#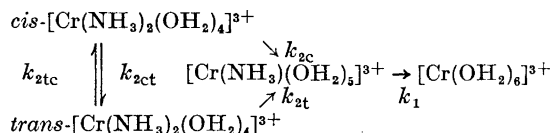 Reaction Rate Studies of the Acid Hydrolysis of Some Chromium (III) Complexes I. The Acid Hydrolysis of Monoamminepentaaquachromium (III) Ions and of *cis*- and of *trans*-Diamminetetraaquachromium (III) Ions in Aqueous Perchloric Acid

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The acid hydrolysis of monoamminepentaaquachromium(III) and of *cis*- and of *trans*-diamminetetraaquachromium(III) cations has been investigated in 0.5 to 1.0 M $HClO_4$ at an ionic strength of 1.0 in the temperature range $60-80°C$.

In the reaction scheme:

$$cis\text{-}[Cr(NH_3)_2(OH_2)_4]^{3+}$$

$$k_{2tc} \quad \Big\updownarrow \quad k_{2ct} \quad \overset{\searrow k_{2c}}{\underset{\nearrow k_{2t}}{[Cr(NH_3)(OH_2)_5]^{3+}}} \to [Cr(OH_2)_6]^{3+} \quad k_1$$

$$trans\text{-}[Cr(NH_3)_2(OH_2)_4]^{3+}$$

all reaction pathways were well defined, except the *cis*- to *trans*-diamminetetraaquachromium(III) isomerization reaction, and rate constants at 70°C and activation energies were found to be:

k_1:	$(1.110 \pm 0.012) \times 10^{-6}$ sec^{-1},	28.8 ± 0.3 kcal/mol
k_{2c}:	$(3.30 \pm 0.19) \times 10^{-6}$ sec^{-1},	27.8 ± 0.3 kcal/mol
k_{2t}:	$(17.6 \pm 0.3) \times 10^{-6}$ sec^{-1},	26.3 ± 0.4 kcal/mol
k_{2tc}:	$(5.2 \pm 0.2) \times 10^{-6}$ sec^{-1},	28.1 ± 1.1 kcal/mol

For the *cis* to *trans* isomerization reaction the rate constant was found to have an upper limit of 0.6×10^{-6} sec^{-1} at 70°C. Hence this path contributes less than 20 % to the disappearance of the *cis*-diamminetetraaquachromium(III) ion, and the equilibrium value for the concentration of *trans*-diamminetetraaquachromium(III) isomer is estimated to be less than 10 % of the total amount of diamminetetraaquachromium(III) ions present.

All rate constants were found to be independent of the hydrogen ion concentration in the acidity range studied.

As all the isomers in the ammineaquachromium(III) system are known, this system should prove ideal for a systematic investigation of some of the geometrical factors which influence the kinetic behaviour of octahedral substitution reactions. We report here, as the first part of an investigation of the acid hydrolysis of all the ammineaquachromium(III) ions, results for the acid hydrolysis of cis- and trans-diamminetetraaquachromium(III) and of monoamminepentaaquachromium(III) ions in 0.5 to 1.0 M perchloric acid at an ionic strength of 1.0, adjusted with sodium perchlorate.

This system has been studied previously by Jørgensen and Bjerrum[1] and also by Jørgensen[2] in nitrate containing media. However, later results of Espenson and Carlyle[3] for the monoamminepentaaquachromium(III) hydrolysis, show that nitrate ions have an accelerating effect on this reaction. The easy accessibility of the cis-diamminetetraaquachromium(III)[4] and the monoamminepentaaquachromium(III) ions,[5] compounds not readily available to Jørgensen and Bjerrum at the time of their investigations, together with the catalytic effect of nitrate ions, made a reinvestigation in perchlorate containing media seem worthwhile.

