (5)$$

derived for the concurrent–consecutive reactions

$$\begin{tikzcd} A \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & B \\ & C \arrow[ur, "k_3"'] & \end{tikzcd} \quad (6)$$

to represent the *possible* concurrent–consecutive reactions

$$\begin{tikzcd} \text{1,2,6-Cr(trienH)(OH}_2)_3{}^{4+} \arrow[rr, "k_{3t4}"] \arrow[dr, "k_{3t3c}"'] & & \text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+} \\ & \text{1,2,3-Cr(trienH)(OH}_2)_3{}^{4+} \arrow[ur, "k_{3c}"'] & \end{tikzcd} \quad (7)$$

and together with the condition $X_A + X_B + X_C = 1$ for the mole fractions of A, B, and C, one can calculate values of R ($R = X_B/X_C$) at arbitrary reaction times. The relevant rate constants for eq 7 at 35° (k_{3c} extrapolated from 40° by Arrhenius plot) lead to a predicted product ratio R of 2.48 at the longest reaction time (1.5 half-times, $X_A = 0.354$) at which 1,2,6-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ decomposition was so studied. This value of R is in satisfactory agreement with the observed chromatographic value of 2.34 ± 0.26 at 35° (Table I) and shows that our treatment of the 1,2,6-triaquo rate data is satisfactory whether or not the aquation of 1,2,3-$\text{Cr(trienH)(OH}_2)_3{}^{4+}$ is occurring at its maximum rate k_{3c}.

---

[8] R. J. A. M. Van der Borg, *Kon. Ned. Akad. Wetensch. Proc., Ser. B*, **62**, 299 (1959).

Although aquation of the tetraaquo product is relatively slow (see below) compared with the disappearance of 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$, calculations based on the relevant rate constants indicate that *ca.* 12% of the total Cr would be present as $Cr(trienH_3)(OH_2)_5^{6+}$ after 2 half-times of the 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ reaction. The observed linearity of the first-order rate plots for the 1,2,3-triaquo reaction up to 2 half-times is not in conflict with the formation of up to 12% pentaaquo complex, since the relative extinction coefficients ϵ of 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$, $Cr(trienH_2)(OH_2)_4^{5+}$, and $Cr(trienH_3)(OH_2)_5^{6+}$ at 500 nm (the wavelength used in kinetic analysis) show that 12% pentaaquo complex would affect the 1,2,3-triaquo kinetic analysis negligibly.

Within the experimental errors there is no change in k_{3c} in going from 1.8 to 0.5 *F* $HClO_4$ at ionic strength 1.8 *M* and 45° or in changing the ionic strength from 1.8 to 3.0 *M* at 1.8 *F* $HClO_4$ and 45°.

A linear Arrhenius plot was obtained from the temperature dependence of k_{3c} at $\mu = 1.8\ M$. The activation parameters are $E_a = 21.2 \pm 2.2$ kcal mol^{-1}, log $[PZ\ (\text{sec}^{-1})] = 10.0 \pm 1.5$, and $\Delta S°_{298}{}^{\ddagger} = -15 \pm 7$ cal deg^{-1} mol^{-1}; extrapolation of k_{3c} to 25° gives $(3.4 \pm 1.0) \times 10^{-6}$ sec^{-1}.

Aquation of $Cr(trienH_2)(OH_2)_4^{5+}$.—There were no complications with the interpretation of the spectral scans during reaction of the tetraaquo complex. An isosbestic point was observed at 586 ± 2 nm (ϵ 16.5 ± 0.9) up to at least 65% reaction, in good agreement with the values 588 ± 1 nm (ϵ 16.0 ± 0.4) predicted from Figure 2 for the reaction

$$Cr(trienH_2)(OH_2)_4^{5+} + H_3O^+ \xrightarrow{k_{45}} Cr(trienH_3)(OH_2)_5^{6+} \quad (8)$$

First-order rate plots (analyzed at 510 nm) with A_∞ values calculated from the spectrum of the pure pentaaquo complex were linear to *ca.* 65% reaction, at which time <1% of the granddaughter, $Cr(OH_2)_6^{3+}$, would be present (see below). Table III gives the values of k_{45}, which are essentially independent of acid concentration over the range 0.5–2 *F* $HClO_4$ ($\mu = 2\ M$) at 70° and show only a 4% decrease in going from ionic strength 2 to 3 *M* for 2 *F* $HClO_4$ at 70°

TABLE III

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Cr(trienH_2)(OH_2)_4^{5+}$

Temp,[a] °C	$[HClO_4]$, *F*	C_0,[b] m*M*	μ,[b] *M*	$10^5 k_{45}$,[b] sec^{-1}
70.10	1.98	4.05	1.98	8.43 ± 0.28
70.10	0.96	3.86	2.0	8.95 ± 0.33
70.10	0.52	5.07	2.0	8.88 ± 0.28
70.10	1.99	4.40	3.0	8.13 ± 0.16
60.04	2.00	2.74	2.0	3.07 ± 0.06
50.03	2.00	2.74	2.0	0.951 ± 0.028

[a] Deviations: ±0.10° at 70°; ±0.03° at 60 and 50°.
[b] Footnotes are the same as for corresponding columns in Table II.