EXPERIMENTAL

Chemicals. Ion exchanged water, distilled from alkaline permanganate in an all quartz apparatus, was employed throughout. Sodium perchlorate (Fluka *puriss. p.a.*) and perchloric acid (Merck 70 % *p.a.*) were used without further purification for the kinetic experiments.

Chromium complexes were prepared by literature methods [1,4-6] with insignificant modifications, except that the previously unreported *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_2$(OH)$_2$]ClO$_4$ was prepared from *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_2$(OH)$_2$]Br by dissolving this compound in dilute perchloric acid, and precipitating the perchlorate by addition of pyridine. After two reprecipitations with pyridine from dilute perchloric acid, no trace of bromide ions could be detected. Small amounts of polymeric chromium species were not readily removed by this method of purification, but were easily removed by the ion exchange chromatographic method described below, so that no further purification of the solid compound was attempted.

Preparation of solutions. K$_2$Cr$_2$O$_7$, Cs[Cr(NH$_3$)(OH$_2$)$_5$](SO$_4$)$_2$.12H$_2$O, *cis*-[Cr(NH$_3$)$_2$(OH$_2$)$_2$Cl$_2$]Cl and *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_2$(OH)$_2$]ClO$_4$, were used as the initial materials for the preparation of [Cr(OH$_2$)$_6$]$^{3+}$, [Cr(NH$_3$)(OH$_2$)$_5$]$^{3+}$, *cis*-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$, and *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$ ions, respectively, in solution. Except for the dichloro complex, where the diamminetetraaqua complex was obtained after mercury(II) assisted chloride hydrolysis, and for potassium dichromate, where the hexaaquachromium(III) ion was obtained by reduction with hydrogen peroxide in dilute perchloric acid solution, the other ammineaqua complexes were formed directly by dissolving the substances in dilute perchloric acid.

Further purification of solutions obtained in this way was carried out as follows: an amount of solution containing about 1 mequiv. of chromium complex was charged onto a column (2 cm × 10 cm) packed with Dowex 50 W X8 200/400 mesh cation-exchanger prewashed with 2 M sulphuric acid and water. Excess hydrogen peroxide was now removed from the column with water, and excess mercury(II) with 0.5 M hydrochloric acid. The complexes were then displaced with 2 M sulphuric acid, as this solvent was able to separate the diammines from the monoammine and the monoammine from the hexaaquachromium(III) complex. The complexes were eluted in the following order: first hexaaqua-, then monoamminepentaaqua-, and last the diamminetetraaquachromium(III) ions. Although the separation of complexes with different numbers of coordinated ammonia molecules proceeded without difficulties, it proved rather difficult by this method to achieve separation between the isomeric diamminetetraaquachro-