Activation parameters from a linear Arrhenius plot ($\mu = 2\ M$) are $E_a = 24.2 \pm 0.7$ kcal mol^{-1}, log $[PZ\ (\text{sec}^{-1})] = 11.34 \pm 0.47$, $\Delta S°_{298}{}^{\ddagger} = -9 \pm 2$ cal deg^{-1} mol^{-1}, and, by extrapolation, $k_{45} = (4 \pm 14) \times 10^{-7}$ sec^{-1} at 25°.

Aquation of $Cr(trienH_3)(OH_2)_5^{6+}$.—The pentaaquo complex aquates (reaction 9) in acid solution to the hexaaquo complex, as shown by the good agreement between the isosbestic point predicted for reaction 9 from Figure 2, namely, 607 ± 1 nm (ϵ 10.8 ± 0.3), and the isosbestic point observed experimentally at 607 ± 1 nm (ϵ 10.5 ± 0.2) for the first 50–60% reaction; also, $Cr(OH_2)_6^{3+}$ was isolated chromatographically from the aged reaction solutions.

$$Cr(trienH_3)(OH_2)_5^{6+} + H_3O^+ \xrightarrow{k_{56}} Cr(OH_2)_6^{3+} + trienH_4^{4+} \quad (9)$$

Table IV presents the values of k_{56} obtained from first-order rate plots (analyzed at 540 nm) with A_∞ values calculated from the spectrum of pure $Cr(OH_2)_6^{3+}$; these plots were linear as far as followed (50–60% reaction). There appears to be no effect of acid concentration over the range 0.5–2 *F* $HClO_4$ ($\mu = 2\ M$) on k_{56}. At 70°, increase of ionic strength from 2 to 3 *M* decreases k_{56} about 20%, within the normal range of salt effects at high ionic strengths.

TABLE IV

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $Cr(trienH_3)(OH_2)_5^{6+}$ [a]

Temp, °C	$[HClO_4]$, *F*	C_0, m*M*	μ, *M*	$10^5 k_{56}$, sec^{-1}
80.06	2.01	3.92	2.0	2.28 ± 0.08
80.11	0.91	2.47	2.0	2.27 ± 0.08
80.11	0.46	2.49	2.0	2.29 ± 0.08
70.30	2.01	2.46	2.0	0.812 ± 0.030
69.92	0.91	2.49	2.0	0.694 ± 0.025
69.92	0.46	2.47	2.0	0.741 ± 0.023
70.11	1.96	3.06	3.0	0.645 ± 0.016
60.03	2.01	3.92	2.0	0.208 ± 0.007
60.03	0.91	2.47	2.0	0.200 ± 0.007
60.03	0.46	2.49	2.0	0.225 ± 0.007

[a] Footnotes of Table III apply to same columns here.

Activation parameters from a linear Arrhenius plot ($\mu = 2\ M$) are $E_a = 28.1 \pm 0.8$ kcal mol^{-1}, log $[PZ\ (\text{sec}^{-1})] = 12.77 \pm 0.52$, and $\Delta S°_{298}{}^{\ddagger} = -2 \pm 2$ cal deg^{-1} mol^{-1}. Extrapolation of k_{56} gives $(1 \pm 7) \times 10^{-8}$ sec^{-1} at 25°

Discussion

A reaction scheme incorporating the aquation and isomerization reactions found to occur in the stepwise "unwrapping"[9] of the triethylenetetramine ligand from 1,2,3- and 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ to give $Cr(OH_2)_6^{3+}$ is shown in Figure 3.

The rates of isomerization of 1,2,6-$Cr(trienH)(OH_2)_3^{4+}$ and (upper limit for rate only) 1,2,3-$Cr(trienH)(OH_2)_3^{4+}$ found in this research are within an order of magnitude of the rates of isomerization of some bis(ethylenediamine)chromium(III) complexes at 25°[10] and require no further comment.