mium(III) complexes. All separations were conducted at 15 − 20°C, as further cooling proved to be unnecessary (see Table 2). They were, however, made in the dark, as the *trans*-diammine when illuminated by daylight, but much less so in artificial light, isomerized to form the *cis*-isomer. After elution on the Dowex-column the main fraction was diluted approximately 100 times with water and adsorbed on about 5 ml of Sephadex SE-C-25. After washing with water, the chromium(III) complexes were displaced with 1 M sodium perchlorate solution. This last purification serves a multiple purpose. Firstly, it removes the sulphuric acid necessary for the separation of the tripositive ions, but unwanted in the kinetic investigations. Secondly, if small amounts of sulphato complexes were present, these complexes would by this treatment, because of their lower charge, be separated from the tripositive main species. However, spectral comparison between the sulphuric acid effluents and solutions of the purified compounds, gave no indication of sulphate complex formation during the time necessary for the elution to take place. Also the results of Table 2, which do not show any difference between elution experiments at 0°C and 20°C, indicate the absence of sulphato complexes. Thirdly, the small amount of UV-absorbing materials given off by the Dowex column are being disposed of. After dilution with an appropriate amount of 1 M perchloric acid, the solutions obtained were used either to measure the spectra of the purified ammineaqua complexes, see Table 1 and Fig. 1, or for the kinetic investigations.
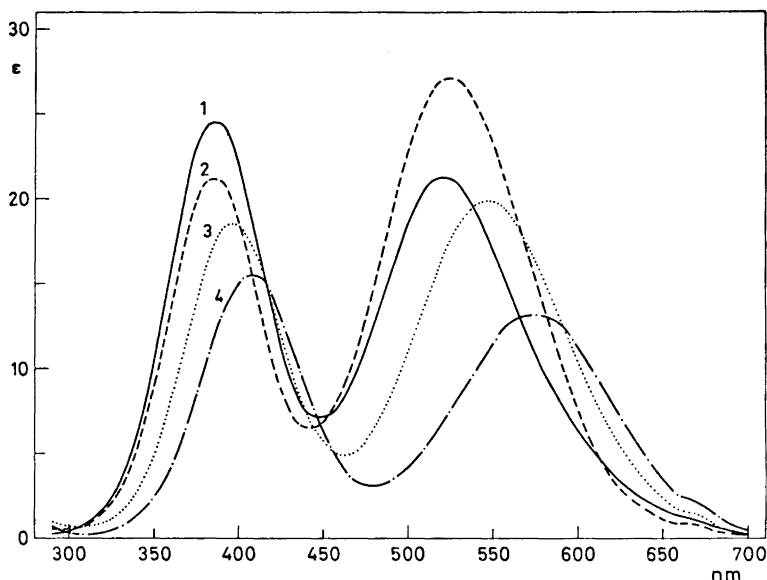

Fig. 1. Visible absorption spectra of compounds prepared and purified as described in the text. 1: *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$, 2: *cis*-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$, 3: [Cr(NH$_3$)(OH$_2$)$_5$]$^{3+}$ and 4: [Cr(OH$_2$)$_6$]$^{3+}$. The spectra measured are identical in 1.0 M HClO$_4$ and in 0.5 M HClO$_4$ + 0.5 M NaClO$_4$.

For different methods of purification the differences in reaction rates were insignificant. This is seen from experiments 1, 3, and 4 (Table 3) where the initial solutions of the *trans*-diamminetetraaquachromium(III) ion were obtained in three different ways: by direct dissolution of the *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_2$(OH)$_2$]ClO$_4$ in perchloric acid (expt. 1), by purification of the *trans* solution by passing it through a Sephadex column only (expt. 3), and by the method used for all remaining experiments and described above (expt. 4).

Table 1. Comparison of spectral characteristics of compounds, prepared and purified as described in the text, with literature values.

Complex	Medium	λ_1 max nm	ε_1 max l/(mol cm)	λ_2 max nm	ε_2 max l/(mol cm)	ε_1 max/ε_2 max	Ref.
trans-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$	0.5 M HClO$_4$ + 0.5 M NaClO$_4$	522	21.3	387	24.6	0.865	a
	0.5 M HNO$_3$	520	22	385	24.5	0.895	1 [b]
	3 M HClO$_4$	530	21.0	390	18.9	1.11	8 [c]
cis-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$	0.5 M HClO$_4$ + 0.5 M NaClO$_4$	526	27.0	386	21.3	1.27	a
	0.4 M HClO$_4$ + 0.4 M Hg(ClO$_4$)$_2$	525	26.8	386	21.5	1.25	4
[Cr(NH$_3$)(OH$_2$)$_5$]$^{3+}$	0.5 M HClO$_4$ + 0.5 M NaClO$_4$	547	19.9	396	18.6	1.07	a
	~0.5–2 M HClO$_4$	547	20.5	397	19.0	1.08	3
	1 M HClO$_4$	545	22.1	397	21.8	1.03	5
[Cr(OH$_2$)$_6$]$^{3+}$	0.5 M HNO$_3$	550	19	390	18	1.06	1 [b]
	0.5 M HClO$_4$ + 0.5 M NaClO$_4$	574	13.2	407	15.5	0.852	a
	1 M HClO$_4$	574	13.4	408	15.8	0.848	5

a This work. *b* Estimated from the graph in this reference. *c* Reported as the *trans*-[Cr(NH$_3$)$_2$(OH$_2$)$_4$]$^{3+}$, but see text.

Table 2. Separation behaviour of *trans*- and a mixture of *cis*- and *trans*-diamminetetraaquachromium(III) ions. Absorbances of first and second spin-allowed band (A$_1$ and A$_2$) of the fractions, measured in 2.0 M H$_2$SO$_4$.

Fraction No.	Experiment at 20°C						Experiment at 0°C					
	trans A$_2$	A$_1$	Δ^a	Mixture A$_2$	A$_1$	Δ^a	*trans* A$_2$	A$_1$	Δ^a	Mixture A$_2$	A$_1$	Δ^a
0	0	0	−0.8	0	0	−1.5	0	0	0.5	0	0	−0.1
1	0.557	0.476	0.9	0.508	0.450	−2.2	0.042	0.036	0.6	0.010	0.009	0.0
2	0.880	0.749	−1.1	0.803	0.712	−1.9	0.180	0.153	−0.2	0.047	0.040	−1.8
3	0.708	0.604	0.4	0.568	0.509	3.6	0.306	0.261	0.2	0.230	0.202	−2.3
4	0.346	0.296	0.6	0.287	0.258	1.9	0.241	0.205	−0.3	0.281	0.250	0.4
5	—	—	—	—	—	—	0.151	0.129	0.6	0.227	0.202	0.3
6	—			—			0.065	0.054	−1.0	0.157	0.141	1.5
7	—			—			0.022	0.018	−0.3	0.100	0.091	2.1
8	—			—			—			0.053	0.047	−0.1
α	0.8515±0.0015			0.887±0.005			0.854±0.002			0.888±0.005		

a $\Delta = 1000(A_1 - \alpha A_2 - \beta)$; with α and β determined as slope and intercept of a straight line, determined by the method of least squares, through the points.

Table 3. Rate constants and initial complex concentrations calculated for individual kinetic experiments in a reaction scheme with *cis-* to *trans-*diamminetetraaquachromium(III) isomerization absent.

Run No.	$10^6 \times C_0$ (M)	$10^6 \times k_{2t}$ (sec⁻¹)	$10^6 \times k_{2tc}$ (sec⁻¹)	$10^6 \times k_{2c}$ (sec⁻¹)	$10^6 \times k_1$ (sec⁻¹)	Temp (°C)	t_{max} (h)
trans-[Cr(NH₃)₂(OH₂)₄]³⁺							
1	2260±16	55.4±1.4	16.8±1.4	10.0±1.4	3.7±0.3	80.20	29
2[a]	1959±11	50.2±2.3	14.5±2.5	8.8±1.0	—[b]	80.00	7
3	2431±19	53.3±1.3	17.4±1.5	11.2±1.6	3.5±0.3	80.20	29
4	1278±6	56.9±1.8	17.8±1.8	11.1±1.6	3.4±0.2	80.35	47
5	1285±4	17.4±0.3	4.5±0.3	2.9±0.3	0.91±0.09	69.70	98
6	1611±4	5.54±0.10	1.53±0.11	1.10±0.17	0.258±0.023	60.18	336
cis-[Cr(NH₃)₂(OH₂)₄]³⁺							
7	1021±4	—	—	11.51±0.18	3.50±0.10	80.20	264
8[a]	862±4	—	—	10.7±0.3	3.82±0.15	80.35	311
9	854±4	—	—	3.15±0.05	1.07±0.03	69.70	98
10	1586±6	—	—	1.026±0.013	0.315±0.009	60.18	819
[Cr(NH₃)(OH₂)₅]³⁺							
11	1654±4	—	—	—	3.83±0.06	80.20	167
12[a]	1808±4	—	—	—	3.86±0.04	80.20	168
13	3661±9	—	—	—	0.327±0.004	60.18	819

[a] Kinetic runs in 0.5 M HClO₄ + 0.5 M NaClO₄; all other in 1.0 M HClO₄.
[b] Experiment followed for too short a time for this constant to be well defined.