The absence of significant hydrogen ion dependence of the rates in the range 0.5–2 *F* $HClO_4$ ($\mu = 2\ M$) for aquation of the triethylenetetramine complexes is in line with the absence of such an effect with the ethylenediamine and all but one of the diethylenetriamine complexes (there is a small H^+ effect in aquation of $Cr(en)(OH_2)_4^{3+}$ and a larger effect for $Cr(dienH_2)$-

---

(9) The term "unwrapping" is used here, as in ref 3, to denote that the multidentate amine ligand undergoes successive rupture of its N bonds to the metal atom center, without regard to which Cr–N bonds are broken. Examination of Fisher–Hirschfelder models suggests that breaking 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 taken into consideration for the proton which must be taken up by the freed amino N atom to stabilize each isolable intermediate; *i.e.*, the unwrapping appears to start at one primary N atom and after that the next Cr–N bond broken is to the amino N atom next to it or at the opposite end of the amine chain and so on.

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

$$\begin{tikzcd}
(3t)\ 1,2,6\text{-Cr(trienH)(OH}_2)_3{}^{4+} \arrow[r, "120^a"] \arrow[d, shift right, "37^a"'] & (4)\ \text{Cr(trienH}_2)(\text{OH}_2)_4{}^{5+} \arrow[r, "3.07"] & (5)\ \text{Cr(trienH}_3)(\text{OH}_2)_5{}^{6+} \arrow[r, "0.208"] & (6)\ \text{Cr(OH}_2)_6{}^{3+} \\
(3c)\ 1,2,3\text{-Cr(trienH)(OH}_2)_3{}^{4+} \arrow[u, dashed, shift right, "\leqslant 13^b"'] \arrow[ur, dashed, "\leqslant 13^b"'] & & &
\end{tikzcd}$$

Figure 3.—First-order rate constants (10^5k_1, $\sec^{-1}$) for aquation and isomerization reactions in 2 *F* $HClO_4$ at 60° in the absence of light. [a]Extrapolated from 20–35° values. [b]Extrapolated from 40–50° values.

$(OH_2)_5{}^{5+}$). Apparently the acid dissociation constants for proton loss from the aquo ligands of these triethylenetetramine complexes are insufficiently large to generate sufficient hydroxoaquo species (of expected greater lability) at the acidities investigated kinetically.

Table V compares the rate parameters for multidentate amine "unwrapping" from Cr(III) centers for all such complexes investigated so far. As in aquation of the aquoethylenediamine and aquodiethylenetriamine analogs, the "unwrapping" of the triethylenetetramine ligand becomes progressively slower with each successive stage of aquation. This behavior contrasts seemingly with the stepwise aquation of $Cr(NH_3)_6{}^{3+}$ to $Cr(OH_2)_6{}^{3+}$, where the limited data[11] fail to show (at 40°) a systematic trend and the total rate change appears not to exceed a factor of 10. The successive rate decreases for the above amine complexes and the lack of such decreases for the ammine analogs, together with faster aquation for the 1,2,6- than for the 1,2,3-triaquo complexes, suggest that chelate ring strain may play a role, since strain is presumably reduced with each successive aquation and could lead to increasing activation energies. Indeed, it is seen from Table V that the activation energies and activation entropies increase progressively in the order $18.0 < (21.2) < 24.2 < 28.1$ kcal mol^{-1} and $-20 < (-15) < -9 < -2$ cal deg^{-1} mol^{-1}, respectively, for the successive triethylenetetramine aquations starting with 1,2,6-$Cr(trienH)(OH_2)_3{}^{4+}$ (values inside parentheses are for the 1,2,3-triaquo complex). Similarly, for the successive diethylenetriamine aquations starting with 1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ the order is $19.2 < (24.3) \sim 24.0 < 26.5$ kcal mol^{-1} and $-11 < (-7) > -10 < -6$ cal deg^{-1} mol^{-1} ($\Delta S^{\circ\ddagger}$ for either the 1,2,3-triaquo or tetraaquo species seems not to fit the trend). These trends may be in the opposite direction for the ethylenediamine analogs, but the errors in E_a and $\Delta S^{\ddagger}$ are very large for them, and even for the other series some trends are partially obscured by the experimental errors. However, ring strain is only one factor. The increasing organic "grease" of the chelate ligand in going from the ammines to the ethylenediamine to the diethylenetriamine to the triethylenetetramine complexes presumably renders solvation of both the ground state and the transition state increasingly difficult in the aqueous medium; in the transition state the separating freed amino group must make an increased demand for solvation.