It is also noteworthy that the calculated total chromium concentrations are the same for experiments 4 and 5 and for experiments 8 and 9 (Table 3) and that both pairs were prepared from the same stock solutions.

Kinetic measurements. Aliquots of solutions prepared as described above in a suitable number of sealed glass ampoules were immersed into a thermostated water bath maintained at the desired temperature with an accuracy of $\pm 0.05°C$. During the advancing hydrolysis the solutions were kept protected from light. At suitable time intervals ampoules were withdrawn from the thermostat, and the reactions quenched by cooling the reaction mixtures in an ice bath. Spectra of the reacted solutions were measured on a Cary 14 recording spectrophotometer equipped with a $0-0.2$ A slidewire. These measurements were performed at room temperature, that is $23 \pm 2°C$, as the temperature independence of the spectra in the range measured, $700-290$ nm, made a more careful thermostating unnecessary. Spectra of the pure substances were obtained analogously, except that these stronger solutions permitted the use of a $0-1$ A or $0-2$ A slidewire.

Methods of analysis. Chromium concentrations were determined by spectrophotometric measurements at the chromate(VI) absorption maximum at 373 nm after oxidation of the chromium(III) containing solutions with hot alkaline hydrogen peroxide solution. In good agreement with earlier results the molar extinction coefficient for our particular instrument was found to be 4826 ± 8 l/(mol cm).

Hydrogen ion concentrations and the sum of concentrations of hydrogen and sodium ions were determined by titrating with sodium hydroxide solution prior to and after exchange of sodium ions with hydrogen ions.

Method of calculation. The method of calculation was that of a nonlinear regression analysis. This will be described at length elsewhere.[7] Here we direct attention only to some points of particular interest for the present study.

The large number of individual measurements (approximately 5000) obtained over an extended period of time precluded the simultaneous reduction of all the primary data, and the datareduction, which ultimately yielded the contents of Tables 4 and 5 was

Table 4. Rate constants and activation energies for all kinetic experiments of Table 3.

	60°C	70°C	80°C	E_A(kcal/mol)
$10^6 \times k_{2t}$ (sec^{-1})	5.51 ± 0.15	17.6 ± 0.3	52.5 ± 1.0	26.4 ± 0.4
$10^6 \times k_{2tc}$ (sec^{-1})	1.52 ± 0.12	5.2 ± 0.2	16.8 ± 0.9	28.0 ± 1.2
$10^6 \times k_{2c}$ (sec^{-1})	0.986 ± 0.018	3.34 ± 0.04	10.6 ± 0.2	27.7 ± 0.4
$10^6 \times k_1$ (sec^{-1})	0.315 ± 0.006	1.115 ± 0.012	3.67 ± 0.05	28.7 ± 0.3

Table 5. Rate constants and activation energies calculated for all kinetic experiments in a reaction scheme with the *cis-* to *trans*-diamminetetraaquachromium(III) isomerization reaction included.

	60°C	70°C	80°C	E_A(kcal/mol)
$10^6 \times k_{2t}$ (sec^{-1})	5.51 ± 0.17	17.6 ± 0.3	52.4 ± 1.0	26.3 ± 0.4
$10^6 \times k_{2tc}$ (sec^{-1})	1.51 ± 0.11	5.2 ± 0.2	16.7 ± 0.8	28.1 ± 1.1
$10^6 \times k_{2c}$ (sec^{-1})	0.97 ± 0.06	3.30 ± 0.19	10.5 ± 0.6	27.8 ± 0.3
$10^6 \times k_{2ct}$ (sec^{-1})	0.00 ± 0.09	0.0 ± 0.3	0.0 ± 0.9	–
$10^6 \times k_1$ (sec^{-1})	0.313 ± 0.006	1.110 ± 0.012	3.66 ± 0.04	28.8 ± 0.3

therefore carried out in the following three steps. Firstly, the composition of quenched reaction mixtures was calculated from the spectra of these solutions and those of the four pure components. Absorption spectra from 290 nm to 700 nm measured at 10 nm intervals were employed in all the experiments. In this reduction of the primary data to yield concentrations of reaction products as function of time, the additional requirement, that in order to be chemically significant the concentrations had to be greater than or equal to zero, was applied.

Secondly, the concentrations as function of time permitted the calculation of the rate constants and of the initial complex concentrations for kinetic runs at various temperatures and hydrogen ion concentrations (Table 3).

Thirdly, rate constants (k_{T_0}) at a series of fixed temperatures (T_0), which were close to those at which the actual experiments were made, were calculated together with activation energies (E_A). These calculations were based upon the rate constants estimated for the individual kinetic runs (k_T), as a function of temperature(T), according to eqn. (1):

$$k_T = k_{T_0} \exp[-E_A(1/RT - 1/RT_0)] \tag{1}$$

Table 4 gives rate constants at 80, 70, and 60°C and activation energies calculated from the data of Table 3.*
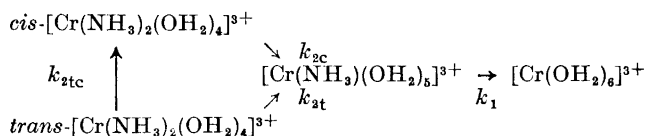
RESULTS AND DISCUSSION

When a solution approximately 50 mM in *trans*-diamminetetraaquachromium(III) and 1 M in perchloric acid was kept in the dark at 80°C for 4 h, and the resulting mixture separated as described in the experimental section, three bands resulted. The two substances eluted first were identified as the hexaaquachromium(III) and the monoamminepentaaquachromium(III) ions, respectively. As the total amount of hexaaquachromium(III) in this particular experiment amounted to only a few percent of the total chromium ions present, this ion was only identified from its elution behaviour (known of course from columns with greater hexaaquachromium(III) ion content) whereas the monoamminepentaaquachromium(III) ion was identified through its visible absorption spectrum. The last eluate was identified from the visible absorption spectrum as containing a mixture of the *cis* and the *trans*-diamminetetraaquachromium(III) ions. The *cis*-diamminetetraaqua- and the monoamminepentaaquachromium(III) ions were studied in the same way except for reaction times of 24 and 48 h, respectively. With the former no *trans* was observed but *cis*-diamminetetraaqua-, monoamminepentaaqua-, and hexaaquachro-

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* It should be noted that nondiagonal variance matrices were always employed in the latter two data reductions described above. Consequently, the data of Table 4 are not directly obtainable from those of Table 3 without knowledge of nondiagonal elements of the variance matrix for the data of Table 3.

The importance of these nondiagonal elements is particularly well illustrated by the data obtained when k_{2ct} is included in the calculations. As no significant amounts of *trans*-diamminetetraaquachromium(III) was ever obtained in experiments started with the *cis*-diamminetetraaquachromium(III) the normal equations became almost singular for these kinetic runs. Consequently rather large standard deviations were always obtained upon the highly correlated rate constants (k_{2t}, k_{2tc}, k_{2c}, and k_{2ct}) in these experiments. This can be illustrated by values of 12.7 ± 3.1, 6.1 ± 5.4, 3.3 ± 0.6, and 0.99 ± 0.15 sec^{-1} found for $10^6 k_{2c}$ in experiments 7 to 10. Had correlation terms been neglected in the following computation, the significantly better defined values for k_{2c} of Table 5 would never have been obtained. This of course is also the reason why the data reductions described by the above modified equation of Arrhenius (eqn. 1), resulting in Tables 4 and 5 in this investigation, have been chosen, as rate constants for individual kinetic runs seldom reflect the total content of information in a kinetic investigation when reaction schemes become sufficiently complicated.

mium(III) ions were all three identified from their visible absorption spectra. In the monoamine experiment only monoamminepentaaqua- and hexaaquachromium(III) ions could be detected.