TABLE V

RATE PARAMETERS FOR AQUATION OF SOME Cr(III) AQUOAMINE COMPLEXES AT 60°

Complex	Medium	k, $\sec^{-1}$	E_a, kcal mol^{-1}	$\Delta S^{\circ\ddagger}$, cal deg^{-1} mol^{-1}
1,2,6-$Cr(trienH)(OH_2)_3{}^{4+}$ [a]	2 *F* $HClO_4$	1.2×10^{-3} [b]	18.0 ± 2.6	-20 ± 9
1,2,6-$Cr(dien)(OH_2)_3{}^{3+}$ [c]	1 *F* $HClO_4$	1.6×10^{-2} [d]	19.2 ± 0.6	-11 ± 2
1,2,3-$Cr(trienH)(OH_2)_3{}^{4+}$ [a]	2 *F* $HClO_4$	$\leqslant 1.3 \times 10^{-4}$ [e]	21.2 ± 2.2 [f]	-15 ± 7 [f]
1,2,3-$Cr(dien)(OH_2)_3{}^{3+}$ [c]	1 *F* $HClO_4$	5.89×10^{-5}	24.3 ± 0.7	-7 ± 3
Pink $Cr(en)(NH_3)(OH_2)_3{}^{3+}$ [g]	3 *F* $HClO_4$	1.33×10^{-4}	27.5 ± 0.3	$+4 \pm 1$
$Cr(trienH_2)(OH_2)_4{}^{5+}$ [a]	2 *F* $HClO_4$	3.07×10^{-5}	24.2 ± 0.7	-9 ± 2
$Cr(dienH)(OH_2)_4{}^{4+}$ [c] (1,2,3,6-tetraaquo)	1 *F* $HClO_4$	2.16×10^{-5}	24.0 ± 0.6	-10 ± 2
$Cr(en)(OH_2)_4{}^{3+}$ [h]	3 *F* $HClO_4$	3.0×10^{-6}	27.7 ± 1.5	-3 ± 5
$Cr(trienH_3)(OH_2)_5{}^{6+}$ [a]	2 *F* $HClO_4$	2.08×10^{-6}	28.1 ± 0.8	-2 ± 2
$Cr(dienH_2)(OH_2)_5{}^{5+}$ [c]	1 *F* $HClO_4$	2.6×10^{-6}	26.5 ± 0.8	-6 ± 3
$Cr(enH)(OH_2)_5{}^{4+}$ [h]	3 *F* $HClO_4$	1.9×10^{-6}	25.4 ± 2.3	-11 ± 7

[a] This research. [b] Extrapolated from 20–35° values. [c] Reference 3. [d] Extrapolated from 15–30° values. [e] Extrapolated from 40–50° values. [f] Reaction may include concurrent isomerization. [g] T. J. Williams and C. S. Garner, *Inorg. Chem.*, **8**, 1639 (1969); complex has unknown configuration. [h] Reference 2.

The negative entropies of activation can probably be correlated with aquation *via* dissociation to a tetragonal-pyramidal transition state or intermediate, in analogy with the persuasive arguments of Tobe[12] relating to steric change and $\Delta S^{\circ\ddagger}$ values in aquation of Co(III) complexes of type $Co(en)_2ACl^{n+}$ and similar Co(III) complexes with four amine Co–N bonds.[13] To the extent that the analogy is valid, one may conclude that pink $Cr(en)(NH_3)(OH_2)_3{}^{3+}$, the only complex of Table V for which the activation entropy of aquation is clearly positive, may aquate *via* dissociation to an incipient trigonal-bipyramidal intermediate.

The data of Table V also suggest that the 1,2,6-triaquo complexes aquate abnormally faster than the tetraaquo and pentaaquo species. If the trend were to continue to be accelerated, this could perhaps explain why experiments have failed so far to detect the existence of $Cr(trien)(OH_2)_2{}^{3+}$.[5] Preliminary kinetic studies of the tetraethylenepentamine analogs indicate a similarly greater than expected lability for $Cr(tetrenH)(OH_2)_2{}^{4+}$ ($t_{1/2} \approx 1$ hr in 3.5 *F* $HClO_4$ at 20°).[14] It will be interesting to determine the rates of the rest of the aquation stages for the tetraethylenepentamine complexes.

Acknowledgment.—S. C. T. wishes to thank the National Science Foundation for financial support as an NSF undergraduate summer research participant, 1970, during the last month of this research.

---

(11) See ref 10, Table 23 and Figure 24.

(12) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968); V. Ricevuto and M. L. Tobe, *ibid.*, **9**, 1785 (1970), have reported that the aquation of *cis*-$Co(en)_2(N_3)Cl^+$ is an apparent exception to their rule.

(13) See ref 10, Table 25 and pp 205–206, for expansion of this idea to include Cr(III) analogs.

(14) S. J. Ranney and C. S. Garner, unpublished research.