The following reaction scheme:

$$cis\text{-}[Cr(NH_3)_2(OH_2)_4]^{3+}$$

$$k_{2tc} \uparrow \qquad \searrow k_{2c} \atop [Cr(NH_3)(OH_2)_5]^{3+} \to [Cr(OH_2)_6]^{3+}$$
$$\qquad \nearrow k_{2t} \qquad\qquad k_1$$

$$trans\text{-}[Cr(NH_3)_2(OH_2)_4]^{3+}$$

although it could have accommodated the experimental results was not immediately accepted because isomerization reactions of chromium(III) complexes, in which monodentate ligands only are present, are not commonly encountered. As the absence of the isomerization reaction would require contamination of the supposed *trans*-isomer with the *cis*-isomer, the isomeric purity of the *trans*-diamminechromium(III) compounds employed to generate the *trans*-diamminetetraaquachromium(III) ion in solution was investigated in more detail.

cis-Diamminechromium(III) compounds may in fact be obtained as products of the oxidation of Reinecke salt (ammonium *trans*-diamminetetrakis-(isothiocyanato)chromate(III) monohydrate). This is demonstrated by the results of House:[8] by oxidation of Reinecke salt with *aqua regia*, and treatment of the oxidation product with concentrated hydrobromic acid a dibromo compound precipitated, and after hydrolysis of the bromide ligands in this compound he obtained a diamminetetraaquachromium(III) solution, said to be that of the *trans*-isomer. The visible absorption spectrum of solutions thus generated did not agree with that of neither the *cis*- nor the *trans*-diamminetetraaquachromium(III) ions prepared by other methods (Table 1 and Fig. 1). Therefore solutions obtained by the method of House were investigated further. Ion exchange experiments revealed appreciable amounts of the monoamminepentaaquachromium(III) ion, and from the visible absorption spectrum of the diammine fraction this was interpreted as a mixture of the isomeric diamminetetraaquachromium(III) ions with the *cis*-isomer as main constituent. This result indicates that *cis*-diamminechromium(III) compounds may well be present in the *trans*-diamminechromium(III) compounds prepared by the oxidation of Reinecke salt. In order to answer this question some separation experiments using the supposed *trans*-isomer product prepared according to Werner and Klien[6] and also this product mixed with a known amount of the *cis*-isomer prepared according to Andersen and Berg[4] were carried out.

It was found that diamminediaquadihydroxochromium(III) perchlorate prepared from a mixture of the dichloro compounds of the two diammines, containing the *cis*- and the supposed *trans*-diammine in the ratio 1:4, was indistinguishable from that prepared from the dichloro compound of the supposed *trans*-diammine alone. This was shown by comparing the visible absorption spectra of the diamminetetraaquachromium(III) ion generated by dissolving the dihydroxo compounds in dilute perchloric acid. As this spectrum did not change on further reprecipitation it must either be concluded that we have a pure isomer or a crystal reprecipitating with a constant ratio

between *cis*- and *trans*-isomer. From kinetic experiments the content of *cis*-isomer in *trans*-diamminetetraaquachromium(III) solutions prepared as described in the experimental part is found to be 25.0 ± 0.8 %, if the isomerization reaction is disregarded as a source of the *cis*-isomer. Thus a *cis*- to *trans* ratio of 1:3 in diamminediaquadihydroxochromium(III) perchlorate is predicted.

Ion exchange experiments with the *trans*-isomer and a mixture containing about 85 % of the *trans*- and about 15 % of the *cis*-isomer gave, when the diamminetetraaquachromium(III) effluent was fractionated, the results of Table 2. In this table results of a plot of the absorbance at the maximum of the second band against the absorbance at the maximum of the first band are shown for four fractionation experiments. The deviations from linearity are seen to be particularly systematic in the solutions known to be mixtures, whereas in the fractionation of the *trans*-solutions, no systematic trends are observed. The separation results are seen to be in agreement with the *cis trans* assignment of the isomeric diamminetetraaquachromium(III) ions based upon their mode of formation and visible absorption spectra, as *trans*-complexes are generally eluted more readily than the corresponding *cis*-isomers. From the 1:3 ratio of *cis* to *trans*, predicted from the kinetic experiments, *trans*-isomer contents in the two sets of solutions employed in the ion exchange experiments of 75 % and 64 % were calculated. These values are far too little different to account for the observed elution behaviour. It is therefore concluded that the *trans*-compounds prepared by bromine and chlorine oxidation of Reinecke salt are isomerically pure, and consequently that *trans* to *cis* isomerization does occur in the absence of light in diamminetetraaquachromium(III) solutions. Also the high reproducibility of the visible absorption spectrum of the *trans*-diamminetetraaquachromium(III) ion, whether this was prepared from dibromo-, dichloro-, or dihydroxo-diamminediaqua-chromium(III) compounds,[6] renders possible reprecipitation of the dihydroxo compound with a constant ratio of *cis*- to *trans*-isomer unlikely.

Table 3 shows rate constants and initial complex concentrations calculated for a series of kinetic experiments. The reaction rates are seen to be the same within the experimental error in 0.5 M and 1.0 M acid, when some small temperature differences are taken into consideration, so that at these high acidities reactions of deprotonated species need not be considered.

From Table 4 it is seen that k_{2t} is appreciably larger than k_{2c}. This means that a significant amount of *cis*-isomer may well hydrolyze *via* the *trans*-isomer, as the magnitude of k_{2t} prevents the build up of significant concentrations of the *trans*-isomer. In order to estimate to what extent this took place the *cis* to *trans* isomerization rate constant, k_{2ct}, was included in the calculations. Results of these calculations are shown in Table 5. As could be expected, no well defined value of k_{2ct} was obtained, as the kinetic experiments were already adequately described within the simpler reaction scheme with k_{2ct} absent. Some important conclusions may, however, be drawn by comparing Tables 4 and 5. The significant difference between the two tables lies in the standard deviation associated with k_{2c}, which is seen to be about three times larger in Table 5 than in Table 4. This is not unexpected since the high negative correlation between k_{2c} and k_{2ct} (as a result of the magnitude of k_{2t}) with a

correlation coefficient of about -0.98 should have this effect. Had k_{2t} been much greater almost complete correlation between k_{2c} and k_{2ct} would have existed. This would have rendered standard deviations upon k_{2c} and k_{2ct} as individual parameters so large as to invalidate the quantitative information in these separated parameters completely. In this case only the sum $k_{2c} + k_{2ct}$ could have been obtained with reasonable accuracy from the experiments. This is in agreement with the intuitive chemical considerations on the reaction scheme and also with the data of Table 4 as values of k_{2c} in this table are values of the sum $k_{2c} + k_{2ct}$ when the *cis* to *trans* isomerization reaction is included in the reaction scheme.

If two standard deviations are taken as an upper limit for k_{2ct} two interesting results emerge from Table 5. Firstly, less than about 20 % of the *cis*-diammine disappears *via* the *trans*-diammine, and secondly, in solutions at equilibrium with respect to the diamminetetraaquachromium(III) ions less than 10 % is present as the *trans*-isomer.

A more thorough discussion from a stereochemical and kinetic point of view, of the data presented here will be presented when our current studies of the acid hydrolysis of the other $[Cr(NH_3)_n(OH_2)_{6-n}]^{3+}$ ions ($n = 3$, 4, 5, and 6) have been concluded.

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